1 of 7

CATALYTIC TWO-STAGE LIQUEFACTION (CTSL™) PROCESS BENCH STUDIES
AND PDU SCALE-UP WITH SUB-BITUMINOUS COAL

FINAL

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ABSTRACT

Reported herein are the details and results of Laboratory and Bench-Scale experiments using sub-bituminous coal conducted at Hydrocarbon Research, Inc., under DOE Contract No. DE-AC22-88PC88818 during the period October 1, 1988 to December 31, 1992. The work described is primarily concerned with testing of the baseline Catalytic Two-Stage Liquefaction (CTSLTM) process with comparisons with other two stage process configurations, catalyst evaluations and unit operations such as solid separation, pretreatments, on-line hydrotreating, and an examination of new concepts.

In the overall program, three coals were evaluated, bituminous Illinois No. 6, Burning Star and sub-bituminous Wyoming Black Thunder and New Mexico McKinley Mine seams. The results from a total of 16 bench-scale runs are reported and analyzed in detail. The runs (experiments) concern process variables, variable reactor volumes, catalysts (both supported, dispersed and rejuvenated), coal cleaned by agglomeration, hot slurry treatments, reactor sequence, on-line hydrotreating, dispersed catalyst with pretreatment reactors and CO₂/coal effects. The tests involving the Wyoming and New Mexico Coals are reported herein, and the tests involving the Illinois coal are described in Topical Report No. 2.

On a laboratory scale, microautoclave tests evaluating coal, start-up oils, catalysts, thermal treatment, CO₂ addition and sulfur compound effects were conducted and reported in Topical Report No. 3. Other microautoclave tests are described in the Bench Run sections to which they refer such as: rejuvenated catalyst, coker liquids and cleaned coals. The microautoclave tests conducted for modelling the CTSLTM process are described in the CTSLTM Modelling section of Topical Report No. 3 under this contract.

PROJECT DESCRIPTION

In October of 1988, HRI was granted a contract to expand the two-stage, close-coupled catalytic liquefaction of coal data base by further exploring catalytic effects, optimizing reactor conditions, and investigating coal pretreatment and solids separation methods. The statement of work consisted of the following:

TASK 1 - PROJECT MANAGEMENT PLAN

TASK 2 - LABORATORY STUDIES

- A. Coal Feedstock Qualification
- B. Catalyst Qualification
- C. Catalyst Deactivation Studies
- D. Solvent Quality Testing
- E. Product Reactivity Testing

TASK 3 - CONTINUOUS BENCH-SCALE OPERATIONS

- 3.1 Reactor Configurations
- 3.2 Feedstock Effects
- 3.3 Catalyst Studies
- 3.4 Solids Separation
- 3.5 Additional Process Developments

TASK 4.0 PDU SCALE-UP

TASK 5 - TECHNICAL ASSESSMENT

ORGANIZATION OF REPORT

The description of the work performed and the results achieved under this contract are discussed in three separate topical reports. These are:

Topical No. 1 - Sub-bituminous Coal Bench-Scale and PDU Studies

Topical No. 2 - Illinois Coal Bench-Scale Studies

Topical No. 3 - Laboratory-Scale Studies, Modelling,
and Technical Assessment

Final Report - Presents a Summary, Conclusions and Recommendations
from the Entire Program

In this report, Topical No. 1, the bench-scale runs that used sub-bituminous coal are discussed first, followed by a discussion of the PDU preparations and operations. There are ten separate sections for the bench runs, each essentially

an independent report, with tables, figures and appendices at the end of each section. The results for each bench run are discussed with respect to the specific objectives for the run.

Tasks 3 and 4 are addressed in this report, Topical No. 1. Work performed under Task 2, Laboratory Support, is discussed in Topical Report No. 3, but when the laboratory work was integral with the bench runs, the results are included in this report.

In this report, dealing with sub-bituminous coal, all of subtasks under the Continuous Bench-Scale Operations and PDU Scale-Up tasks were addressed as follows:

Task 3.1 - Reactor Configurations

- Run CC-1 - examined different first and second stage temperature patterns (low/high, equal, and high/low).
- Run CC-2 - tested a first stage volume that was twice the second stage volume.
- Run CC-7 - compared catalytic/thermal and thermal/catalytic operations

Task 3.2 - Feedstock Effects

- Run CC-5 - tested pretreatment of coal in a hot slurry mix tank for possible removal of carbon oxides or other effects.
- Run CC-10 - tested the performance of an alternative sub-bituminous coal (McKinley Mine, New Mexico Coal)

Task 3.3 - Catalyst Studies

- Run CC-3 - tested iron molybdenum spherical catalyst
- Run CC-4 - tested two forms of dispersed iron catalyst (iron oxide and pyrrhotite) for incremental activity with supported catalyst also in both reactors.
- Run CC-7 - tested iron oxide dispersed catalyst with supported catalyst only in the low temperature reactor.
- Run CC-12 - evaluated the performance of rejuvenated catalyst that had been recovered from previous bench runs.
- Run CC-15 - evaluated the performance of iron oxide hydroxide predispersed catalyst with supported catalyst only in the final stage.

Task 3.4 - Solids Separation

- Run CC-11 - generated atmospheric bottoms for filtration tests at British Coal Board.

Task 3.5 - Additional Process Developments

- Run CC-10 - evaluated on-line hydrotreating of New Mexico coal light distillates.
- Run CC-11 - evaluated on-line hydrotreating of Black Thunder coal light distillates.
- Run CC-13 - evaluated the effect of CO₂ addition and the kinetics of increasing the coal concentration in the reactor by using a vaporizing solvent to slurry the feed coal.

Task 4.0 - PDU Scale-up - scaled up extinction recycle and solids separation by filtration.

PROGRAM OBJECTIVES

The objective of this program was to achieve higher distillate yields and better quality products at lower capital and production costs in comparison to existing technologies. Specific approaches to accomplish this objective were to:

- ◆ Improve understanding of the complex reactions in coal liquefaction, which may lead to further process improvements.
- ◆ Identify catalysts of increased effectiveness and potentially lower cost.
- ◆ Further improve hydrogen management and cost.
- ◆ Identify and demonstrate coals with the greatest potential for liquefaction in the CTSL[™] Process.
- ◆ Develop scale-up data in a PDU.

EXECUTIVE SUMMARY

INTRODUCTION

In a recently completed DOE sponsored research program at HRI (1985-88) distillate yields were improved from 4.3 bbls/MAF ton of bituminous coal to 5.0 barrels while reducing the cost per barrel of oil produced by more than 10%. The process upon which this is based consists of a two stage low severity, directly coupled equal volume ebullated bed reactor system. Separation and recycle of the heavy oils results in nearly complete conversion of the residual oils to distillates. Process studies have also shown that the low-temperature, first-stage catalytic hydrogenation of coal followed by catalytic upgrading can lead to higher conversion, greater heteroatom removal, and more effective and selective hydrogen utilization. The result is the production of syncrude of lower molecular weight and superior quality to that obtainable in single-stage coal liquefaction.

These results were very encouraging; and a more complete assessment of the technical and economic viability of two stage liquefaction was recommended. Further effort was needed to explore catalytic effects, to investigate process operations such as coal pretreatment and solids separation and to expand the data base to find further process improvements.

The major objective of the program was to improve the Catalytic Two-Stage Liquefaction (CTSL™) Process in order to achieve higher distillate yields and better quality products at lower capital and production costs.

The CTSL™ process consists of two ebullated-bed reactors close coupled in series with the first reactor operating at a lower temperature than the second. Thus the lower temperature first-stage favors catalytic hydrogenation through the maintenance of donor solvent quality. Further conversion and heteroatom removal occurs in the second stage at a higher thermal severity selected to minimize dehydrogenation of first-stage products. *Figure 1* depicts the process without defining a method of solid separation. The equipment used for the bench-scale studies consists of two close-coupled 2000 cc ebullated-bed reactors with vapor/liquid separation, continuous atmospheric distillation, filtration and a 1000 cc on-line hydrotreater. Operations are continuous excluding coal preparation, solid separation and heavy recycle oil preparation. A single batch of supported catalyst is used for a run; therefore, each experiment must account for deactivation in the interpretation of results. At a nominal capacity of 50 lbs/day this unit clearly defines process chemistry and scales directly to larger size units.

HRI EBULLATING-BED CATALYTIC TWO-STAGE COAL LIQUEFACTION (CTSL) PROCESS

SIMPLIFIED FLOW PLAN

BENCH UNIT DESCRIPTION

Process development studies have been conducted in HRI's continuous two-stage Bench Unit 227, shown in *Figure 2*. It is necessary to study the process in a continuous unit with self-sustained recycle solvent generation in order to fully understand the results and avoid the pitfalls of smaller batch or once-through experimental units. The unit features two 2,000 cc ebullated-bed reactors in series. A special high pressure, on-line sampling system on the first-stage reactor obtains the data required to independently assess the effectiveness of the two reactor stages. A continuous atmospheric still provides accurate control of recycle solvent cut points. The atmospheric still bottoms are subjected to further batch filtration and/or vacuum distillation operations to study various recycle oil preparation techniques. These operations would be replaced by suitable continuous solids separation processes at a larger scale. System inventories are minimized in order to provide a rapid lineout response to condition changes. The ability to conduct multi-variable studies over relatively short term periods (two to five days per condition set) while obtaining accurate, material balanced yield and product property data, was effectively demonstrated throughout the program. Hydrogen was used on a once-through basis.

EBULLATED-BED BENCH UNIT 227

MAJOR CONCLUSIONS

The major objective of this contract was to improve the CTSL™ Process in order to achieve higher distillate yields and better quality products of lower capital and production costs.

In support of this objective bench studies were conducted with various catalysts, additives and different process configurations. Generally, higher yields and throughputs were achieved by the use of H₂S and iron additives. Production costs were lowered by the use of catalyst rejuvenation, lower capital costs by using filtration for solid separation and improved quality by on-line hydrotreating the naphtha overhead products. Some of these improvements have been quantified in economic studies which will be further addressed in Topical #3 and the Final Contract Report.

During the sub-bituminous portion of this program, a total of 11 bench runs and 1 PDU run encompassing over 195 operating days were completed. Supporting work has included laboratory studies and technical assessments. The major conclusions from the bench unit and PDU operations with the sub-bituminous coal are highlighted below and in *Table 1*, and discussed in detail in the body of this report.

- ◆ Different processing conditions such as high temperature/low temperature, equal temperature, second stage with twice the first stage volume, thermal/catalytic, and catalytic/thermal reactor configurations all had quantifiable effects on the yield pattern, conversions, and product quality, but none of the variations had higher distillate liquid yields than the low temperature/high temperature catalytic/catalytic configuration with equal volume reactors.
- ◆ Iron oxide additive improves distillate yields slightly, but pyrrhotite does not.
- ◆ Iron molybdate promoted supported catalyst has definite catalytic activity in coal liquefaction, but is inferior to nickel molybdate when compared on an equal volume basis. Its lower cost on a weight basis makes it worthy of future consideration.
- ◆ Most of the fresh-catalyst activity can be recovered through rejuvenation (acid wash and carbon burnoff), but improvements in the procedure are required to retain catalyst strength and promoter metals.
- ◆ Reactor coal concentrations can be increased (if the appropriate carrier for coal injection can be found) for improved coal conversion kinetics. Operability and product quality are not adversely affected.

- ◆ On-line hydrotreating improves product quality yielding distillates from naphtha with less than 10ppm nitrogen and sulfur while reducing aromatic content.
- ◆ Predispersed iron oxide hydroxide catalyst combined with second stage supported catalyst in a high temperature/low temperature configuration gives similar liquid yields as CTSL™ operations.
- ◆ The addition of H₂S reduces the rate of catalyst deactivation.
- ◆ Filtration can be successfully applied as a solid separation and oil recovery unit operation.
- ◆ Adding CO₂ to the CTSL™ process increases coal conversion and promotes shift reactions to CH₄, CO and H₂O. On-line hydrotreating is very effective in reducing heteroatoms and upgrading distillates.

RECOMMENDATIONS

Further studies and development is recommended as follows:

- ◆ Investigate process configurations incorporating dispersed catalysts in combination with supported catalysts.
- ◆ Conduct more on-line hydrotreating studies with other catalysts and with higher boiling fractions.
- ◆ Continue studies with different additives, H₂S, DMDS, to understand their catalytic behavior and to improve kinetics.
- ◆ Study the use of syngas as a source of hydrogen and for improved coal conversion.
- ◆ Continue development and scale-up of filtration as a process for solid separation.

BENCH UNIT STUDIES

Table 1 shows an overview of all of the bench runs in this program. The objectives, basic conditions, and observations are identified. The results and conclusions for the bench runs with sub-bituminous are described below. These runs included CC-1 through CC-5, CC-7, CC-11 through 13, and CC-15 with Black Thunder mine (Wyoming) coal and Run CC-10 with McKinley mine (New Mexico) coal. Task 4 was the PDU operation with the Black Thunder coal.

RUN 227-55(CC-1) - CTSL™ EVALUATION OF BLACK THUNDER MINE COAL

This evaluation was referenced to the more extensive evaluation of a similar sub-bituminous coal from the Clovis Point mine. In addition, the Run 227-55(CC-1) operation studied a wider range of first and second stage temperatures than had been used previously, with the second stage temperature lower than, equal to, and higher than the first stage temperature.

The Black Thunder coal had good liquefaction performance very close to that of the Clovis Point coal, with a probable processing advantage of having about 3 W% lower ash content. The processing results for the various configurations of first and second stage temperatures appeared to follow a common trend when the combined severity of the two stages was held at a nominally common value.

The maximum yield of C₄-975°F distillate oil was 67.9 W% of maf coal, which was obtained during the first operations at the higher combined stage severity using the higher second stage temperature. Catalyst deactivation lowered this distillate yield by 0.2-0.4% per day of coal operations (0.7-1.4% decrease per 100 pounds coal processed per pound of catalyst). The distillate yields with the equal first and second stage temperatures and with lower second stage temperature appeared to follow the deactivation trend indicated by the reference operation with the higher second stage temperature.

Samples of first stage products indicated that hydrogenation was favored in the lower temperature stage, whether that stage was the first or second stage.

Comparison with the results with the Clovis Point coal, indicates an advantage in C₄-975°F distillate yield of about 2 W% of dry coal for the Black Thunder Mine coal. This difference reflects for the most part the lower ash content of the Black Thunder coal, in part offset by 0.5-1.0% lower coal conversion, and 0.5-1.0% higher light gas yield with the Black Thunder coal. Residual oil yield and catalyst deactivation were essentially the same for the two coals. The hydrogen contents and nitrogen contents of the liquid products from the Black Thunder coal were comparable to those of the Clovis Point coal products. The sulfur contents were somewhat lower in the Black Thunder coal products.

RUN 227-57(CC-2) - CTSL™ EVALUATION OF BLACK THUNDER MINE COAL WITH REDISTRIBUTED STAGE VOLUMES

This evaluation was with the first stage volume double that of the second stage, for comparison with Run 227-55(CC-1) with the same coal where the stage volumes were equal.

In general operations with the higher proportion of low temperature first stage reactor volume had possibly slightly lower total distillate yield, reflecting countervailing effects of lower light gas yield and lower residual oil yields against lower coal conversion. The product liquids were of somewhat improved quality with lower nitrogen content and higher hydrogen content.

The first condition, a comparison with an equal-stage-volume operation at a common second stage coal space velocity (doubled first stage volume), indicated 1.2% increased coal conversion, 1.1 W% lower residual oil yield, less than 0.5 W% increase in gas yield, and 1.8 W% increase in C₄-975°F distillate yield. Nitrogen contents were about one-half to two-thirds of those of the reference equal-stage-volume operation, while hydrogen contents were slightly higher by 0.04-0.19 W%.

The second condition, a comparison with an equal-stage-volume operation at a common overall coal space velocity (redistributing the stage volumes), indicated 2% lower coal conversions, 1 W% lower residual oil yield (although product residual oil concentrations were very nearly the same), possibly equal gas yields (modelling projects 1 W% lower gas yield), and 1.6 W% lower C₄-975°F distillate yields. Nitrogen contents were lower than in the equal-stage-volume reference operation by a factor of two-thirds to three-fourths, while hydrogen contents were higher by an average of 0.3 W%.

The third condition, a comparison with an equal-stage-volume operation at a higher common overall two-stage coal space velocity, indicated 1.6 W% lower coal conversion, 0.5 W% lower residual oil yield, 0.3 W% lower gas yield, and 1.6 W% lower C₄-975°F distillate yields. The relative nitrogen contents were lower than in the equal-stage-volume reference operation by the same proportion noted above in the Condition 2 comparisons, while the difference in hydrogen contents was even greater with 0.9 W% higher hydrogen contents than in the reference operation. Another comparison for this condition, with an equal-stage-volume operation at a common first-stage coal space velocity (halving the second stage volume), indicated 5 W% lower coal conversion, 1 W% higher residual oil yield, 1-2 W% lower gas yield, and 3-4 W% lower C₄-975°F distillate yields.

RUN 227-58 (CC-3) - CTSL™ EVALUATION OF IRON-MOLYBDENUM CATALYST WITH BLACK THUNDER MINE COAL

A developmental catalyst from UOP, RCM-1-123, Fe-Mo supported on alumina, was used in both stages. This catalyst offers the possibility of lower catalyst replacement costs because it would be less expensive than a nickel-based catalyst. The test was conducted over 12 days, using a space velocity of 44 lb coal/ft³ of catalyst. The liquefaction performance was evaluated at two temperature conditions, 750°F/800°F and 750°F/825°F.

The 975°F⁺ conversion was 82.5-87.3 w%. Compared to Shell S-317 NiMo catalyst, the 975°F⁺ conversion and the C₄-975°F yield were only slightly lower with FeMo catalyst. However, considering the much lower catalyst charge weight (due to the lower bulk density), the difference was not very large. The quality of the product obtained with the FeMo catalyst was significantly lower.

RUN 227-61 (CC-4) - CTSL™ EVALUATION OF IRON-BASED DISPERSED CATALYSTS WITH BLACK THUNDER MINE COAL

The objective of this run was to investigate the performance of iron-based additives (dispersed catalyst) for liquefaction of sub-bituminous coal in the presence of supported catalyst.

Two dispersed catalysts were tested. The first additive was an iron oxide labelled magnetic pigment by its supplier. The second additive was a pyrrhotite concentrate. These additives were added at the rate of 5 W% (equivalent FeS) of coal rate. Hydrogen sulfide was injected continuously to provide sulfur at S/Fe atomic ratio of two. Partially deactivated supported catalyst (Shell S-317 NiMo) recovered from the previous runs was used. The test was conducted using constant conditions of space velocity (67 lb coal per hour per ft³ of supported catalyst per stage) and reactor temperatures (750°F in the first stage and 825°F in the second stage).

The process performance was marginally better with the iron oxide additive than with no additive. Coal conversion was higher by about 1.5 W% (MAF), and 975°F⁺ conversion and C₄-975°F yield were higher by about 2 W% (MAF). With pyrrhotite additive, coal and resid conversions were higher by less than 1 W%, and the distillate yield was lower due to significantly higher gas yield.

RUN 227-62(CC-5) - CTSL™ EVALUATION OF BLACK THUNDER MINE COAL AFTER THERMAL PRETREATMENT

This run examined the atmospheric pressure slurry pretreatment of the coal at 500-600°F, drying of the coal when mixed with slurry oil, and addition of H₂S during liquefaction operations to find the effect upon catalytic performance. The catalyst for this run was presulfided using TNPS as the presulfiding agent, in place of the DMDS that had been used in previous runs.

The pretreatment did not have a detrimental impact upon coal convertibility or liquid product distribution. While some carbon oxides were generated in the pretreatment operations, any consequent reductions in overall process water and light gas yields as well as hydrogen consumption were not apparent. Initiation of H₂S addition during the run reversed declines in hydrogenation and denitrogenation performance, as well as stabilizing a trend of increasing residual oil yield, that had occurred earlier in the run.

The pretreatment produced some carbon oxides, 2-3% of coal, a very small amount of C₁-C₃ hydrocarbons, less than 0.1%, and water in excess of the nominal water content of the coal fed (D-2961 method), by 2-4%. There was very little difference in these results for the 500°F and 600°F pretreatment temperatures, excepting that the higher amounts of water were obtained at the higher pretreatment temperature.

The experimental coal conversions for the Run 227-62(CC-5) operations using pre-dried coal averaged 0.1% higher than the conversions for similar operations with coal that had not been thermally pretreated. For the operations with undried coal to the pretreater, and finally with H₂S addition to the feed gas, the experimental conversions averaged 0.3% lower than the projected values. These results indicate that there was essentially no impact upon the coal reactivity of the 500 to 600°F pretreatment, or of slurry drying the coal, or of H₂S addition to the process gas.

The combined pretreatment/CTSL™ operation produced 3-4 W% carbon oxides compared to yields of 0.3-1.4 W% obtained in the reference operation of Run 227-55(CC-1). However, the concurrent impacts of the pretreatment upon product structure that might be expected were not apparent from the run data. That is, water yields that might be expected to be lower by 1-2 W%, because of greater elimination of oxygen in the carbon oxides, actually averaged 0.7 W% higher in these operations with coal pretreatment than in the reference operations. Also, light gas yields which might have been expected to be lowered by about 1 W%, because of reduced opportunity for hydrocarbon synthesis reactions of the carbon oxides, actually averaged 1 W% higher in the operations with coal pretreatment. However, calculated water yields, using an oxygen balanced normalization procedure, indicate that the pretreatment lowered water yields by about 2 W%.

In this run, before the use of H_2S addition, hydrogen contents of the liquids were lower, while nitrogen contents were higher, than during the reference operations in earlier runs. Rather than reflecting the use of coal pretreatment or of TNPS presulfiding, the probable cause of these differences was the substantial quantities of a relatively low hydrogen content, high nitrogen content, distillate obtained from the Wilsonville Coal Liquefaction Facility which was used as make-up oil to compensate for the oils vaporized at the pretreatment temperatures.

In conclusion, the hot pretreatment produced in a minor reduction in oxygen but did prove that operation in the temperature range of 500-600°F has no detrimental effect on performance, in fact has no noticeable effect either positive nor negative on process performance. Commercially, however, a hot slurry mix system would conserve energy and improve overall process efficiency.

It was also noted that continuous addition of H_2S improved performance by stabilizing HDS, HDN and resid conversion.

**RUN 227-64 (CC-7) - REACTOR CONFIGURATION STUDY:
CATALYTIC/THERMAL VS. THERMAL/CATALYTIC
WITH DISPERSED IRON OXIDE ADDITIVE**

The objective of this run was to study the effect of two different reactor configurations, catalytic/thermal and thermal/catalytic, in a two-stage liquefaction system with sub-bituminous coal. The catalytic stage is the normal ebullated-bed reactor holding supported catalyst while the thermal stage does not contain any supported catalyst. The run was conducted using an iron oxide additive (dispersed catalyst). This additive had been tested before in Run 227-61(CC-4) and was found to improve process performance. This additive would provide the only catalytic activity in the thermal stage and would provide an incremental activity in the catalytic stage. The catalytic stage contained partially deactivated NiMo catalyst. Hydrogen sulfide was injected continuously at about 5 W%.

In catalytic/thermal mode of operation, increasing the thermal stage temperature from 825°F to 840°F increased the C_4 -975°F distillate by 2.0 W% (maf) as the 3.5 W% (maf) higher 975°F+ conversion outpaced the 1.9 W% (dry coal) higher gas yield. With the thermal stage at 840°F, the catalytic/thermal configuration gave higher coal and 975°F+ conversions relative to the thermal/catalytic configuration. The coal and 975°F+ conversions were 93.3 W% and 89.0 W% for the catalytic/thermal configuration and 91.2 W% and 87.8 W% for the thermal/catalytic configuration.

The 975°F+ conversion, distillate yield, and product quality in Run 227-64(CC-7), with only one catalytic stage, were inferior to these measures of performance in Run 227-61 (CC-4), with supported catalyst in both stages. Compared with the

catalytic/thermal configuration in Run 227-64(CC-7) Condition 1, the 975°F conversion was 2.0 W% (maf) higher, the C₄-975°F distillate yield was 6.1 W% higher, and the denitrogenation was 19.5 W% higher for the catalytic/catalytic operations.

RUN 227-68 (CC-10) - CTSL™ PROCESSING OF NEW MEXICO COAL WITH ON-LINE HYDROTREATING

The objectives of this run were to study on-line hydrotreating of CTSL™ liquid products and to evaluate the performance of New Mexico McKinley Mine coal in the CTSL™ process. The concept of on-line hydrotreating is attractive because one can make use of the high hydrogen partial pressure in the reactor effluent vapor stream to hydrotreat the light liquid products without having to use a separate high pressure section.

The on-line hydrotreating was very effective in reducing the heteroatom contents of the distillate and caused significant saturation of the aromatics, especially in the middle distillate range. The sulfur contents of the hydrotreated Separator Overhead were between 2 and 14 ppm. The nitrogen contents were reduced to 9 ppm with the lightest hydrotreater feed, but were 89 and 72 ppm with the heavier hydrotreater feeds.

The New Mexico coal was not as active as the Wyoming coal in terms of coal or resid conversion, but it yielded more distillate because of slightly less gas production and much less water production.

RUN 227-69 (CC-11) - PREPARATION OF PRODUCT SLURRY FOR FILTRATION TESTS

The primary objective of this run was to produce about 20 kg of atmospheric bottoms to evaluate an alternative solids-separation technique, namely the pressure filtration technique developed by British Coal Board. Another objective was to obtain data on the on-line hydrotreating of Black Thunder coal.

The hydrotreater did not perform as well in this run with Black Thunder coal as it had in Run 227-68(CC-10) with New Mexico coal. The nitrogen contents of the Separator Overhead were reduced to 50 and 60 ppm for the hydrotreater temperatures of 640 and 670°F, respectively. However, the hydrotreater temperatures were not accurately known due to the failure of the thermocouple in the center section of the hydrotreater.

The run was conducted with a continuously injected H_2S stream because prior runs had indicated that it might mitigate catalyst deactivation. There was indeed very little decrease in resid conversion in the first 11 days of the run. The heavy liquid products also showed stable H/C ratios. However, hydrodenitrogenation was affected by catalyst deactivation.

Filtration tests were conducted by British Coal Board. They found that the bottoms could be filtered effectively, and they optimized variables such as filtration temperature and pressure. Filter aids to reduce cake resistance were found not to be beneficial. Filter screens with apertures of size larger than the solids size could be used; however, sluicing to remove partial screen blinding was found to be necessary. Washing of filter cake with a light liquid was required to recover trapped liquid product.

RUN 227-70 (CC-12) - EVALUATION OF REJUVENATED CATALYST

The objective of Run 227-70 (CC-12) was to evaluate the performance of rejuvenated catalyst that had been recovered after earlier CTSL™ bench unit operations on Black Thunder Mine (Wyoming) coal. The rejuvenation process, developed by HRI for H-Oil catalysts, removes contaminant metals by acid washing and recovers the surface area by carbon burnoff. Most previous rejuvenation process development involved cobalt molybdate catalysts. This run was the first operational test of a rejuvenated nickel molybdate catalyst and the first use of rejuvenated catalyst for coal liquefaction.

The 12-day run included a single condition of 750°F first stage temperature, 800°F second stage temperature, and 45 lb/hr/ft³ (each reactor) catalyst space velocity. These conditions were identical to those in Run 227-55(CC-1) Condition 1, with which the results were compared.

The rejuvenated catalyst had residual oil conversion activity, hydrogenation activity, and denitrogenation activity essentially that of fresh catalyst and markedly greater than that of catalyst aged in CTSL™ operations. There were slightly lower yields of distillate product with the rejuvenated catalyst because of lower coal conversion and higher carbon oxides yields, factors which might not be associated with the catalyst performance.

The rejuvenated catalyst was of much lower physical strength, and very much shortened particle length, than fresh catalyst, and a more durable initial catalyst might be more appropriate if rejuvenated catalysts are to be used commercially. The fact that the rejuvenated catalyst showed superior performance despite its diminished physical and chemical properties indicates that the rejuvenation process has potential. Modifications of the rejuvenation process to decrease this degradation could lead to even better performance.

RUN 227-71 (CC-13) - CO₂ AND LIGHT DISTILLATE SLURRYING

The objectives of Run 227-71(CC-13) were to evaluate CO₂ or a vaporizable distillate as feed slurring agents for coal to the CTSL™ operation.

A feed slurring agent that would vaporize in the reactor would afford less dilution, than with the usual slurring agents, of the resulting slurry phase in the reactor and promote more complete reaction of the coal and heavy primary liquid products to lighter liquids. CO₂ has been demonstrated as a feasible slurring agent for pipeline transport of coal and might be applied for this use in CTSL™ liquefaction. However, on the small scale of Bench Unit operations it was not possible to maintain CO₂/slurry feed to the unit, and the test program was modified to study the impact of CO₂ feed to the process while using the conventional CTSL™ practice of slurring the coal with recycled filtered liquid. Also, there was an attempted operation using a light gas oil as slurring agent in place of the filtered liquid, which was maintained for 40 hours before problems developed in maintaining feed slurry flow.

The CO₂ fed in the operations ranged from 0 to 0.6 lbs/lb of the coal fed, while there was an additional solvent feed of about 1.2 lbs/lb coal, either recycle filtered liquid obtained by filtration of the reactor product slurry, or an extraneous naphtha/light gas oil solvent that had been produced in other coal liquefaction operations.

The added CO₂ was largely reacted with hydrogen to form, about 58%, CO, CH₄, and H₂O. As a result, an increase in hydrogen consumption of 3.8 W% dry coal was observed. Increased coal conversions, by 1-2%, were obtained during the operations with CO₂ addition. The addition of CO₂ had no clear impact upon the conversion of residual oil to distillates, so that distillate oil yields were increased only by the degree of increased coal conversion. In the final operations with CO₂ addition with the highest proportion of CO₂ addition, the products hydrogen contents, nitrogen contents, sulfur contents, cyclohexane and toluene insolubles contents were poorer than in any other CTSL™ operations with Black Thunder Mine coal.

In the operation using light gas oil as coal slurring oil the coal conversion, 94.0%, was the highest of any CTSL™ operation with the Black Thunder Mine coal. There was probably little impact upon the kinetics of conversion of residual oil to distillates, although there was a relatively high yield of residual oil because of the lack of residual oil recycle. With recycle of some residual oil along with the use of light distillate as the principal coal slurring agent, it is considered that increased coal conversion can be obtained while maintaining low residual oil yield. The type of oil used for this purpose in this run, 480°F volume average boiling point, is probably nearly optimum in maintaining an acceptable slurry environment at reactor conditions.

RUN 227-75 (CC-15) - EVALUATION OF A PRE-DISPERSED IRON CATALYST IN TWO-STAGE LIQUEFACTION

The objective of this run was to evaluate the performance of the dispersed iron-based catalyst in the liquefaction of Black Thunder Mine Coal in a bench-scale continuous flow unit with a thermal-catalytic configuration.

The iron catalyst precursor was impregnated on the coal matrix using an incipient wetness technique developed by Pittsburgh Energy Technology Center (1). Black Thunder Mine coal was impregnated with hydrated iron oxide (FeOOH) at 5000 ppm of iron using this technique and was liquefied in thermal-catalytic mode. The iron catalyst precursor was activated in a pretreating stage (at 527 or 570°F) prior to the thermal stage at 800°F. The catalytic stage was an ebullated bed reactor at 775°F consisting of Shell S-317 NiMo catalyst. The space velocity was 43 lb/hr/ft³ catalyst. The performance of this system was compared with that obtained without the use of any dispersed iron catalyst.

Run CC-15 (227-75) was successfully completed with three conditions with FeOOH impregnated coals and one condition with untreated Black Thunder Mine coals. At relatively low concentration of 0.5 W%, the dispersed iron additive improved distillate yield, coal and 975°F+ conversion. Compared to the condition with no dispersed catalyst, the coal conversions were 1.9 W% higher, averaging 92.6 W% (maf), and the resid conversions averaged 3.4 W% higher, declining from 89.1 W% (maf) in Period 5 to 85.3 W% in Period 14. Similarly, the C₄-975°F distillate yield, which decreased from 66.1 W% (maf) to 60.2 W%, was significantly lower in Condition 3, with no dispersed catalyst. The hydrogenation activity of the dispersed iron catalyst was evident in the lower hydrogen contents of both the first and second stage products. Overall performance was similar to that of the two stage CTSL™ process.

However, the impregnation procedure introduced additional nitrogen to the coal matrix and resulted in a higher nitrogen product. The economics of the improved process performance should be evaluated against the costs for impregnating the iron catalyst precursor as well as additional hydrotreating cost.

- (1) Cugini, A.V., et al, DOE/PETC, "A Highly Active Disposable Iron Catalyst for Coal Liquefaction", 201st National ACS Meeting, Atlanta, GA, April 14-19, 1991.

RUN 260-03 - PDU CATALYTIC TWO-STAGE LIQUEFACTION OF BLACK THUNDER COAL

The objective of the PDU operation was to scale-up the CTSL™ process with subbituminous coal and to demonstrate resid and heavy gas oil extinction in catalytic two-stage liquefaction with equilibrated catalyst using a commercially viable solids separation process. A 26-day run in HRI's Process Development Unit 260 was planned using Black Thunder mine (Wyoming) coal. The major modification of the PDU for this operation was installation of a vertical-leaf pressure filter for separation of solids from the reactor liquid flash bottoms slurry.

Pumping and filter-leaf sealing problems with the filtration system caused initial delays in the PDU operations. Later the run was interrupted several times, most often because of catalyst particles in downstream valves. A total of 13 days of coal operations were completed with five interruptions. The original run plan had specified 28 days of operation with the ultimate conditions of 775°F first stage temperature, 825°F second stage temperature, 44 lb coal/hr/ft³ (ea. stage) catalyst space velocity, and 1.5 lb catalyst/ton dry coal catalyst replacement rate for each stage.

Because of the short duration of continuous operations, accurate product yields could not be calculated. As required for resid extinction, the goal of returning all of the vacuum bottoms to the process was achieved. However, there was significantly more residual oil net product remaining on the filter cakes than had been expected. The coal conversions varied between 78 W% and 88 W% of maf coal in these abbreviated operations, which had not attained full severity.

After repairs, modifications, and improvements were made to the filtration system, approximately 30 filtrations were completed. All of the filtration steps were operational, but the cakes generally remained sticky, presenting some problems in forming a consistent, dry cake, and probably causing the relatively high quantity of liquid remaining on the cake. Generally, the filter cakes were 45 to 60 W% solids. Further modifications in procedure are required to make filtration a viable solids separation technique.

TABLE 1					
Bench-Scale Runs					
Run	Coal	Objectives	Conditions	Remarks	
CC-1 22 Days	Black Thunder	Temperature sequencing	1st: 750-817°F 2nd: 796-825°F	Six conditions completed, yields and conversions similar for same nominal combined severity; 2 W% higher dist. than Clovis Point.	
CC-2 15 Days	Black Thunder	Volume Experiment	$V^{\text{stage1}} = 2 \times V^{\text{stage2}}$	Same combined residence time gives slightly lower coal conversion and dist. yield due to lower severity. Larger volume provides more hydrogen.	
CC-3 12 Days	Black Thunder	Iron-Mo spherical catalyst test	CTSL™ 750/800°F, 750/825°F	On volume basis, Fe-Mo is poorer than Ni-Mo (especially product quality).	
CC-4 18 Days	Black Thunder	Dispersed catalyst + supported catalyst Continuous H ₂ S feed	Iron oxide (magnetite), iron pyrrhotite	Cont. H ₂ S improves yields with sub-bit. coals; 5% Fe ₃ O ₄ improves yields.	
CC-5 20 Days	Wyoming	Hot slurry pretreatment	500-600°F soaking	No significant reduction in O ₂ content; increases CO _x by 3 W%; reduces water by 2 W%.	
CC-6 12 Days	Illinois #6	Oil Agglomeration cleaned coal	Coal cleaned by spherical agglomeration with heptane and asphalt	Increases conversion by 1 1/2% and distillate yield by 6%.	

TABLE 1

Bench-Scale Runs

Run	Coal	Objectives	Conditions	Remarks
CC-7 20 Days	Black Thunder	Dispersed/Support catalyst and reverse sequence	Iron oxide and NiMo on alumina catalyst	Disp/Support configuration decreases dist. yields slightly compared to support/dist, but improves product quality; both configurations are inferior to support/support.
CC-8 17 Days	Illinois #6	*OTISCA* micronized, cleaned coal	Added coal water slurry drying system.	Improves conversion; however, not as good as spherical agglomeration.
CC-9 8 Days	Illinois #6	Collect sample for delayed coking test	750-/815°F Foster-Wheeler coking test	Delayed coker conversion is 40% of resid to oil.
CC-10 16 Days	New Mexico Coal	On-line hydrotreating of distillates	CTSL™ 750/815° Hydrotreater 650°F	Nitrogen and sulfur contents are reduced to under 10 ppm.
CC-11 13 Days	Black Thunder	Collect sample for filtration study	Point of Ayre; U.S. filter arrangement	Acceptable filtration rates.
CC-12 12 Days	Black Thunder	Rejuvenated Catalyst Evaluation	Spent NiMo catalyst, acid washed, carbon burn-off	Very good performance; better hydrogenation.
CC-13 14 Days	Black Thunder	CO ₂ /coal slurries	Various CO ₂ concentration Different solvents	Low-boiling solvent. Increases conversion by 3% max at 94%; more CH ₄ (14%), CO (11%), water (43%).

TABLE 1

Bench-Scale Runs

Run	Coal	Objectives	Conditions	Remarks
CC-14 21 Days	Illinois No. 6	PETC pre-dispersed iron oxide hydroxide catalyst	Pretreatment 527°F 1st stg: 800/825°F 2nd stg: 775°F (with supported cat.)	First condition at mild temperature; yields equal to CTSL™.
CC-15 14 Days	Black Thunder	PETC pre-dispersed iron oxide hydroxide catalyst	Pretreatment 570°F 1st stg: 800/825°F 2nd stg: 775°F (with supported cat.)	High coal conversion; equivalent yields to CTSL™; higher gas make.
CC-16 14 Days	Illinois No. 6	Evaluation of AO60 NiMoly Catalyst	CTSL 1st stg: 800/825°F 2nd stg: 775°F	Catalyst performance equivalent to Shell 317 and Amocat catalysts.

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SECTION I

RUN 227-55(CC-1) - CTSL™ EVALUATION OF BLACK THUNDER MINE COAL

INTRODUCTION

Run 227-55(CC-1) was a CTSL™ bench unit evaluation of Black Thunder Mine, Wyodak Anderson Seam (Wyoming), sub-bituminous coal obtained from the Thunder Basin Coal Co. This evaluation was referenced to the more extensive evaluation of a similar coal from the Clovis Point Mine. In addition, the Run 227-55(CC-1) operation studied a wider range of patterns of first and second stage temperatures than had been used previously in the CTSL™ program, with the second stage temperature lower than, equal to, and higher than the first stage temperature.

The Black Thunder coal had good liquefaction performance very close to that of the Clovis Point coal, with a probable processing advantage of having about 3 W% lower ash content. The processing results for the various configurations of first and second stage temperatures appeared to follow a common trend when the combined severity of the two stages was held at a nominally common value.

SUMMARY

The Black Thunder Mine Coal was tested in a 23-day run in the CTSL™ Bench Unit. This operation studied 4 conditions of various first and second stage temperature, with one replication to evaluate catalyst aging, first using a second stage temperature 50°F higher than the first stage temperature, then a more severe condition with second stage temperature 75°F higher than the first, and then the same combined stage severity using equal stage temperatures, and the last with 50°F lower second stage temperature. A fifth set of conditions used a coal feed rate 50% higher than had been used in the other operations.

The maximum yield of C₄-975°F distillate oil was 67.9 W% of maf coal, which was obtained during the first operations at the higher combined stage severity using the higher second stage temperature. Catalyst deactivation lowered this distillate yield by 0.2-0.4% per day of coal operations (0.7-1.4% decrease per 100 pounds coal processed per pound of catalyst). The distillate yields with the equal first and second stage temperatures, and with lower second stage temperature appeared to follow the trend indicated by the reference operation with the higher second stage temperature.

Samples of first stage products indicated that hydrogenation was favored in the lower temperature stage, whether that stage was the first or second stage.

Comparison with the results with the Clovis Point coal, indicates an advantage in C₄-975°F distillate yield of about 2 W% of dry coal for the Black Thunder Mine coal. This difference reflects for the most part the lower ash content of the Black Thunder coal, in part offset by 0.5-1.0% lower coal conversion, and 0.5-1.0% higher light gas yield with that coal. Residual oil yield and catalyst deactivation were essentially the same for the two coals. The hydrogen contents and nitrogen contents of the liquid products from the Black Thunder coal were comparable to those of the Clovis Point coal products. The sulfur contents were somewhat lower in the Black Thunder coal products.

Apart from a mechanical failure of the internal recycle pump drive in the seventh day of the run there were no operating problems during the run. The amount of deposits found in the reactor and separators after the run were relatively small. The catalyst recovered from the reactors after the run was in good condition, and the amount of catalyst recovery was reasonably high indicating acceptable catalyst attrition when processing this coal.

SCOPE OF WORK

The coal used in Run 227-557(CC-1) was characteristic of commercial shipments from the Black Thunder Mine. The catalyst for both stages was Shell S-317 $\frac{1}{32}$ " nickel molybdate on alumina extrudates, a commercially available catalyst. This catalyst shipment was the same as that used in the CTSL™ demonstration run for Illinois coal, Run 227-47(I-27).

The operating conditions for the six Conditions used during the run are summarized in *Table 1*. Four combinations of first and second stage temperature were used: 750 and 800°F, then 750 and 825°F (replicated for definition of catalyst deactivation), followed by 796 and 796°F, and finally 817 and 767°F (the last two sets giving the same nominal combined stage severity as the second set assuming 45,000 Btu/lb mole activation energy). The final Condition was with the coal feed rate increased by 50% from the value used in other operations. After the Condition 1, solvent recycle was changed from entirely filtered liquid (solids free) to a blend containing about one-third solids-containing unfiltered Topped Separator bottoms product slurry from the system. The change was prompted by difficulty in maintaining the target expansion of the ebullated catalyst beds in the reactors, because of the light product that was being generated. Solids were included in the solvent recycle to get a higher density material circulating in the reactor. Also, the temperature of the atmospheric still, removing middle distillates from the Topped Separator Bottoms, was lowered at this time to put this fraction in the solvent recycle pool so as to maintain solvent balance for the operation.

Samples of the slurry circulating in the first stage were taken for each of the Conditions for use in evaluating the performance of the individual stages.

PROGRAM RESULTS AND ANALYSES

RUN 227-55(CC-1)

This section discusses the conversions, product yields, process performance and product quality for Run 227-55(CC-1). *Table 2* is the operating summary for the run, giving the principal operating conditions for each Period (day) and normalized product distributions for periods which were considered to represent equilibrated results. (Note in this table the ash values are on an SO₃-free basis, for reasons which are discussed below in the section concerning coal analyses.)

COAL CONVERSION

Figure 1 graphically summarizes the coal conversions against operating period, identifying the principal operating conditions for each of the points.

Coal conversion ranged from 86.4 to 92.4% of maf (moisture and ash free) coal for the equilibrated intervals of operation. The highest level of coal conversions, averaging 91.8%, were maintained in the Condition 2 through Condition 5 interval of the run, Periods 9 through 19, with the varied configurations of first and second stage temperatures having a nominally equivalent combined severity. The initial Condition 1 operations with 25°F lower second stage temperature and with no solids-containing TSB in the recycle, gave the lowest level of coal conversions, averaging 86.7%. The final Condition 6 operation, with coal rate increased by 50% at the more severe temperature configuration, gave a coal conversion of 87.3%, a reduction of 4-5% because of the increase in coal feed rate.

The trends in coal conversion follow a rational kinetic pattern in which increased coal conversion is obtained with increased temperature, with inclusion of some unreacted solids in the recycle solvent, and with lower coal feed rates. The coal conversions with Black Thunder coal were generally lower, by about 3%, than would have been expected with the Clovis Point Wyoming coal, tested previously, using the same operating conditions. The following tabulation compares the Black Thunder coal results of Run 227-55(CC-1) with those that would have been expected with the Clovis Point coal on the basis of the kinetic correlation of the Clovis Point coal operating results:

227-55 (CC-1)	227-55 (CC-1)	Clovis Point
Condition	Coal Conversion	Projected Conv.
1	87.2	90.5
2	91.1, 91.4	94.9
3	92.3, 91.4	94.7
4	92.4, 92.3	95.4
5	92.0, 91.8	94.9
6	88.6, 87.3	91.7
Average	90.4	93.7

In kinetic terms the difference in performance can be rationalized by assuming that the reaction rate constants for the Black Thunder coal were 66.3% of those for the Clovis Point coal.

The increase in coal conversion between the Condition 1 operation and the Condition 2 operation was in part due to the increase in second stage temperature from 800°F to 825°F, and in part due to incorporating some solids containing Topped Separator Bottoms in the solvent recycle. The kinetic model with the modified reaction rate constants give some insight into the relative impact of these two factors, as shown in the following tabulation projecting the impact of stepwise changes in recycle flows and then reactor temperatures:

<u>Condition</u>	<u>Second Stage Temperature, °F</u>	<u>Solv. Recy., Lb/Lb</u>		<u>Projected Conversion</u>
		<u>PFL</u>	<u>TSB</u>	
1	800	1.19	0.00	86.3
1 (mod)	800	0.84	0.38	88.6
2	825	0.84	0.38	92.0

Ostensibly about $\frac{2}{5}$ of the increase in coal conversion was due to substituting Topped Separator Bottoms (TSB) for a portion of the Pressure Filter Liquid (PFL) solvent recycle, and the balance of the increase was due to the increased second stage temperature.

The experimental impact of increasing the coal feed rate between Condition 5 and Condition 6 operations, lowered conversion by about 3.2-4.7%, is in reasonable accord with a projected change of 4.0%. The apparent small impact upon coal conversion of differing configurations of the stage temperatures in Conditions 2, 3, 4, and 5 is also in accord with the projections from the modified kinetic model.

975°F* CONVERSION

Figure 2 is a summary of the 975°F* Conversions (100 minus unconverted coal minus residual oil yield) through the run, plotted against operating period (Days) with identification of the principal changes in operating conditions.

975°F* conversion ranged from 81.5% to 89.6% of maf coal. The highest level of 975°F* conversion, an average of 88.6%, was apparently maintained over the Condition 2 through Condition 5 interval of the run with the various stage temperature configurations with a nominally common combined severity. The lowest level of this conversion, averaging 82.1%, was in the final operations of the run during Condition 6 with the coal feed rate increased by 50%. The initial operation of the run, Condition 1 with the second stage temperature lower by 25°F gave an average 975°F* conversion of 84.6%. There was no definite trend

of this parameter with increasing catalyst age through the operations of Condition 5, at 19 days of coal operations having processed 540 lbs coal/lb catalyst(single stage inventory).

The impact upon 975°F+ conversion of the various changes in conditions principally reflect the corresponding changes in coal conversion. The change of 4% between Condition 1 and the Condition 2/5 results is the same as the change in coal conversion, indicating virtually the same 975°F+ residual oil yield for the two modes. The change of 6.5% in 975°F+ conversion between the Condition 2/5 and Condition 6 was 2% greater than the difference in coal conversion for the two operating modes, indicating about 2% higher residual oil yield for the higher coal rate operations of Condition 6.

Normalized Product Distribution

Normalized product distributions for periods of equilibrated operations are included in *Table 2*. Yields, as a percentage of dry coal fed, are plotted against catalyst age (days) in *Figures 3 through 16*.

C₁-C₃ Gas Yields

Figure 3 summarizes the normalized yield of C₁-C₃ hydrocarbon gases through the run. The gas yields were very erratic through the run; particularly evident in Condition 5 (Periods 18 and 19 results) where the gas yield differed by 3.6 W% (a factor of 1.4) in operations at common conditions with no apparent upsets. A similar pattern to a lesser degree was evident during other operating intervals of the run.

Samples of product gas are taken three times each day (once each shift) and are in effect grab samples taken into flow through sample bottles. This practice has been satisfactory in past CTSL™ operations in that the consecutive samples have been reasonably consistent in analysis. However, in Run 227-55(CC-1) a very erratic pattern appeared exemplified by the six gas analyses from Periods 18 and 19, where the hydrocarbon content changed by a factor of as much as 2.6 for consecutive gas samples.

The problem in sampling the vent gas stream, which has three constituents: 1) the high pressure vent gas, 2) flash gas from depressuring the hot separator bottoms, and 3) flash gas from depressuring the cold separator liquids. The latter two streams (relatively hydrocarbon rich, 75% and 30% hydrogen content compared to 90-95% hydrogen in the high pressure vent, when these streams were sampled during single stage coal liquefaction tests) are intermittent while the first flow is continuous. Observation of action of the hot separator bottoms let-down valve indicates a pattern where this valve is closed for up to 80% of the time, on a cycle of about 7 minutes. This pattern would indicate a 20% probability of getting a hydrocarbon rich sample, and 80% probability of a lean sample.

To improve the sampling of the gas there will be modification of the sampling system to get a more representative sample, probably by inducing a mixed sample by installing a surge volume upstream of the sample bottle. The characteristic sample could be obtained by adding about 1-2 cubic feet surge volume in the sample line upstream of the sample tube. Whether this surge would require mechanical mixing or whether diffusion effects would be sufficient for homogenization of the sample has still to be determined.

The C_1 - C_3 gas yields during Run 227-55(CC-1) ranged from 5.7 to 12.5 W% of dry coal (or 5.7 to 10.3 W% if Period 18, Condition 5, result is ignored). This yield was at a more or less common level, averaging 8.9 W%, for the Condition 2 through 5 operations at nominally constant combined two-stage severity. The yield was 0.9-3.2 W% lower than this average during the Condition 1 operations, with 25°F lower second stage temperature. The yield was 1.2-2.7 W% lower than that average during the Condition 6 operations with 50% increased coal feed rate.

The gas yields, as determined, with Black Thunder coal in Run 227-55(CC-1) were generally higher than would have been expected in comparable operations with Clovis Point (Wyoming) coal. A kinetic model based on the Clovis Point CTSL™ operations projected yields for the various modes of operation used in Run 227-55(CC-1) that averaged 1.5 W% lower than the yields obtained during Run 227-55(CC-1), 6.6 W% compared to 8.2 W%.

It is not clear which parameters in the Clovis Point correlation should be adjusted to give better correspondence to the Black Thunder gas yields. However, for additional insight into the effect of the changes in operating conditions during Run 227-55(CC-1), projections were made after simple adjustment involving the apparent rate of gas formation from the slurry phase components. With this adjustment, to give the same projected average gas yield during Run 227-55(CC-1) as obtained experimentally, projected yields were obtained for each of the Conditions of the run, which are indicated by the lines shown in *Figure 3*. These latter projections indicate somewhat different impacts of the changes in operating conditions than those noted above. The increase in second stage temperature from 800 to 825°F, between Condition 1 and Condition 2, is projected to increase gas yields by 3.2 W%. The operation with equal stage temperatures, Condition 3, is projected to give a gas yield 2.0 W% lower than that for the reference operation with 75°F higher second stage temperature, Conditions 2 and 5. The operation with 50°F higher first stage temperature, Condition 4, is projected to give a gas yield 0.7 W% lower than that reference operation. The operation with 50% higher coal feed rate, Condition 6, is projected to give a gas yield 2.0 W% lower than that of the reference operation. These projected changes are somewhat greater than the differences in the nominal average yields for each of the Conditions, and better correspondence would be expected if a lower activation energy were employed than the one used in the correlation, 102,000 Btu/lb mole. The activation energy of 45,000 Btu/lb

mole, as used in setting the temperature configurations of Conditions 3 and 4, gave a fairly close correspondence to the apparent impacts of the temperature changes between Conditions 1 through 5. However, the considerable scatter of the gas yields during Run 227-55(CC-1) is fairly weak support for such a modification.

C₄-390°F Naphtha Yields

Figure 4 summarizes the C₄-390°F naphtha yields through Run 227-55(CC-1). C₄-390°F naphtha yields ranged from 15.6 W% of dry coal in Condition 6 operations, with the higher coal rate, to 22.7 W% in Condition 4 operations, with the first stage temperature 50°F higher than that of the second stage.

In part, the erratic gas analyses, discussed above in connection with the C₁-C₃ gas yields, contributed to some scatter in the naphtha yield. This scatter was in the C₄-C₇ in gases which amounted to about one-fourth of the naphtha yield. Considerably less scatter was evident in the portion of the naphtha that was collected in separator overhead condensate from the reactor product vapors, the IBP-390°F product fraction. *Figure 5* summarizes the IBP-390°F naphtha yields through the run, which showed more regular pattern than that of the C₄-390°F yields. The correlating lines for C₄-390°F yields of *Figure 4* are based on the IBP-390 correlations of *Figure 5* with an adjustment for C₄-C₇ yields, which were taken to be 0.34 times as great as the IBP-390°F yields for the corresponding operation, on the basis of the averaged results of the run.

Considering the IBP-390°F yields as presented in *Figure 5*, the increase in second stage temperature from 800°F to 825°F between Condition 1 and Condition 2 resulted in an increase in IBP-390°F naphtha yield of about 3 W% of dry coal (or about 4 W% increase in C₄-390°F naphtha yield). In the interval between the Condition 2 and Condition 5 operation, there was apparent a slight down trend in these yields by about 0.12 %/day (statistical confidence level of 94.5% and a similar trend was indicated in the CTSL™ operations with Clovis Point Wyoming coal). The Condition 3 result, with equal stage temperatures, was not clearly different from this trend. However, the Condition 4 results, with the first stage temperature 50°F higher than that of the second stage, had naphtha yields about 2-3 W% higher than that of the Condition 2/5 trend. The operations of Condition 6, with 50% increase in coal feed rate, had naphtha yields that were lower by 3.5-4.5 W%.

These naphtha yields correspond fairly closely to those that would have been expected with the Clovis Point Wyoming coal, although there were some differences in the degree of the impact of the condition changes. The following tabulation compares, for representative operations, the experimental naphtha yields with Black Thunder coal in Run 227-55(CC-1) with the yields projected on the basis of the kinetic correlation of the Clovis Point coal CTSL™ results.

Run 227-55 (CC-1)		C ₁ -390°F Yield, W% of Dry Coal	
<u>Condition/Period</u>	Experimental	Projected	Projected
	<u>Smoothed Data</u>	<u>Clovis Corr.</u>	<u>Mod. Act. Energy</u>
1/6	17.2	16.0	17.1
2/10	21.1	21.5	21.5
3/13	20.6	17.6	18.6
4/16	22.7	19.3	19.8
5/19	19.7	20.0	20.0
6/22	15.4	16.6	16.6
Average	19.5	18.5	18.9

The experimental results for Conditions 2 and 5, with 750 and 825°F stage temperatures, correspond closely to projections from the Clovis Point coal correlation. However, the experimental impact of the change in second stage temperature from 800°F to 825°F between Condition 1 and Condition 2, here 3.9 W% yield, was less than expected from the Clovis Point correlation, 5.5 W%. Lowering the value of activation energy used in the correlation, 118,000 Btu/Lb-Mole, to a value of 83,000 Btu/mole gives the results in final column of the above tabulation, resulting in a closer correspondence to the apparent impact of the change in second stage temperature. Even with this change of activation energy, the experimental naphtha yields of Conditions 3 and 4, with the modified configurations of the temperatures of the two stages, were 2-3 W% higher than the projected yields. Also, the experimental impact of the 50% increase in feed rate between Condition 5 and condition 6 was higher than projected, a 4.3 W% change compared to 3.4 W%.

While the naphtha yield of Condition 4 was notably higher than those of the other Conditions, it does not necessarily reflect an improved selectivity to naphtha. *Figure 6* plots naphtha yields for the various modes of operation in Run 227-55(CC-1) against the C₁-C₃ yields for those operations. It is evident in *Figure 6*, that none of the modes of operation in the run had significantly improved selectivity of naphtha yield relative to gas yield.

390-650°F Light Distillate Yield

Figure 7 summarizes the yield of 390-650°F light distillate through Run 227-55(CC-1). The 390-650°F light distillate yield ranged from 25.3 to 29.7 W% of dry coal. The highest yield was obtained during the first operations of the run in Condition 1 and also during Condition 2 operations. The lowest yield was obtained during the Condition 5 operation after an extended interval through the Condition 2 to Condition 5 operations during which this yield declined steadily.

The trends during the run were predominately this decline in yield at a rate of about 0.33% per day of operations (99.0% statistical confidence level), a possibly lower yield by about 1.9 W% for Condition 1 operation with 750 and 800°F stage temperatures (87.3% statistical confidence level), and higher yield by about 3.1 W% for Condition 6 operations with the coal rate increased by 50% (98.0% statistical confidence level). The results for the various stage temperature configurations during Condition 2 through 5 operations appeared to follow a common trend.

The nominal increase in yield with increased second stage temperature between Condition 1 and Condition 2, corresponds to a reaction model much as that used for correlating naphtha yields, where a major factor in the product fraction formation is secondary reaction of slurry phase components which would be favored by higher stage temperatures. However, the higher yield of the light distillate fraction during Condition 6 operations with the higher coal rate is not consistent with such a simple model. A factor in the change could be the increase in the atmospheric still temperature for the Condition 6 operation, which lowered the concentration of the 390-650°F fraction in the solvent recycle from about 25% to 10%, affording less opportunity for secondary reactions of this component to lighter products.

650-975°F Heavy Distillate Yield

Figure 8 summarizes the yield of 650-975°F heavy distillate through Run 227-55(CC-1). The 650-975°F heavy distillate yield ranged from 8.5 to 15.5 W% of dry coal. Within this range these yields have a considerable scatter that cannot be definitely associated with changes of operating conditions during the run. Nominal trend lines are indicated in *Figure 8*, but the correlation as presented is uncertain, with a statistical confidence level of only 72%, and these trends are considerably different from the apparent impact of the variables indicated in earlier CTSL™ operations. Namely, in this run the yield of this fraction apparently decreased with increasing catalyst age (days of operations), but the earlier work showed little change or, if there was any, a small increase with increasing catalyst age. Also, here a possible increase in the yield of this fraction with an increase in second stage temperature is indicated, where the earlier work showed a considerable decrease in the yield with comparable increases in stage temperatures. The apparent impact in this run of increased yield of this fraction with increased coal feed rate is the same as the effect observed in the earlier CTSL™ operations.

975°F+ Residual Oil Yield

Figure 9 summarizes the yield of 975°F+ residual oil through Run 227-55(CC-1). The residual oil yield ranged from 1.5 to 6.7 W% of dry coal. The lowest yield was obtained in the first operations of the run, in Condition 1 with the 750/800°F configuration of stage temperatures, and the highest yield was obtained during

the final operations of the run, in Condition 6 with the coal feed rate increased by 50%. During the Condition 2/5 interval of the run the residual oil yield increased from about 2 W% to 4 W% following a trend that appeared to be common for three configurations of stage temperatures that were used over this interval. There is some scatter to these residual oil yield data, probably due to period-to-period material-balance fluctuations which impact after normalization largely upon the apparent net yield of PFL, the product stream containing the residual oil. A considerably more regular pattern respecting residual oil trends during the run is reflected in *Figure 10*, which presents the concentration of residual oil in the separator bottoms slurry downstream of the second stage reactor.

Referring to *Figure 10*, for the Condition 2/5 interval of the run, with a nominally common combined two-stage severity with various configurations of stage temperatures, there was a very regular increase in the residual oil concentration, by a factor of about 1.6 between the 9th day and 19th day of operations. During the Condition 1 operations with the lower second stage temperature, this concentration was higher, by a factor of about 1.4, than the extrapolated Condition 2/5 trend. The Condition 2/5 trend corresponds to that expected on the basis of the correlated Clovis Point CTSL™ results for Run 227-27, which projects, because of catalyst deactivation, an increase in residual oil concentration by a factor of 1.8 over a similar interval of operation with 750 and 825°F stage temperatures. The impact of lower second stage temperature in Condition 1 of Run 227-55(CC-1) upon residual oil concentration was somewhat greater than the effect indicated by the Clovis Point correlation, which projects a factor of 1.2 change in residual oil concentration, which might indicate a higher activation energy than used in the correlation, 23,000 Btu/lb mole.

Neither the residual yield plot of *Figure 9*, nor the residual oil concentration plot of *Figure 10* indicate a definite effect upon these residual oil parameters of the increase in coal rate between Condition 5 and Condition 6. The Clovis Point correlation projects an increase in residual oil concentration by a factor of 1.5 with such an increase in coal feed rate, and about 2 W% increase in residual oil yield, while the experimental results indicate a concentration ratio factor of no more than 1.1 and a yield change of 0.2-2.5 W%. Possibly the dilution of the residual oil content of the system as a consequence of the use of makeup oil, containing no residual oil, in Periods 20 and 21 was not sufficiently overcome during Period 22 to be considered and equilibrated condition.

This analysis indicates that catalyst deactivation with the Black Thunder coal feed is essentially the same as exhibited with the Clovis Point Coal in Run 227-27.

C₄-975°F Distillate Yield

Figure 11 summarizes the yield of C₄-975°F distillate through Run 227-55(CC-1). The C₄-975°F distillate yield ranged from 59.8 to 67.9 W% of dry coal. The highest yield was obtained during the Condition 2 operations with 750 and 825°F

stage temperatures, and the lowest yield was obtained in the Condition 6 operations with the higher coal feed rate. The results for the Condition 2/5 interval of the run appeared to follow a common trend with this yield declining by about 0.4 W% per day of coal operations. During Condition 1, with 750 and 800°F stage temperatures, the C₄-975°F distillate yield was about 5 W% below this trend line. In Condition 6, with 50% higher coal feed rate, this yield was about 2 W% below the trend line.

The nominal increase of 5 W% in the C₄-975°F distillate yield with the change in second stage temperature 800°F to 825°F reflected an increase in coal conversion by 5 W%, and a slightly lower residual oil yield, which was greater than the increase of about 2 W% in C₁-C₃ gas yield. However, as noted above, about 2 W% of the increase in coal conversion was ascribable to the substitution of solids-containing Topped Separator Bottoms for a portion of solids-free Pressure Filter Liquid solvent recycle. After this consideration, the apparent impact of the increase in second stage temperature would then be a 3 W% increase in C₄-975°F Distillate yield, with all other operating parameters unchanged.

The common trend in the yield of C₄-975°F Distillates through the Condition 2/5 interval of the run with the various configurations of stage temperatures corresponds to the small effect of the stage temperature changes upon coal conversion, light gas yield, and residual oil yield. The trend indicated in *Figure 11*, an 0.4% decrease per day of coal operations, is about twice the increase in residual oil yield over this interval, 0.2 W% per day, which might be considered a more realistic estimate of the rate of decrease in distillate yield over this interval.

The lower distillate yield for the higher coal rate operation of Condition 6, by 2 W%, is consistent with the lower coal conversion of that operation, by 4%, and the lower gas yield, by 2 W%, that were noted above. However, such a difference would correspond to no impact of the change upon yield of residual oil, which probably did increase by about 2 W% with the change in coal rate, but was not equilibrated in the time allowed for this operation. With such an adjustment the possible impact of the increase in coal rate was a decrease of 4 W% in C₄-975°F distillates yield.

Water and Carbon Oxides Yields

Figure 12 summarizes the water formation through Run 227-55(CC-1). Water formation ranged from 17.6 W% to 21.0 W% of dry coal. In large part this range is probably experimental scatter due to uncertainties in the amount vaporization of water from the feed slurry holder.

To evaluate this vaporization samples of the slurry being pumped to the reactors were taken at a number times during the run, with the following results:

<u>Cond.</u>	<u>Period</u>	<u>Feed Slurry Temperature</u>	<u>Water Contents, W%</u>		<u>Water Loss % of Coal</u>
			<u>Coal to Slurry</u>	<u>In slurry % of Slurry</u>	
1	7A	193	5.55	2.79	0.03
2	11A	180	5.52	1.55	2.36
3	14A	189	6.69	2.55	1.46
4	17B	200	5.37	1.88	1.50
5	20A	211	5.51	1.51	2.44
6	23A	306	5.36	No Sample	(4.5)

From change in collected water Yield.

These data, discounting the Period 11A samples, indicate a small degree of vaporization with the slurry held at 200°F or below, a moderate increase in vaporization with the temperature at 211°F, and virtually complete vaporization at 306°F. These measurements were used in the normalization calculations for water formation, summarized in *Figure 12*, which assumed that the water remaining with slurry in the Condition 6 corresponded to 0.5 W% of the coal fed.

The normalized net water yields do not present any clear reflection of the impact of the changes in operating conditions. However, inspection of the elemental analyses available permits a judgment as to the possible changes. One effect might be an effect of catalyst age manifest as increased oxygen content of the liquid products. While no direct analyses for such oxygen contents were made, the summation of the carbon, hydrogen, sulfur, and nitrogen analyses (reflecting an oxygen-by-difference value) indicate no appreciable trend through the run, see *Table 5 "Product Stream Analyses."* On this basis, it is judged that there would be little trend in water yield, at most the order of a minor fraction of one percent. A larger impact would be in changing proportions of unconverted coal for the various operating conditions, since this material still contains a high proportion of oxygen, with oxygen-by-difference values of 15.6 to 17.5 % of the ash-free products, see *Table 6 "First and Second Stage Product Fraction Analyses."* On this basis, it is judged that the Condition 1 operation, averaging 86.7% conversion, had a water yield about 0.9 W% lower than for the Condition 2/5 operations, which averaged 91.9% conversion. Also, the Condition 6 operation, averaging 88.0% conversion, had a water yield 0.7 W% lower than that of the Condition 2/5 interval. The correlating lines of *Figure 12* reflect this interpretation.

There was a possible upward trend in yield of the carbon oxides which is reflected in the tabulation below, although the problems with gas sampling, noted above, would also have an impact on this factor. The tabulation summarizes the oxygen contents of the water product, the carbon oxides, and total oxygen content, all as a percent of coal fed, for the six Conditions of the run:

<u>Condition</u>	Oxygen Content, W% of Coal Feed		
	<u>Water</u>	<u>Carbon Oxides</u>	<u>Total</u>
1	16.86	0.37	17.23
2	15.69	0.21	15.90
3	17.02	0.38	17.41
4	16.88	0.47	17.35
5	17.70	0.76	18.46
6	16.69	0.58	17.26
Average			17.27
O in Coal			1.46
Total			18.73

This accounting of oxygen is somewhat less than the oxygen-by-difference value of the feed coal, 20.18 W%. Some of the difference is in the oxygen content of the liquid products, although available analytic data indicate that this factor is of the order of 0.5 W% of the coal fed.

650-850°F Distillate, 850-975°F Distillate and 850°F⁺ Residual Oil Yields

The yields of 650-850°F distillate (MGO middle gas oil), 850-975°F distillate (VGO vacuum gas oil), and 850°F⁺ residuum through Run 227-55(CC-1) are summarized in *Figures 13, 14 and 15*, respectively. The yield of 650-850°F distillate followed the pattern of the yield of 650-975°F distillate, discussed above, and the yield of 850°F⁺ residuum followed the pattern of the yield of 975°F⁺ residuum, also discussed above.

The yield of 850-975°F distillate ranged from 0.9 to 2.6 W% of dry coal, averaging 1.8%, with no definite pattern within that range because of catalyst age or the changes in operating conditions during the run.

The yield of 650-850°F distillate ranged from 7.2 to 13.2 W% of dry coal. The trend lines shown in *Figure 15* have the same poor statistical justification that was noted above in the correlation of the 650-975°F distillates yield. The highest yields were generally obtained in the early operations of Condition 1 and Condition 2. There was a possible decline of about 3 W% over the Condition 2 through Condition 5 interval of the run. This yield possibly increased by 2 W% with the increase in feed rate during the Condition 6 operation.

The yield of 850°F⁺ residual oil ranged from 3.4 to 7.6 W% of dry coal. There was a probable upward trend in this yield by about 1.5 W% through the Condition 2 to Condition 5 interval of the run, essentially the trend in 975°F⁺ residual oil yield, as discussed above. There is no clear impact upon this yield either of the lower second stage temperature during the Condition 1 operation, or of the higher feed rate during the Condition 6 operation.

PROCESS PERFORMANCE

Conversion and normalized product distribution have been discussed in detail above. Coal conversion varied from 86.4 to 92.4% of maf coal with significant effects of the changes in stage temperatures, solids content of the recycle solvent, and coal feed rate, but no evident effect of catalyst age. 975°F+ conversion and C⁴-975°F distillate yield decreased with increasing catalyst age, increased with increased second stage temperatures, and decreased with increased coal feed rate. The changes in the configuration of the two stage temperatures, with nominally the same combined stage severity, had no clear impact upon the trends of these performance parameters.

The following table summarizes the averaged results for the various conditions during the two runs:

Cond.	Coal Feed	Solvent Recycle	Temper. °F		Catal. Age	W% of maf Coal		
	Lb/Hr /F ²	W% Solids Lb Coal	First Stage	Second Stage	Lb Coal /Lb Cat	Coal Conv.	975°F Conv.	C ⁴ -975°F Yield
1	44.9	0.00	751	800	140	86.7	84.6	63.7
2	45.1	3.44	750	824	270	91.2	88.6	67.6
3	46.8	3.70	796	794	356	91.8	88.4	64.8
4	45.3	3.64	817	767	442	92.3	89.0	64.6
5	45.4	3.56	750	824	532	91.9	88.5	61.8
6	69.2	5.58	752	824	642	88.0	82.1	59.5

Hydrogen Consumption

Figure 16 summarizes the hydrogen consumption through Run 227-55(CC-1). The hydrogen consumption ranged from 6.2 W% of dry coal to 8.3 W%. The highest hydrogen consumptions were during the Condition 2/5 interval of the run in the operations with various stage temperature configurations with nominally at the same combined severity. Over this interval the hydrogen consumption averaged 7.8 W% of dry coal. The correlating line in Figure 16 for this interval indicates a slight downward trend over the interval, which is only weakly supported by the points on the graph, but does correspond to the trends in the hydrogen contents of the products, which is discussed below.

For the Condition 1 operation, with 800°F second stage temperature, the hydrogen consumption averaged 7.5 W%, which is 0.3 W% lower than during the Condition 2/5 interval, probably a significant difference.

During the Condition 6 operation, with 50% higher coal feed rate, the hydrogen consumption averaged 6.4 W% of dry coal, about 0.9-1.3 W% lower than that for the Condition 2/5 interval. This change was principally because of lower hydrogen content of the distillate products, which is reflected in the following

tabulation, which summarizes the distribution of hydrogen for representative operating periods of the run:

<u>Period</u>	<u>6</u>	<u>10</u>	<u>19</u>	<u>22</u>
Operating Conditions				
First Stage Temp., °F	750	750	750	750
Second Stage Temp., °F	800	825	825	825
Coal Rate, Lb/Hr/Ft ³	44.9	44.7	44.9	69.6
Hydrogen Content				
W% of Dry Coal Fed				
C ₄ -975 Distillate	7.93	7.75	7.24	6.55
C ₁ -C ₃ Gas Product	1.56	1.65	1.88	1.63
Residual Oil Prod.	0.21	0.20	0.29	0.29
Unreacted Coal	0.63	0.42	0.37	0.50
H ₂ O, NH ₃ , H ₂ S	2.20	2.18	2.31	2.23
Total	11.98	12.20	12.10	11.20
In Feed Coal	4.54	4.54	4.54	4.54
Consumption	7.44	7.66	7.57	6.66
Total	11.98	12.20	12.11	11.20
Performance Parameters				
C ₄ -975°F Dist. Yield, W%	59.93	63.79	59.73	56.18
H ₂ In C ₄ -975°F Dist, W%	12.32	12.14	12.12	11.98
H ₂ In Dist./total H ₂	0.617	0.635	0.598	0.583
C ₄ -975°F Yield/Consumption	8.05	8.33	7.89	8.43

The principal indication of this tabulation is that the changes in hydrogen consumption correspond for the most part to changes in the total hydrogen content of the C₄-975°F distillate produced. The changes in total hydrogen content of the distillate are in part due to a progressively lower hydrogen percentage through the run and in part because of changes in the quantity of distillate produced. The penultimate line of the table, in effect a "hydrogen efficiency" parameter, indicates a fairly narrow range of performance in these terms, with possibly some advantage for the Condition 2/5 operating conditions over those of Condition 1, and only a slight impact of the increased coal rate of the Condition 6 operation.

The second hydrogen efficiency parameter given above, the ratio of C₄-975°F distillate yield to hydrogen consumption, shows a small advantage for the Condition 2/5, Periods 10 and 19 operations, over the Condition 1, Period 6, operation which had the lower second stage temperature. In these terms the Condition 6, Period 22, operation, with the higher coal feed rate, had a small advantage over the Condition 2/5 operation. Both forms of characterizing hydrogen efficiency indicate a decline in performance with increased catalyst age in Period 19.

Nitrogen Removal

Nitrogen removal, calculated for the operating periods for which nitrogen contents of all of the product streams were available, ranged from 66 to 80% of the nitrogen in the feed. The following tabulation summarizes the distribution of nitrogen in the products for the 6 Conditions of the run:

<u>Condition</u>	<u>Period</u>	<u>C₊-975</u>	Nitrogen Distribution, %		
			<u>975°F*</u> <u>Resid.</u>	<u>Unconv.</u> <u>Coal</u>	<u>Ammonia</u> <u>(Removal)</u>
1	6	10.7	0.9	15.7	71.9
2	10	14.4	1.3	8.6	75.4
3	13	13.5	2.1	9.0	74.9
4	16	10.5	1.9	9.7	80.0
5	19	12.4	2.9	8.4	75.7
6	22	16.2	3.4	13.2	65.4

The greatest nitrogen removal was in the Condition 4 operation with the first stage temperature 50°F higher than that of the second stage. While this pattern suggests that this temperature configuration is the most efficient in this respect, not all of the product analyses support such an advantage for this temperature configuration. (See below in the "Product Quality" Section.) The lowest nitrogen removal was in the Condition 6 operation with the higher coal feed rate, in part because of a relatively high nitrogen retention in the distillate product, and in part because of low coal conversion which retained a proportional amount of the nitrogen. The nitrogen removal during the Condition 1 operation was lower than the general level attained in the Condition 2/5 operation, principally because of lower coal conversion.

Sulfur Removal

Sulfur removal averaged 71% for all of these operations, with a very narrow range of performance in this regard, 70 to 72% removal. The unreacted sulfur was predominately in the unreacted solids. In fact, it was in the ash/mineral matter component of the solids, which appeared to retain sulfur amounting to about 30% of the sulfur in the coal feed. (See below in the "Product Quality" Section). The total sulfur in the product liquids amounted to about 1% of the sulfur in the feed for the operations of Conditions 1 through 5. In the Condition 6 operation there was some increase in the sulfur content of the liquid product to about 2% of the sulfur in the feed:

Comparison With Clovis Point, Wyoming, Coal CTSL™ Results

The analysis of the Black Thunder Mine coal is very similar to that of the Clovis Point, Wyoming, coal that was previously tested in CTSL™ operations, particularly in hydrogen and oxygen content and in heating value, as summarized in *Table 9*, which gives the analyses of these coals. The most appreciable difference between the two coals is that the Black Thunder coal contains about 7% ash (6% SO₃-free-ash), while the Clovis Point Coal contains over 10% ash (over 8% SO₃-free-ash), which would give some processing advantage to the Black Thunder coal.

Table 3 compares the results of specific CTSL™ operations with the Black Thunder coal in Run 227-55(CC-1) with closely matched operations with the Clovis Point coal, particularly with respect to stage temperatures and coal feed rate. Reasonable matches were made to the Condition 1 (although the Clovis Point operation has 10°F higher second stage temperature), Condition 2 and 5, and Condition 6 operations of Run 227-55(CC-1).

Coal Conversion - The coal conversions during the Black Thunder operations were 0.5-1.0% lower than those in the Clovis Point operations. Consideration of the differences between the operations with the two coals might modify this difference; viz, the higher second stage temperature for the Clovis Point operation matching the Condition 1 might account for 0.5% higher coal conversion in that operation. However, the differences in recycle solvent flows for the other two Conditions being compared (higher filter liquid and topped separator bottoms recycle for the Clovis Point operations) are projected, through the Clovis Point correlation, to result in lower conversions, by as much as 2%, for the Clovis Point operations than would be the case if recycle flows had been identical to those used in the Black Thunder operations. Thus, even after considering these factors it is probable that the degree of conversion with the Black Thunder coal is slightly lower than with the Clovis Point coal.

Residual Oil Yield - Residual oil yield with both coals were relatively low, in the range of 2-5 W% of dry coal. For the data summarized in *Table 3*, which have the same average residual oil yield for the two coals within a small fraction of 1 W%, there is no clear difference in the performance of the two coals in this respect. In the above discussion of residual oil yields for Run 227-55(CC-1) it was noted that apparent catalyst deactivation for this run was very close to indicated for Run 227-27 with the Clovis Point Coal.

C₁-C₃ Gas Yield - The gas yields with the Black Thunder coal were generally higher than those with the Clovis Point coal, by about 0.8 W% of dry coal for the data compared in *Table 3*.

C₄-975°F Distillate Yield - For data compared in *Table 3*, with Black Thunder coal the yield of C₄-975°F distillate was slightly higher than with the Clovis Point coal, averaging 59.3 W% of dry coal (a range of 56.2 to 63.8 W%) compared to 57.6 W% (a range of 54.9 to 61.5 W%) for the Clovis Point coal. The reason for this advantage is the lower ash content of the Black Thunder coal. When the results are expressed on an maf basis there is little difference in the performance of the two coals, the C₄-975°F distillate yield with Black Thunder coal averaged 63.1 W% of maf coal, compared to 62.9 W% for the Clovis Point coal.

PRODUCT QUALITY

The elemental analyses of the net product fractions were made only on the heavy gas oil and residual oil constituents of the filtered liquid produced in excess of solvent recycle requirements. These analyses for Run 227-55(CC-1) product fractions are summarized in *Table 4*. In addition, *Table 5* summarizes the analyses that were obtained for the lower boiling product streams, namely the Separator Overhead Product of about 130°F to 700°F boiling range, and the Atmospheric Still Overhead product of about 250°F to 675°F boiling range.

Hydrogen Contents

Figure 17 graphically summarizes the hydrogen contents of the heavy liquid product fractions against catalyst age (days of coal operations). Similarly, *Figure 18* summarizes the hydrogen contents of the light product streams (in this case the data are adjusted to a common volume average boiling point using a factor of 0.99% decrease per 100°F increase in boiling point based on a multiple linear least squares correlation of the data).

Figures 17 and 18 indicate a general downward trend in the hydrogen content of the liquid products as the run continued, with no definite impact of the changes in stage temperatures and coal feed rate. The light products, about 420°F volume average boiling, point decreased in hydrogen content from about 12.7 W% to 12.2 W%, between 6 days and 22 days of coal operations. Similarly, over the same interval, the 650-850°F product fraction declined from about 11.0 W% to 9.5 W% hydrogen content, the 850-975°F product fraction declined from 9.4 W% to 8.0 W% hydrogen content, and the 975°F+ residual oil declined from 8.8 W% to 5.9 W% hydrogen content. There appears to be no consistent deviation from these patterns involving the changed parameters of the various Conditions. Particularly, these results for the Condition 2/5 interval of the run, involving the changing configurations of stage temperature, seem to follow a common pattern of performance. That is, none of the three temperature configurations used appears to result in a notably superior hydrogenation performance.

The hydrogen contents for the liquid products from the Black Thunder Mine operations of Run 227-55(CC-1) correspond very closely to those of the liquid products from the earlier operations with Clovis Point Mine coal. The following compares the average hydrogen contents for the product streams considered for the two coals (Run 227-26 and 227-27 for the Clovis Point coal) over the same interval of operations up to 23 days of coal operations:

<u>Stream/Fraction</u>	<u>Black Thunder</u>	<u>Clovis Point</u>
Sep Ovhd/Atm Ovhd	12.47	12.32
650-850°F	10.21	10.18
850-975°F	8.69	8.91
975°F+ Residuum	7.15	7.05

Also, the decline in hydrogen contents with time of coal operations had the same pattern for the products with the two coals.

Figure 19 summarizes the hydrogen analyses of the product solids from Run 227-55(CC-1) as related to the nominal mineral matter content (SO_3 -free ash content) of those solids. An interesting pattern is evident in that a very nearly linear relation holds which intercepts the x-axis at zero hydrogen content at a value that correspond to 75% mineral matter. Statistical analysis indicates that the 95% confidence range for this intercept is between 71% and 80% mineral matter. Ostensibly, at such a point the solids remaining would be mineral matter and a virtually hydrogen-free carbonaceous component, presumably unreactive. A similar relation appears to hold for the nitrogen content of the product solids, see *Figure 20* and the discussion below.

Nitrogen Contents

Interpretation of the nitrogen analyses is complicated by the different results obtained by the two alternative methods used in analyzing the products. Most of the reported results are based on analyses with a Perkin-Elmer 240B elemental analyzer, in conjunction with the carbon and hydrogen values reported. In some cases, the wet-chemical Kjeldahl method was used. The two methods appear to check reasonably well for the heavier liquid products, boiling above 500°F. However, for lighter products, with lower nitrogen contents such as the separator overhead product results reported in *Table 5*, there is frequently a very marked discrepancy, with the Kjeldahl method giving considerably lower nitrogen content values. It is considered that Kjeldahl results are more reliable.

The reported nitrogen contents of heavy product fractions given in *Table 4* show a fairly uniform pattern, with a consistent upward trend as the run continued. For each of the four product fractions, the nitrogen content increased by a factor of approximately two between the 6 day and the 22 day of coal operations. There was no clear advantage in this respect for any of the three stage temperature configurations used in the Condition 2/5 interval of the run between the 10th and 19th days of coal operations. The Kjeldahl analyses of the light product streams, summarized in *Table 5*, show even more marked change in nitrogen contents during the run with an increase from 0.04-0.05%, in the 6th day, up to 0.31-0.32 W% in the 22 day.

Figure 20 summarizes the nitrogen analyses of the product solids from Run 227-55(CC-1) as related to the nominal mineral matter content (SO_3 -free ash content) of those solids. Here, the pattern is similar to that discussed above concerning the hydrogen analyses of the solids. Again, a very nearly linear relation holds with an intercept on the x-axis at zero nitrogen content at a value that corresponds to 66% mineral matter. Statistical analysis indicates that the 95% confidence range for this intercept is between 61% and 72% mineral matter, a slight overlap of the confidence range for this intercept indicated by hydrogen

analyses. Again, the organic character of the non-mineral constituent appears to have been lost at this point. Possibly, this intercept, which corresponds to 2-3% of the maf coal fed, is an indicator of the proportion of unreactive non-mineral coal.

Sulfur Contents

The reported sulfur contents of all of the liquid product fractions through Period 19 (Condition 5) of the run were all of the order of 0.01 W%. The only deviation in this pattern was in the sulfur contents of the products of Period 22 (Condition 6), where the 850-975°F Heavy Gas Oil product and the 975°F+ Residuum product contained about 0.04 W% sulfur.

Figure 21 summarizes the sulfur analyses of the product solids from Run 227-55(CC-1) as related to the nominal mineral matter content (SO_3 -free ash content) of those solids. Here, the pattern differs from that discussed above concerning the hydrogen analyses of the solids. A linear relation holds, with an intercept of 0.19 W% sulfur (95% confidence range of 0.05-0.33 W%) at zero nominal mineral matter content), and a value of 2.44 W% (95% confidence range of 2.22-2.67 W%) at 100% nominal mineral matter content. The 2.44 W% value, the apparent sulfur content of the mineral matter constituent of the product solids, corresponds to 0.146 W% sulfur on the feed coal (based on 6.01% SO_3 -free ash), which is about the total of reported pyritic sulfur content of the coal, 0.11 W%, plus sulfate sulfur, 0.04 W%. However, it is somewhat less than if all of the iron in the feed coal were converted to FeS, which, with 4.85% Fe in the coal ash, would require 0.198 W% sulfur (on coal), without allowance for the reported sulfate sulfur content of 0.04 W% (on coal).

Comparison With Clovis Point Coal Products

There is only a limited amount of comparable data for the CTSL™ products from the Clovis Point coal. The most significant set of analyses is of the product fractions from the composited products of the process demonstration run on that coal, Run 227-27. For comparison, the average of the similar analyses for the Black Thunder Coal given in *Table 4* were used, with the following indications:

The hydrogen contents of the product fractions for the Black Thunder coal range from 0.6 W% lower to 0.2 W% higher than those for the Clovis Point coal, with an average difference of 0.05 W% lower content for the Black Thunder coal products.

The nitrogen contents for the Black Thunder coal product fractions ranged from 0.11 W% lower to 0.06 W% higher than those for the Clovis Point coal, with essentially the same average.

Sulfur contents of the light products boiling to about 600°F for both coal were in the minimal range of the analytical technique, 0.01 W%. For the high boiling oils, the Black Thunder products were also in this range of sulfur content, while the Clovis Point coal products had slurry contents from 0.03 W%, in the light vacuum gas oil, to 0.28 W% in the residuum.

FIRST STAGE SLURRY ANALYSES AND INTERPRETATION

Samples of the first stage slurry were obtained during each of the Conditions in Run 227-55(CC-1). The analyses of the samples that were obtained were used in conjunction with the second stage net product and recycle solvent analyses to characterize the performance of the individual stages. The analyses were conventional D-1160 distillation characterization of the filterable portion, and solvent fractionation of the 975°F+ residuum as 975°F+ Oil (cyclohexane soluble), 975°F+Asphaltenes (toluene soluble, cyclohexane insoluble), and 975°F+ Pre-asphaltenes (toluene insoluble). The THF insoluble solids were characterized as ASTM ash and unconverted coal (the balance of the quinoline insoluble portion). Elemental analyses were obtained on the THF washed solids, the total filtered portion, and product fractions obtained in a D-1160 distillation.

Table 6 summarizes the distillation characterization of the first and second stage slurry phase liquids and the elemental analyses that were obtained on these liquids, some product fractions, and on the oil-free solids obtained.

Table 7 interprets the distillations and solids content analyses in terms of first and second stage product fraction flows relative to the amount of coal feed to the operating system.

Table 8 interprets the flows of *Table 7* as individual stage performances in terms of apparent formation or reaction of the product fractions as a percentage of the coal fed to the operation. It should be noted that the quantities given in *Tables 7 and 8* are only for the slurry phase, and that any vapor phase content, particularly significant for the lighter distillate fractions, is not included.

An estimated vapor phase flow for the first stage is included in *Table 7*, the value used is based on the experimental vapor flow from the second stage, by assuming that the vapor generation in each stage was proportional to the amount of coal reacted in that stage. This value differs from the values used in the interpretation of the stage performances of the previous runs of the CTSL™ program, where it was assumed the first stage vapors equal the second stage vapors. The current procedure attempts to deal with the considerable variations in the first stage severity in Run 227-55(CC-1). The alternative of basing the first stage slurry phase flow (and apparent vapor flow) on the apparent ash content of the first stage sample and an ash balance, gave very erratic results corresponding to apparent vapor flows ranging from 15.6 to 91.6% of feed flow, with no clear relation to first stage severity.

Hydrogenation and Heteroatom Removal

Hydrogenation - The hydrogen contents of each of the second stage product fractions were lower than those of the corresponding first stage products for the Condition 1, 2, 5, and 6 operations which used first stage temperature of 750°F and second stage temperature of 825°F (800°F for Condition 1). However, for the Condition 4 operation, with 817°F first stage and 767°F second stage temperatures, the second stage values were all higher than the first stage hydrogen contents. The Condition 3 operation, with both stages at 797°F, had relatively small differences in hydrogen contents for the two stages.

Figure 22 graphically summarizes, for the four product fractions analyzed, the change in hydrogen content between stages to the change in temperature between stages. Clearly, hydrogenation reactions were favored at the lower stage temperature, whether that was in the first stage (with a temperature increase between stages) or in the second stage (with a temperature decrease between stages). The range of the change of hydrogen content between stages was a gain in hydrogen content of 0.47 W% in residual oil hydrogen content in the second stage with first stage at 817°F and the second stage at 767°F, to a loss of 0.7-1.1 W% with the first stage at 750°F and the second stage at 825°F. For the lighter product fractions the first stage-second stage differences in hydrogen content were generally smaller, but with the same pattern as noted for the residual oil.

Denitrogenation - *Figure 23* summarizes the nitrogen contents of the four product fractions analyzed, in both the first and second stages, in the course of the run (against days of coal operation). A general upward trend of nitrogen contents against time is evident. There is a more pronounced change for the second stage nitrogen contents, which were lower than the first stage nitrogen contents early in the run, but were higher than the first stage nitrogen contents at the end of the run. There is possibly some modification of this pattern for the Condition 4 (Period 16) analyses, with the second stage temperature 50°F lower than that of the first stage, where all second stage nitrogen contents were lower than those of the first stage, while the Condition 3 (Period 13) and Condition 5 (Period 19) analyses generally indicate higher second stage values.

In general terms this pattern indicates effective second stage denitrogenation for relatively fresh catalyst, which decreased to a degree by the end of the run. The increase in nitrogen contents between the first and second stages at the end of the run probably does not represent reversion reactions, but rather only limited denitrogenation of the additional production of these fractions occurring in the second stage. The nominal improvement of denitrogenation for the Condition 4 (Period 16) operation may reflect a relatively small second stage production of these fraction, consequent of the low proportion of the coal conversion occurring in that stage (see below), so that such denitrogenation reactions that were

occurring could become more apparent. It appears that first stage denitrogenation capability was retained in large part to the end of the run.

Desulfurization - In general, for the lighter product fractions (IBP-650, 650-850°F, 850-975°F) sulfur contents in both stages were at low levels, of the order of 0.01 W%, and at this level no definite first stage-second stage pattern could be established. However, there was a clear difference between the stages of the sulfur contents of the residual oil fractions. Through Condition 5 (Period 19) the sulfur content of the first stage residual oil generally ranged from 0.045 W% to 0.091 W%, while of the second stage ranged from 0.000 W% to 0.012 W%, indicating appreciable second stage desulfurization to that point, and probably some first stage desulfurization as well. In the Condition 6 (Period 22) operation the same level of first stage sulfur content was maintained, but the second stage sulfur content increased to 0.036 W%, indicating decreased second stage desulfurization effectiveness, possibly due to increased catalyst age or to the higher coal feed rate during the Condition 6 operation.

For the Condition 1, Period 6, operation the reported sulfur contents of the first stage liquid and product fractions are all extraordinarily high, a full order of magnitude greater than the other sulfur contents reported. In the absence of a rationale for this discrepancy this result has been discounted, presuming a mis-sampling of the system.

Coal Conversion

The coal conversions for the individual stages summarized in *Table 8* follow a fairly rational kinetic pattern. The coal conversion in the first stage ranged from 65.4% to 87.7% of maf coal to the process, with the lowest values with the first stage temperature at 750°F, the highest value with the first stage at 817°F, with an intermediate value with the first stage at 796°F. The proportion of coal reacted in the second stage ranged from 4.6 to 25.0% of maf coal fed to the process, or from 31.5 to 70.2% of the coal fed to that stage, the lowest value being obtained in the Period 16 (Condition 4) operation with that stage at the lowest temperature, 767°F, and the higher values with 800-825°F second stage temperatures.

However, this pattern does exactly correspond to simple first-order CSTR (Continuous Stirred Tank Reaction) kinetics. Consider, the Period 13 (Condition 3) results with essentially equal stage temperatures, where the conversion in the first stage was 79.8% of the maf coal feed to that stage, while the conversion in the second stage was only 45.8% of the maf coal feed to that stage. In a simple first order model regime, these values would be equal.

There are a number of kinetic schemes that would allow for this deviation, the most simple being assumption of a reaction order other than first order. In this case, the difference in first and second stage performance corresponds to a

reaction order of 3.3. Such a high order is difficult to justify, especially for a cracking reaction, although a preliminary analysis indicates this order would give reasonable correspondence to the effects upon conversion of coal feed rate, and of the substitution of solids-containing TSB for a portion of the solids-free PFL solvent recycle. There is the possibility of regressive reactions of reversion to insoluble, unfilterable components of the heavier liquefied products, which would have the greatest apparent impact with relatively highly converted products. However, such a mechanism would be expected to result in lowered conversions as the concentration of residual oil increased with increased catalyst age, which was not the case, apparently. Also, in other CTSL™ and single stage experiments using solvent recycles with increased proportions of distillate components, there has been no impact upon coal conversion, such as would be expected if reversion reactions of residual oil components were an important factor.

This pattern of relatively higher degree of conversion in the first stage has been encountered in the CTSL™ operations with other coals, most notably with the Clovis Point coal. The correlation of those results, retaining a first-order kinetics model, recognized that the maf coal is not a uniform material, but consists of several species of differing reactivity, exemplified by the components of the petrographic analyses, such as vitrinite, exinite, inertinite, fusinite, etc. The interpretation of the Black Thunder Mine results was based on this conception of three major species, two reactive species of differing reactivity following first order kinetics with respect to the weight fraction concentration in reactor slurry phases, with the third species inactive. The values of the correlating parameters were developed by extension of the correlation of the Clovis Point coal conversion results. The comparison of the final Black Thunder correlating parameters and those in the Clovis Point correlations is as follows:

	<u>Black Thunder</u>	<u>Clovis Point</u>
Coal Distribution, W%		
High Reactivity	55	60
Low Reactivity	42	40
Unreactive	3	0
Kinetic Parameters		
Low Reactivity Constant		
Lbs/hr/ft ³ @750°F	17.1	18.5
Act. Energy, Kcal/mole	38.5	38.5
High Rate/Low Rate	56.7	56.7

Direct use for the Black Thunder coal of the distribution parameters for the Clovis Point coal required lowering the 750°F rate constant to 11.5 Lbs/hr/ft³ and gave a good fit to the two stage conversions (standard error of 0.61% conversion, with a variance reduction of 91.9%), and to the portion of conversion observed in the first stage (an average of 72.7% compared to an experimental average of 72.8%

conversion). The adjusted distribution parameters tabulated above resulted in a small improvement in the correlation with a standard error of 0.53% conversion, which would not be considered a significant improvement statistically. However, the adjustment does allow for the possible presence of an unreactive portion as indicated by nitrogen and hydrogen analyses of the unreacted solids that were discussed above. Also, preliminary results in microautoclave testing of the product solids from Run 227-55(CC-1) indicate that maf coal cannot be completely converted to liquids. It was considered that the available data base was too small to warrant modification of the activation energy parameter and relative reactivity parameter from the Clovis Point coal parameters.

Figure 24 is parity plot comparing the experimental two stage conversions for Black Thunder coal with the values projected using the above kinetic parameters. The projections were made by means of a reaction system model with input of the coal feed rate, stage temperatures, recycle flows of PFL and TSB, the atmospheric overhead removal in generating to TSB, and the vapor flow from the second stage (to fix the slurry flow). The parity plot includes data from the first operations of the run with lower stage temperatures, which were not used in fixing the kinetic parameters. The parity plot indicates very good correspondence of experimental and projected values over the range of the bulk of the data, and a reasonable extrapolation to the more extreme conditions represented by the early data of the run.

Figure 25 is parity plot comparing the experimental and projected first stage conversions. The scatter from the parity line is slightly greater than for the two stage conversions, but still does represent a good correspondence over the full range of conversions encountered. The variation in first stage conversion was principally affected by changes in first stage temperature, so that the correspondence of experimental and projected effects indicates that the value of activation energy is reasonably close to the best fit.

Residual Oil Formation

The formation of 975°F residual oil in each of the stages, as summarized in *Table 8*, have a general pattern of a moderate formation in the first stage, and net reaction in the second stage. For the Condition 2 through 6 operations the residual oil formation in the first stage ranged from 7.3 to 13.9 W% of dry coal feed. There was a considerably higher formation, 23.5 W%, indicated for the Condition 1 operations, but there were other anomalies in the Condition 1 sample, particularly the sulfur contents noted above, and this result has been discounted in the interpretation of these data.

The net yield of residual oil in the second stage ranged from -10.9 W% of dry coal to -2.8 W% (excepting the Condition 1 result). This pattern of first stage/second stage residual oil formation and reaction corresponds to a model where the primary reaction of the coal forms some residual oil, which under goes

a secondary reaction to lighter products. The net formation of residual oil in the first stage reflects the relatively high proportion of coal reacting in that stage, with consequent residual oil formation greater than the amount of secondary reaction. The net reaction of residual oil in the second stage reflects the lower proportion of coal reacted in that stage. There is apparently a significant amount of secondary reaction of the residual oil even at relatively low reactor temperatures, note the performance of the second stage in the Condition 4 operation with that stage at 767°F, indicating the greatest net consumption of residual oil for the reliable experimental results.

The Condition 2 through 5 results appear to follow a common pattern consistent with first order reaction kinetics after allowance is made for differing stage temperatures, by establishing a satisfactory value of the temperature dependence (activation energy) of the secondary reaction of the residual oil. The best activation energy was estimated by finding the value that gave a common value for the portion of residual oil deriving from the primary reaction of the coal, by equating first and second stage performance by the equations

$$K1 = F * (C1 * S - R1) / Cres1$$

$$K2 = F * (C2 * S - R2) / Cres2$$

$$K2/K1 = \text{Exp} (\text{Acteng} * (T2 - T1) / (T1 + 460) / (T2 + 460) / 1.987)$$

K1, K2 - First and second stage reaction rate constants

F - Dry Coal Feed rate

C1, C2 - First and second stage coal reacted, W% of dry coal

R1, R2 - First and second stage residual oil formation, W% of dry coal

S - Selectivity of residual oil formation from coal reaction, Weight fraction

Cres1, Cres2 - First and second stage residual concentration, W% of slurry phase

By assuming the activation energy (Acteng) a value of the selectivity, S, could be calculated for each of the experimental conditions. *Figure 26* summarizes the relation of calculated selectivity against assumed activation energy for each of the Condition 2 through 6 data sets. The Condition 2, 3, 4, and 5 data sets show a confluence at an activation energy of 6 kcal/mole and a selectivity of 0.43 lbs residuum/lb coal reacted. The Condition 6 relation deviates considerably from those of the other data sets, but this data set is considered less reliable than the

others because of the use of make-up oil during the Condition 6 operation and the possibility of insufficient equilibration time.

These values of activation energy and primary formation of residuum were used to calculate apparent reaction rate constants for the secondary reaction of residuum for each stage for each of the Condition 2 through 6 data sets. These rate constants, adjusted to 750°F using the 6 Kcal/mole activation energy, are plotted against catalyst age (Days of coal operations) in *Figure 27*. For the Condition 2 through 5 interval of the run (10 to 19 days), there was a smooth downward progression of these rate constants, with close correspondence for the two stages of the temperature adjusted rate constants. The second stage rate constant for the Condition 6 operation (22 days) continues this trend, but the first stage rate constant deviates considerably from the trend. To get better correspondence of the Condition 6 results would require a lower value for the primary formation of residual oil and a higher activation energy, but this would increase the scatter for the Condition 2 through 5 correlation.

In *Figure 27* the curve of adjusted rate constant against age corresponds to the equation:

$$K_{750} = 33.26 \text{ Exp}(-0.04852 \cdot \text{Days})$$

To calculate the rate constant at specific reactor temperatures the following relation can be used:

$$K_t = K_{750} \text{ Exp} [4.492 \cdot (T-750)/(T + 460)]$$

which is modified form of the Arrhenius equation using an activation energy of 6 Kcal/mole.

K ₇₅₀	-	First order rate constant at 750°F, Lbs/Hr/Ft ³ , based on weight fraction resid in slurry
K _t	-	Rate constant at Temperature T,
T	-	Temperature, °F

This rate constant equation was used with a reactor model in conjunction with the appropriate operating condition parameters to project residual oil yields for the first stage, second stage, and the combined stages for the final five Conditions, and the combined stage yield for Condition 1. *Figure 28* is a parity plot of the projected yields against the experimental yields. The projected combined stage yields have a good parity correspondence to the experimental values for all six results compared. For the most part the first and second stage yields also have good projected/experimental correspondence. The outlying first stage/second stage points in *Figure 28* are the Condition 6 results.

The values of the above correlating parameters differ considerably from those obtained by similar analyses for the Clovis Point coal, where the primary formation of residuum was taken to be 80-100% of converted coal (indicated by a plot of residuum yield in the first stage against a severity function involving residual oil concentration and the amount of coal reacted) and the activation energy was 19.5 kcal/mole (based upon the impact first stage temperature changes between 650°F and 775°F). To better define the values of these parameters, microautoclave tests were conducted using the products obtained during bench unit Run 227-57(CC-1). See the Modelling Section Report (#3) "Laboratory Scale Studies, Modelling, and Technical Assessment."

DETAILS OF OPERATION

This report summarizes the operations of Run 227-55(CC-1) in the CTSL™ bench unit evaluating Black Thunder Mine Wyoming Coal and investigating various first and second stage temperature configurations. The catalyst used in this run was Shell S-317 1/32" extrudate nickel molybdate. Shell S-317 catalyst had been used in earlier CTSL™ operations with Illinois No. 6 and Ohio 5/6 coals.

Run 227-55(CC-1) completed 536 hours of operation with coal feed, while processing 676 lbs coal/lb catalyst inventory in a single stage. There were no interruptions of the coal feed over this interval. The principal disruption to steady operation was failure of the diaphragm of hydraulic drive of the second stage internal recycle pump during the seventh day (Period 7). This caused some interchange of hydraulic fluid and process liquids and inability to keep the ebullated bed reactor fully expanded. However, there were no permanent consequences, and the unit operated smoothly after the diaphragm was replaced. Operations with coal feed started on January 11, 1989 and were completed on February 2, 1989 as scheduled with an extension of a single day because of the repair of the internal recycle pump in the seventh day.

Preoperational Procedures - Operations were started using HRI 5443 catalytic distillate produced using Illinois No. 6 Coal at the Wilsonville coal liquefaction facility. This feed was used with dimethyl disulfide added in the catalyst presulfiding operation summarized below in the section concerning the fresh catalyst. At the time of coal introduction the slurring oil was recycle material generated during the heatup/presulfiding operations.

Operating Summary - A summary of the six sets of conditions used during the run is given in *Table 1*. The final eight hours at each condition (an "A" period) was used to obtain a sample of slurry from the internal recycle line on the first stage as characteristic of material circulating through the first stage reactor.

Condition 1 (Periods 1A-7A) - The operating conditions were similar to those used in previous operations with Illinois No. 6 coal. The first and second stage temperatures were 750 and 800°F, respectively. The coal feed rate was 44 lbs/hr/ft³(catalyst/stage). The solvent recycle was 1.0 lbs/lb coal consisting of pressure filter liquid obtained by filtration of product slurry which had been topped of light distillate in the atmospheric still which was held at 525°F. This atmospheric still temperature was lower than had been used in the Illinois No. 6 coal operations, about 625°F, and closer to the temperature that had been used in Clovis Point Wyoming sub-bituminous coal operations, since a relatively low boiling product was expected with the Black Thunder coal and such a temperature would be required to retain sufficient middle distillate in the solvent recycle pool to maintain solvent balance during the operations.

The operations were with minimal operating problems through Period 6, although in the latter part of Period 6 discoloration was noted in the hydraulic fluid of the drive of one of the two second stage internal recycle pumps. During Period 7A, in the interval while the first stage liquid sample was being taken, flow from that pump failed and it was necessary to change the diaphragm of the pump because it was cracked.

Condition 2A (Periods 7A-8A) - For this condition the second stage temperature was increased to 825°F, with no other changes in conditions. About 4 hours after the start of this operation, the repaired second stage internal recycle pump was found to be low on hydraulic fluid and it was taken off line for one-half hour for further repair. Two problems were then manifest: 1) insufficient pressure filter liquid was being generated to meet recycle oil requirements, presumably because of the more severe reactor conditions being employed, and 2) the second stage catalyst could not be expanded to the target degree of expansion even with the internal recycle pumps at full flow, ostensibly because a lighter material was being circulated at the more severe conditions.

Condition 2 (Periods 8B-11A) - To deal with obtaining sufficient solvent for recycle, the atmospheric still temperature was lowered to 300°F, reducing the amount of atmospheric still overhead product to virtually zero, so that the production of this material, approximately 8 W% of dry coal to this point, would be retained in the solvent recycle pool. This change did marginally maintain the solvent balance of the operation, with "in hand" generation of the pressure filter liquid (PFL) amounting to just the sample required for its analysis, about 1.8 W% of coal feed.

To obtain improved control of the expansion of the ebullated bed, the circulating materials were made heavier by including some solids in solvent by including in the solvent recycle some unfiltered atmospheric still bottoms slurry (TSB). With one-third TSB and two-thirds PFL in solvent recycle, the solids content of the solvent recycle amounted to about 3.7 W%, and the ash content of the slurry circulating in the reactors increased by a factor of 1.4. With this change the expansion of the ebullated bed in the second stage could be maintained at a satisfactory level, although it still did require full flow from the internal recycle pump through Period 19 of the run.

The operations continued smoothly with minimal operating problems for the balance of the run.

Condition 3 (Periods 11B-14A) - This condition was with equal stage temperatures, 796°F, with no other changes in the operating conditions. This temperature was selected as giving the same total combined first and second thermal severity, on the basis of 45,000 Btu/lb-mole activation energy. The following tabulation rationalizes this pattern, as well that of Condition 4 with the first stage temperature 50°F higher than that of the second stage:

Temperatures, °F		Severity Factor		
<u>First</u>	<u>Second</u>	<u>First</u>	<u>Second</u>	<u>Combined</u>
750	825	0.273	0.816	1.089
796	796	0.545	0.545	1.089
817	767	0.731	0.354	1.089

Unity at 840°F

This activation energy probably corresponds most closely to those applying for catalytic reactions involved.

Condition 4 (Periods 14B-17A) - This Condition was with the first stage temperature 50°F higher than that of the second stage, 817 and 767°F, with no other changes in conditions. The selection of these temperatures is discussed above under Condition 3.

Condition 5 (Periods 17B-20A) - This Condition was with the same set of conditions that had been used during the Condition 2 operation, with first and second stage temperatures of 750 and 825°F.

Condition 6 (Periods 20B-23A) - This Condition was with the coal feed rate increased by 50%, to 67 Lbs/hr/ft³ (catalyst/stage), with the ratio of recycle solvent PFL and TSB also in that proportion. Because of increases in feed slurry viscosity, the temperature of slurry holder was raised from 210°F to 306°F. The attempt to obtain a feed slurry sample was unsuccessful at this time, so direct determination of water vaporization from the holder was not possible. However, the gross collection of water product declined sharply over this interval, by an amount that corresponded to virtually complete vaporization of the water contained with the feed coal, 6.4 W%.

The unit was running smoothly at the completion of scheduled operations with coal feed.

Post Run Unit Inspection - The condition of the catalyst and equipment was very good, overall. The only exception was the seats of the discharge check valves of one of the two first stage internal recycle pumps, which were eroded. The hot separator downstream of the second stage reactor was quite clean with only slight deposits on the walls. The high-pressure receiver for condensate from the vapor product was very clean, but there was a deposit of carbon-like material inside its bottom head.

The first stage reactor was disassembled with no difficulty. The catalyst was found in the normal settled position, with the top level $\frac{1}{2}$ inch below the level after charging the reactor, nominally corresponding to a loss of 1% of the charge.

The catalyst support was removed easily and the catalyst was removed easily, in a free flowing condition with no agglomeration. About 6% of the oil-free solids recovered from the first stage reactor were large (+20 mesh) lumps containing 28.5 W% ash, and 52.0 W% carbon.

The second stage reactor was disassembled with some effort required to remove the top head, but with the catalyst supported coming out easily. The catalyst was found in the normal settled position, with the top level 1- $\frac{1}{4}$ inch below the level after charging the reactor, nominally corresponding to a loss of 2% of the charge. There was a thick layer of caked material coating the reactor wall below the catalyst support, and this material had to be drilled from the reactor before removing the catalyst support. The catalyst was then removed easily from the reactor in a free flowing condition with no agglomeration. About 19% of the oil-free solids recovered from the second stage reactor were large (+20 mesh) catalyst-free lumps, containing 22.3 W% ash, and 60.4 W% carbon.

In general, it is concluded that the Black Thunder coal presents no excessive problems with regard to process depositions. The principal area of accumulation, below the catalyst supports, have frequently developed similar accumulations in past operations, probably because it is the annular area around the riser tube between the bottom flange and the catalyst support and receives little purging flow during operations. This is probably the source of the lumps contained with the catalyst dump. The erosion of the internal recycle pump check valves was quite localized and does not appear to present an exceptional problem with respect to erosion.

COAL FEED

The coal feed for Run 227-55(CC-1) was obtained from the Black Thunder Mine (Wright, Wyoming) of the Thunder Basin Coal Company. The material used in the run, designated HRI-5630, was part of a 3 ton shipment received in drums about 4 weeks before the start of the run. A smaller, 5 gallon, sample, designated HRI-5613, had been received earlier for preliminary evaluation in the HRI microautoclave. Thunder Basin Coal also provided a 5 gallon sample from a second mine in the Wright Area, the Coal Creek Mine, which gave results in the microautoclave very similar to those of the Black Thunder Mine coal.

The HRI-5630 shipment was crushed to - $\frac{1}{2}$ inch, and ground to pass a 70 mesh screen in a micropulverizer. Before the start of Run 227-55(CC-1) the ground coal was dried in a nitrogen swept tray oven at 200°F to an average moisture content of 6.4 W% (from about 27 W%), requiring 8-10 hours. The dried coal was stored in drums under nitrogen blanket until fed to the bench unit. The range of moisture contents for material actually fed to the CTSL™ operation was 5.4-8.9 W%. A single dried batch containing 2.58 W% moisture, was set aside with the prospect of possible degradation because of extended exposure to drying conditions. However, microautoclave tests on this batch did not indicate

a poorer liquefaction performance than the less completely dried material (this point is discussed more fully below).

Table 9 summarizes the analyses obtained on the dried, ground HRI-5630 coal feed to Run 227-55(CC-1). This table also gives the analysis of the HRI-5613 Black Thunder Mine sample (which had been vacuum dried at 100°C for one hour to remove virtually all of the moisture), of the Clovis Point Mine coal used in previous CTSL™ tests of Wyoming sub-bituminous coals, and of the Coal Creek Mine coal. A factor to be noted in this table is the expression of the ash content on an SO₃-free basis. The feed coal ash and the ash obtained from the CTSL™ product solids differ markedly in sulfur contents (6.35 W% sulfur and 2.1-2.9 W%, respectively) so that they are not truly equivalent materials in considering the ash(mineral matter) balance of the CTSL™ operations. The apparent reason for the anomaly is that in the combustion during ash analysis the sulfur oxides formed from organic sulfur and pyritic/pyrrhotite sulfur react with alkali metal oxides and are retained in the ash, apparently over 90% of the available sulfur in both types of samples. Since there is less sulfur available in the product solids because of desulfurization/conversion reactions, less sulfur is retained in those products. It is considered that a reasonable estimate of "true" mineral matter is on this SO₃-free ash basis, and this is the best basis for comparing equivalent materials when calculating yields from the ash (mineral matter) balance.

The most appreciable difference between the Thunder Basin Mine and Clovis Point Mine coals fed to the CTSL™ operations is in the ash content, which is much lower in the Thunder Basin coal, 7.15 W% (6.01 W% SO₃-free) against 10.5 W% (8.3 W% SO₃-free) for the Clovis Point coal. This difference presents a processing advantage for the Thunder Basin coal with reduced product solids separation costs. The potential for liquid yields from the two coals appears to be virtually the same because the very close values of oxygen content and heating value. The dried feed to Run 227-55(CC-1) did not perform as well as the Clovis Point coal in the microautoclave tests that are summarized in *Table 9*. The four measures of liquefaction performance summarized in the table were all lower for the Thunder Basin coal. The HRI-5613 sample of Thunder Basin Coal did somewhat better in the microautoclave tests, effectively the same as the Clovis Point coal results. These recent (1989) microautoclave tests have had a disappointing reproducibility, and have differed in some respects from earlier results with the same samples of coal, so that it is uncertain whether there is an actual difference between Thunder Basin and Clovis Point coals performance, or that the less severely dried HRI-5613 sample actually has better performance characteristics. However, a fair conclusion was that the Thunder Basin coal has a good coal liquefaction potential.

The Coal Creek Mine coal had analyses very close to those of the Thunder Basin Mine coal, and a comparable microautoclave performance.

Start-Up Oil

The start-up oil for Run 227-55(CC-1) was a heavy distillate, HRI-5443, produced during the operations of the Wilsonville Coal Liquefaction facility. It was used to provide the initial inventory of the system, and as the carrier oil during the presulfiding operation prior to the start of coal feed. This oil was also used as makeup oil during the transition in Period 20 from the lower coal rate operations to the higher coal rate operation. A second oil, 227-25 SU, a lighter distillate oil produced during operations at the Catlettsburg H-Coal Pilot Plant and recovered after use in the start-up prior to the CTSL™ operations with Clovis Point coal in Run 227-25. The 227-25 SU oil was considered as an alternative start-up material, but was rejected because of its slightly lower solvent quality than the HRI-5443 oil. The 227-25 SU oil was used as the wash oil during the shut down after completion of CTSL™ operations in Run 227-55(CC-1). Table 10 summarizes the inspections obtained on these two oils.

The HRI-5443 oil was slightly different from the oils used as start-up materials in earlier CTSL™ runs. The following table compares this oil with the earlier start-up oils.

Oil Identif	Source	Start-up Use	-----Inspections-----				Solv. Ill. No. 6	Quality Black Thund
			IBP	% @ 650	% @ 850	Endpt		
HRI-4907	Catlettsburg	Clovis Pt.	486	75			58.0	65.3
L-721	Wilsonville	Ill. No. 6	492	32		800	60.8	63.7
HRI-5443	Wilsonville	Bl.Thund.	205	18	80	975	57.7 69.3	54.7 57.4

Thermal Conversion at 750°F, 30 Minutes, 4/1 solvent/coal - 1989 Tests

The HRI-5443 is of somewhat higher boiling range than the other oils used as start-up materials. It also appears to be of slightly lower solvent quality than the other two oils.

Fresh Catalyst

The catalyst used in both stages for Run 227-55(CC-1) Shell S-317, 1/32" extrudate, nickel-molybdate on alumina. The designation was HRI No.-5394, the same lot that had been used for Illinois Coal and Ohio Coals in previous CTSL™ operations. The inspections on the fresh catalyst are presented in Table 11. This catalyst was different from the charges to the Clovis Point Coal CTSL™ operations, where the first stage catalyst was 1/16" extrudate Amocat 1C nickel molybdate catalyst and the second stage catalyst was 1/16" extrudate Amocat 1A cobalt molybdate catalyst. CTSL™ experiments using Illinois No. 6 coal showed that using nickel molybdate catalyst in both stages was equivalent to nickel

molybdate/cobalt molybdate combination with a process advantage of simplicity and possible staged use of the catalyst. Other CTSL™ experiments showed some advantage for the smaller $\frac{1}{32}$ " most notably in improved heteroatom removal.

The catalyst charged to the reactors was presulfided during the run start-up by treating with startup oil spiked with 1.4 W% dimethyldisulfide. When product oil at the time of the presulfiding became available it was spiked and recycled as the presulfiding solvent. The presulfiding operation consisted of three 6-hour holding periods with the reactors at 450°F, 550°F, and 650°F while feeding the spiked oil at about 1.0 V/Hr/V (total catalyst). The first and second stage reactor temperatures were then increased to 700 and 750°F, respectively, before coal feed was started. The first and second stage temperatures were then increased to the specified initial condition temperatures over a 48 hour period.

Recovered Catalyst

Analyses of the catalysts recovered from the two stages after Runs 227-55(CC-1) are given in *Table 12*.

The catalyst recovery from the first stage was 86% based on the relative volumes of charged and recovered #20 mesh oil-free catalysts, and 89% based on the reported molybdenum contents for the charged and recovered catalyst. There was also some catalyst in the 20/100 mesh material recovered, with the molybdenum content corresponding to 4.3% of the total amount of molybdenum in the catalyst charged. The 20 mesh classification is close the diameter of the $\frac{1}{32}$ " diameter extrudates, so that some of the extrudates may have passed the screen.

The carbon accumulation on the first stage catalyst, 15.6 W%, was higher than the range experienced for first stage operations with this catalyst using Illinois coal, 9.5-14.8 W%. Also, this carbon accumulation was higher than that experienced with Clovis Point Wyoming coal operations using Amocat 1C NiMo catalyst, 8.5-10.0 W% carbon on the recovered first stage catalyst. The titanium accumulation was 0.02 W%, and the iron accumulation was 0.53 W%, while the principal metallic contaminant was sodium at 0.81 W%. The metallic contamination totalling 1.5 W% was fairly moderate, compared to that after Clovis Point Operations, which ranged from 1.3 to 4.1 W%, and that after Illinois Coal operations, which has been over 7 W% in some cases. The total of the analyzed contaminants on the Run 227-55(CC-1) catalyst was 23.6 W%, compared to a value of 26.1 W% indicated by the reported molybdenum contents of the charged and recovered catalysts. The particle density of the first stage recovered catalyst indicated 32.1 W% total contaminants. The pore volume of the recovered catalyst was about 71% of that of fresh catalyst, when compared on a common catalyst content basis, which is in the range of the pore volume retentions experienced in other runs. Ignition of the recovered first stage catalyst increased

the pore volume to 109% of that of fresh catalyst, when compared on a common catalyst content basis, and the calculated surface area of the ignited catalyst was 98% of that of fresh catalyst. The particle density of the ignited catalyst indicated 16% contaminants on the ignited catalyst.

The catalyst recovery from the second stage was 84% based on the relative volumes of charged and recovered #20 mesh oil-free catalysts, and 89% based on the reported molybdenum contents of the charged and recovered catalysts. The molybdenum content of the 20/100 mesh recovered material corresponded to 3.4% of the total amount in the catalyst charged.

The carbon accumulation on the second stage catalyst was 18.9 W%, in the range experienced after CTSLTM operations with Illinois coal, 13.8-19.6 W%, and also in the range of values after Clovis Point coal operations, 15.3-19.3 W%. The titanium accumulation on the second stage catalyst was 0.02 W% and the iron content was 0.07 W%, while the principal metallic contaminant was sodium at 0.81 W%, again indicating moderate metallic accumulation. The metallic contamination totalling 1.4 W% was again fairly moderate, compared to that after Clovis Point Coal operations and that after Illinois Coal operations. The total of the analyzed contaminants of the second stage catalyst was 26.6 W%, while the total contaminants estimated on the basis of the molybdenum content was 27.9 W%. The total contaminants estimated on the basis of the particle density was 35.5 W%. The pore volume of the recovered second stage catalyst was 58% of that of fresh catalyst, when compared on a common catalyst content basis, a relatively low pore volume retention. Ignition of the recovered second stage catalyst increased the pore volume to 104% of that of fresh catalyst, when compared on a common catalyst content basis, and the calculated surface area of the ignited catalyst was 96% of that of fresh catalyst. The particle density of the ignited second stage catalyst indicated 16% contaminants on the ignited catalyst.

The most significant factor in these recovered catalyst analyses was the relatively high carbon content of the first stage catalyst. Possibly it is associated with the Black Thunder Mine Coal. However, a factor to be considered is that the Run 227-55(CC-1) operations had a considerable interval of operations with the first stage temperature at 796°F or 817°F, while in the operations with the other coals this temperature was 775°F or lower. It is thought that the generally higher carbon accumulation on the second stage catalyst in the past has been due to the higher temperatures used in the second stage, and the relatively high carbon content of the first stage catalyst after this run would support this opinion.

TABLE 1

RUN 227-55 OPERATING CONDITIONS

Shell S-317 $\frac{1}{32}$ " Catalyst in Both Stages
 Coal Feed - Black Thunder Mine (Wyoming) Coal, Thunder Basin Coal Co.

CONDITION NUMBER	1	2A	2	3	4	5	6
PERIOD (DAYS)	<u>1A-7A</u>	<u>7B-8A</u>	<u>8B-11A</u>	<u>11B-14A</u>	<u>17B-20A</u>	<u>17B-20A</u>	<u>20B-23A</u>
Hours of Coal Operations							
Nominal Conditions							
Unit Pressure, Psig	2500	2500	2500	2500	2500	2500	2500
Coal Feed, Lb/hr/ft ³ (catalyst)	44	44	44	44	44	44	67
Solvent Recycle, lb/lb Coal							
Filtered Liquid	1.1	1.1	0.76	0.76	0.76	0.76	0.76
Topped Separator Bottoms	0.0	0.0	0.38	0.38	0.38	0.38	0.38
Oil/Solids in Feed	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Atmos. Still Btms. Temp., °F	525	525	300	300	300	300	550
Reactor Temperatures, °F							
First Stage	750	750	750	796	817	750	750
Second Stage	800	825	825	796	767	825	825

TABLE 2

BENCH-SCALE TWO STAGE COAL LIQUEFACTION

COAL: BLACK THUNDER MINE (HRI-5630)
 CATALYST: BOTH STAGES: SHELL S-317 NiMo $\frac{1}{32}$ " (HRI-5394)

	1	2	3	4	5	6	7	8
Period Number	1/11/89	1/12/89	1/13/89	1/14/89	1/15/89	1/16/89	1/17/89	1/18/89
Date (Start of Period)	24	48	72	96	120	144	168	192
Hours of Run (End of Period)	27	55	84	112	140	168	199	228
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat								
TEMPERATURES, °F								
First Stage Reaction	710	735	750	751	750	751	751	750
Second Stage Reaction	759	784	799	800	799	800	807	822
Slurry Mix Tank	173	187	192	189	190	204	193	193
PRESSURES, PSIG								
Unit Back Pressure	2498	2497	2503	2503	2502	2500	2498	2495
Overall DP	12.0	10.8	10.1	9.1	8.5	8.9	12.1	10.6
DRY SPACE VELOCITIES								
Stg. 1, Lb/Hr/Ft ² (catalyst)	42.9	45.3	45.3	45.3	44.4	44.9	46.8	45.6
Two-Stage, Lb/Hr/Ft ² (catalyst)	21.4	22.6	22.6	22.6	22.2	22.4	23.4	22.8
RECYCLES, W% OF DRY COAL								
Pressure Filter Liquid	113.4	108.3	111.4	114.3	114.3	110.0	105.4	82.3
PFL to Buffer - Stage 1	12.6	5.5	6.0	5.0	4.4	4.2	2.6	3.4
PFL to Buffer - Stage 2	17.3	9.1	5.3	4.4	4.5	4.6	3.6	2.6
Separator Bottoms	0.0	0.0	0.0	0.0	0.0	0.0	0.0	29.0
Make-up Oil (HRI-5443)								
TOTAL MATERIAL RECOVERY (GROSS)	92.34	102.86	88.36	97.74	97.77	97.83	96.56	96.04
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED								
C ₁ -C ₃ in Gases				5.74	7.96	7.22		
C ₄ -C ₇ in Gases				4.86	5.50	4.40		
IBP-390°F in Liquids				13.14	12.84	12.44		
390-500°F in Liquids				10.72	10.23	9.67		
500-650°F in Liquids				18.96	18.04	17.90		
650-850°F in Liquids				11.30	10.59	13.95		
850-975°F in Liquids				1.90	1.65	2.47		
Toluene Soluble 975°F Oil				1.47	1.75	2.49		
Toluene Insoluble 975°F Oil				0.01	0.00	0.00		
Unconverted Coal				12.79	12.79	12.04		
Ash (SO ₃ -free)				6.01	6.01	6.01		
Water				18.57	18.52	18.01		
CO				0.27	0.35	0.28		
CO ₂				0.35	0.14	0.19		
NH ₃				0.92	0.92	0.92		
H ₂ S				0.36	0.36	0.36		
Total (100 + H ₂ Reacted)				107.36	107.66	107.44		
PROCESS PERFORMANCE								
C ₄ -975°F Distillates, W% of MAF Coal				64.8	62.6	63.8		
975°F Conversion, W% MAF				84.8				
Coal Conversion, W% MAF		77.2	86.1	86.4	86.4	87.2		90.4
HDS, W%				70.2	70.1	69.9		
HDN, W%				71.9	72.3	71.9		

Normalization for Periods 6, 10, 13, 16, 19, 23 use actual elemental analyses.
 Other periods borrow such analyses from similar operations.

TABLE 2

BENCH-SCALE TWO STAGE COAL LIQUEFACTION

COAL: BLACK THUNDER MINE (HRI-5630)

CATALYST: BOTH STAGES: SHELL S-317 NiMo $\frac{1}{32}$ " (HRI-5394)

	9	10	11	12	13	14	15	16
Period Number								
Date (Start of Period)	1/19/89	1/20/89	1/21/89	1/22/89	1/23/89	1/24/89	1/25/89	1/26/89
Hours of Run (End of Period)	216	240	264	288	312	336	360	384
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	256	284	312	341	371	399	428	456
TEMPERATURES, °F								
First Stage Reaction	750	750	765	797	796	801	817	817
Second Stage Reaction	825	824	812	794	795	786	766	767
Slurry Mix Tank	189	234	180	181	195	189	186	187
PRESSURES, PSIG								
Unit Back Pressure	2497	2499	2507	2507	2506	2503	2503	2505
Overall DP	8.7	9.5	8.6	7.4	7.4	7.8	7.4	7.4
DRY SPACE VELOCITIES								
Stg. 1, Lb/Hr/Ft ² (catalyst)	45.6	44.7	45.3	45.6	48.0	45.6	45.1	45.6
Two-Stage, Lb/Hr/Ft ² (catalyst)	22.8	22.3	22.6	22.8	24.0	22.8	22.6	22.8
RECYCLES, W% OF DRY COAL								
Pressure Filter Liquid	76.3	76.3	76.3	76.3	76.3	76.3	76.3	76.3
PFL to Buffer - Stage 1	2.9	4.8	5.0	5.5	4.7	7.3	4.2	3.6
PFL to Buffer - Stage 2	4.3	3.8	4.0	3.6	3.3	3.5	4.4	3.2
Separator Bottoms	38.1	38.1	38.1	38.1	38.1	38.1	38.1	38.1
Make-up Oil (HRI-5443)								
TOTAL MATERIAL RECOVERY (GROSS)	96.04	96.04	96.04	97.68	97.58	97.36	96.65	98.15
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED								
C ₁ -C ₃ in Gases	8.64	7.74		9.26	8.59		8.66	10.30
C ₄ -C ₇ in Gases	5.06	4.06		4.88	4.66		5.76	5.68
IBP-390°F in Liquids	15.21	15.96		15.38	14.22		16.91	16.68
390-500°F in Liquids	10.21	10.62		10.31	9.37		10.16	9.91
500-650°F in Liquids	18.40	19.12		17.49	18.06		17.26	15.95
650-850°F in Liquids	12.15	12.03		10.42	11.95		10.46	8.63
850-975°F in Liquids	2.11	2.00		1.93	2.63		2.20	1.72
Toluene Soluble 975°F Oil	2.40	2.67		2.80	3.64		3.42	2.99
Toluene Insoluble 975°F Oil	0.02	0.02		0.02	0.03		0.01	0.01
Unconverted Coal	8.35	8.04		7.25	8.11		7.14	7.23
Ash (SO ₂ -free)	6.01	6.01		6.01	6.01		6.01	6.01
Water	17.55	17.79		19.76	18.59		17.72	20.62
CO	0.25	0.20		0.25	0.23		0.19	0.27
CO ₂	0.14	0.08		0.42	0.27		0.38	0.53
NH ₃	0.97	0.96		0.97	0.95		1.00	1.02
H ₂ S	0.37	0.36		0.39	0.36		0.36	0.37
Total (100 + H ₂ Reacted)	107.83	107.66		107.99	107.67		107.64	107.94
PROCESS PERFORMANCE								
C ₄ -975°F Distillates, W% of MAF Coal	67.2	67.9		64.7	64.8		66.8	62.3
975°F Conversion, W% MAF	88.5	88.6		89.3	87.5		88.8	89.1
Coal Conversion, W% MAF	91.1	91.4		92.3	91.4		92.4	92.3
HDS, W%	72.1	71.0		75.6	70.5		70.4	72.1
HDN, W%	76.0	75.4		76.1	74.9		78.4	80.0

Normalization for Periods 6, 10, 13, 16, 19, 23 use actual elemental analyses.
Other periods borrow such analyses from similar operations.

TABLE 2

Part 3 of 3

BENCH-SCALE TWO STAGE COAL LIQUEFACTION

COAL: BLACK THUNDER MINE (HRI-5630)
 CATALYST: BOTH STAGES: SHELL S-317 NiMo $\frac{1}{32}$ " (HRI-5394)

Period Number	17	18	19	20	21	22	23
Date (Start of Period)	1/27/89	1/28/89	1/29/89	1/30/89	1/31/89	2/01/89	2/02/89
Hours of Run (End of Period)	408	432	456	480	504	528	536
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	485	513	541	573	617	660	676
TEMPERATURES, °F							
First Stage Reaction	793	750	750	752	751	752	751
Second Stage Reaction	786	824	824	824	823	826	824
Slurry Mix Tank	200	200	208	211	274	306	306
PRESSURES, PSIG							
Unit Back Pressure	2502	2497	2503	2497	2494	2498	2502
Overall DP	8.4	8.7	8.7	10.1	12.0	11.9	12.7
DRY SPACE VELOCITIES							
Stg. 1, Lb/Hr/Ft ³ (catalyst)	45.6	46.0	44.9	51.3	68.9	69.6	66.2
Two-Stage, Lb/Hr/Ft ³ (catalyst)	22.8	23.0	22.4	25.6	34.4	34.8	33.1
RECYCLES, W% OF DRY COAL							
Pressure Filter Liquid	76.3	75.7	76.3	57.9	58.4	73.0	76.3
PFL to Buffer - Stage 1	6.2	2.7	4.3	3.0	2.6	2.8	5.1
PFL to Buffer - Stage 2	3.2	3.0	3.3	2.4	1.7	1.9	1.9
Separator Bottoms	38.1	38.1	38.1	39.0	38.1	38.1	38.1
Make-up Oil (HRI-5443)				27.2	18.4	3.1	
TOTAL MATERIAL RECOVERY (GROSS)	95.03	96.06	96.05	95.07	100.15	100.48	
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED							
C ₁ -C ₃ in Gases		12.46	8.88		6.19	7.67	
C ₄ -C ₇ in Gases		8.00	5.30		3.77	4.53	
IBP-390°F in Liquids		14.51	14.60		11.82	11.05	
390-500°F in Liquids		10.03	10.16		9.47	8.87	
500-650°F in Liquids		15.31	17.14		19.91	17.88	
650-850°F in Liquids		7.21	10.57		9.76	12.24	
850-975°F in Liquids		1.27	1.97		0.91	1.61	
Toluene Soluble 975°F Oil		2.22	3.88		5.91	4.14	
Toluene Insoluble 975°F Oil		0.04	0.27		0.76	0.25	
Unconverted Coal		7.47	7.71		10.71	11.90	
Ash (SO ₃ -free)		6.01	6.01		6.01	6.01	
Water		20.97	18.90		19.17	18.41	
CO		0.27	0.19		0.10	0.21	
CO ₂		1.10	0.63		0.62	0.72	
NH ₃		1.01	0.97		0.77	0.83	
H ₂ S		0.37	0.36		0.35	0.35	
Total (100 + H ₂ Reacted)		108.27	107.56		106.23	106.66	
PROCESS PERFORMANCE							
C ₄ -975°F Distillates, W% of MAF Coal		59.9	63.6		59.2	59.8	
975°F Conversion, W% MAF		89.6	87.4		81.5	82.7	
Coal Conversion, W% MAF		92.0	91.8		88.6	87.3	
HDS, W%		72.9	71.3		68.5	69.2	
HDN, W%		79.1	75.7		60.7	65.4	

Normalization for Periods 6, 10, 13, 16, 19, 23 use actual elemental analyses.
 Other periods borrow such analyses from similar operations.

TABLE 3

COMPARISON OF BLACK THUNDER AND CLOVIS POINT COALS CTSL RESULTS

Coal Feed	Black Thunder				Clovis Point		
	Shell S-317				Amocat 1C/1A		
Catalyst	1	2	5	6	(1)	(2/5)	(6)
Run 227-55(CC-1) Condition (Clovis Match)							
Run-Period, Unit 227	55-6	55-10	55-19	55-22	21-12	25-12	21-20
Hours of Run (End of Period)	144	240	456	528	311	294	503
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	170	284	541	660	561	444	860
TEMPERATURES, °F							
First Stage Reaction	751	750	750	752	749	750	751
Second Stage Reaction	800	824	824	826	811	824	826
Atmospheric Still	523	294	294	551	537	497	532
PRESSURES, PSIG							
Unit Back Pressure	2500	2499	2503	2498	2511	2511	2516
SPACE VELOCITIES							
Lb/Hr/Ft ³ Cat. (stage)	44.9	44.7	44.9	68.9	46.4	45.6	69.6
RECYCLES, W% OF DRY COAL							
Pressure Filter Liquid	110.0	76.3	76.3	73.0	99.0	120.6	99.0
PFL to Buffer - Stage 1	4.2	4.8	4.3	2.8	10.8	0.0	6.1
PFL to Buffer - Stage 2	4.6	3.8	3.3	1.9	11.1	0.0	4.3
Separator Bottoms	0.0	38.1	38.1	38.1	149.0	0.0	153.4
Make-up Oil				3.1			5.6
Vacuum Distillate							
TOTAL MATERIAL RECOVERY (GROSS)	97.83	97.77	96.05	97.74	98.85	96.98	97.09
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED							
C ₁ -C ₃ in Gases	7.22	7.74	8.88	7.67	6.92	6.88	7.18
C ₄ -C ₇ in Gases	4.40	4.06	5.30	4.53	5.23	3.97	4.85
IBP-390°F in Liquids	12.44	15.96	14.60	11.05	14.20	14.79	13.87
390-500°F in Liquids	9.67	10.62	10.16	8.87	13.75	13.11	12.46
500-650°F in Liquids	17.90	19.12	17.14	17.88	13.01	17.43	14.61
650-850°F in Liquids	13.05	12.03	10.57	12.24	7.53	9.85	7.45
850-975°F in Liquids	2.47	2.00	1.97	1.61	2.87	2.35	1.66
Toluene Soluble 975°F Oil	2.49	2.67	3.88	4.14	2.06	2.67	3.41
Toluene Insoluble 975°F Oil	0.00	0.02	0.27	0.25	0.77	0.00	1.69
Unconverted Coal	12.04	8.04	7.71	11.90	11.26	7.01	10.74
Ash (SO ₃ -free)	6.01	6.01	6.01	6.01	8.30	8.18	8.31
Water	18.01	17.79	18.90	18.41	17.54	18.59	15.77
CO	0.28	0.20	0.19	0.21	0.36	0.26	0.61
CO ₂	0.19	0.08	0.63	0.72	1.50	0.34	2.30
NH ₃	0.92	0.96	0.97	0.83	0.70	0.77	0.65
H ₂ S	0.36	0.36	0.36	0.35	0.86	0.83	0.87
Total (100 + H ₂ Reacted)	107.44	107.66	107.56	106.66	106.86	107.15	106.41
PROCESS PERFORMANCE							
C ₄ -975°F Distillates, W% of Dry Coal	59.9	63.8	59.7	56.2	56.6	61.5	54.9
C ₄ -975°F Distillates, W%MAF Coal	63.8	67.9	63.6	59.8	61.7	67.0	59.9
975°F Conversion, W% MAF	84.5	88.6	87.4	82.7	84.0	89.4	82.7
Coal Conversion, W% MAF	87.2	91.4	91.8	87.3	87.7	92.4	88.3
HDS, W%	69.9	71.0	71.3	69.2	71.0	73.0	76.8
HDN, W%	71.9	75.4	75.7	65.4	62.7	66.8	56.3

TABLE 4
PRODUCT FRACTION ANALYSES - RUN 227-55

Operations With Black Thunder Mine Coal - Shell S-317 Catalyst

Period Number	6	10	13	16	19	22
Catalyst Age, Lbs Coal/Lb Catalyst	168	284	371	456	541	660
LGO (IBP-650°F)						
IBP (D-1160 of Solvent)	505	450	431	401	444	525
Gravity, °API	19.5	21.4	20.8	20.5	19.6	15.9
Carbon, W%	88.47	88.32	88.88	88.61	88.56	88.56
Hydrogen, W%	11.58	11.10	11.30	11.22	10.97	10.64
Sulfur, W%	0.008	0.001	0.003	0.001	0.002	0.010
Nitrogen, W%	0.18	0.13	0.23	0.20	0.22	0.30
H/C Ratio	1.56	1.50	1.51	1.51	1.48	1.43
VGO (650-850°F)						
Gravity, °API	11.4	12.3	12.5	11.9	9.8	9.6
Carbon, W%	89.35	89.82	89.50	89.86	89.64	89.66
Hydrogen, W%	10.94	10.34	10.18	10.13	9.85	9.85
Sulfur, W%	0.008	0.008	0.001	0.003	0.004	0.005
Nitrogen, W%	0.12	0.11	0.22	0.24	0.26	0.31
H/C Ratio	1.46	1.37	1.36	1.34	1.31	1.31
HVGO (850-975°F)						
Gravity, °API	5.1	0.8	0.1	-1.0	-2.4	-3.1
Carbon, W%	90.14	90.74	90.82	90.75	91.10	90.74
Hydrogen, W%	9.08	8.94	8.93	8.58	8.29	8.32
Sulfur, W%	0.015	0.003	0.001	0.012	0.006	0.045
Nitrogen, W%	0.26	0.30	0.39	0.42	0.50	0.54
H/C Ratio	1.20	1.17	1.17	1.13	1.08	1.09
RESIDUUM (975°F)						
Gravity, °API	-4.6	-9.6	-9.8	-11.4	-13.2	-13.0
Carbon, W%	90.40	91.71	91.51	91.72	92.26	91.21
Hydrogen, W%	8.45	7.30	7.23	6.89	6.50	6.55
Sulfur, W%	0.002	0.012	0.009	0.000	0.007	0.036
Nitrogen, W%	0.39	0.51	0.63	0.66	0.74	0.89
Cyclohexane Insolubles, W%	4.35	13.87	13.03	20.59	32.55	38.54
Toluene Insolubles, W%	0.10	0.70	0.73	2.75	6.15	5.43
Ash, W%	0.00	0.00	0.00	0.02	0.12	0.00
H/C Ratio	1.11	0.95	0.94	0.90	0.84	0.86

Nitrogen analyses by Perkin-Elmer 240B Elemental Analyzer.

TABLE 5

PRODUCT STREAM ANALYSES - RUN 227-55 (CC-1)

Operations With Black Thunder Mine Coal - Shell S-317 Catalyst

Period Number	6	10	13	16	19	22
Catalyst Age, Lbs Coal/Lb Catalyst	168	284	371	456	541	660
SEPARATOR OVERHEAD						
Volume Average Boiling Point, °F	449	423	422	408	421	480
Gravity, °API	32.90	33.90	34.20	34.80	33.30	27.80
Watson Characterization Factor	11.06	11.03	11.05	11.04	11.00	10.85
Carbon, W%	86.77	86.73	87.91	87.84	87.26	87.60
Hydrogen, W%	12.46	12.31	12.53	12.31	12.34	11.68
Sulfur, W%	0.00	0.01	0.01	0.00	0.01	0.01
Nitrogen, W% (Perkin-Elmer)	0.24	0.26	0.24	0.19	0.22	0.30
Total	99.47	99.32	100.69	100.34	99.80	99.59
Nitrogen, W% (Kjeldahl)	0.043					0.31
H/C Ratio	1.71	1.69	1.70	1.67	1.68	1.59
ATMOSPHERIC OVERHEAD						
Volume Average Boiling Point, °F	482	363	363	354	361	495
Gravity, °API	28.10	37.80	38.20	38.90	37.70	24.10
Watson Characterization Factor	11.00	11.18	11.20	11.22	11.22	11.17
Carbon, W%	87.66	87.21	86.09	87.27	86.85	87.04
Hydrogen, W%	12.28	12.89	13.12	13.27	13.06	11.38
Sulfur, W%	0.01	0.00	0.00	0.01	0.02	0.00
Nitrogen, W% (Perkin-Elmer)	0.19	0.20	0.21	0.12	0.19	0.38
Total	100.14	100.30	99.42	100.67	100.12	98.80
Nitrogen, W% (Kjeldahl)	0.054					0.32
H/C Ratio	1.67	1.76	1.82	1.81	1.79	1.56
PRESSURE FILTER LIQUID PRODUCT (SOLVENT)						
Gravity, °F	12.10	10.40	9.90	7.50	5.30	0.60
Composition						
IBP-650°F, W%	16.77	30.00	30.67	30.20	25.24	8.49
650-850°F, W%	52.83	44.20	40.66	38.43	40.81	46.78
650-975°F, W%	15.05	10.80	11.69	11.27	10.74	14.38
975°F Residuum, W%	15.15	14.50	16.28	19.61	22.73	29.79
Carbon, W%	89.09	88.89	89.20	89.55	89.98	90.23
Hydrogen, W%	10.38	10.06	9.85	9.45	9.20	8.53
Sulfur, W%	0.01	0.01	0.01	0.00	0.01	0.04
Nitrogen, W% (Perkin-Elmer)	0.18	0.29	0.35	0.37	0.42	0.57
Total	99.66	99.25	99.41	99.41	99.61	99.37
H/C Ratio	1.39	1.35	1.32	1.26	1.22	1.13

Nitrogen, W% (Perkin-Elmer) - Analysis with Perkin-Elmer 240B Elemental Analyzer

Nitrogen, W% (Kjeldahl) - Wet Chemical determination

TABLE 6

Part 1 of 2

COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES
RUN 227-55

	First Stage			Second Stage		
	1 6	2 10	3 13	1 6	2 10	3 13
Condition Period Number						
Catalyst Age, Lbs Coal/Lb Catalyst	204	284	371	204	284	371
TOTAL LIQUID						
Gravity, deg-API	10.4	10.3	6.8	12.1	10.4	9.9
Elemental Analyses, WZ						
Carbon, WZ	88.74	89.16	89.52	89.09	88.89	89.20
Hydrogen, WZ	10.38	10.20	9.58	10.38	10.06	9.85
Sulfur, WZ	0.23	0.008	0.001	0.010	0.009	0.006
Nitrogen, WZ	0.37	0.28	0.32	0.18	0.29	0.35
Total	99.72	99.65	99.42	99.66	99.25	99.41
650 F-, WZ	11.7	22.9	22.0	16.8	30.0	30.7
650-850 deg-F, WZ	39.2	41.6	39.0	52.8	44.2	40.7
850-975 deg-F, WZ	17.3	13.5	14.2	15.1	10.8	11.7
975 deg-F+, WZ	31.3	21.2	24.1	15.2	14.5	16.3
Loss, WZ	0.5	0.8	0.7	0.2	0.5	0.7
LGO (IBP-650 F)						
Gravity, deg-API	20.9	20.1	20.7	19.5	21.4	20.8
Carbon, WZ	88.60	88.52	88.93	88.47	88.32	88.88
Hydrogen, WZ	11.79	11.65	11.23	11.58	11.10	11.30
Sulfur, WZ	0.012	0.005	0.001	0.008	0.001	0.003
Nitrogen, WZ	0.19	0.13	0.17	0.18	0.13	0.23
VGO (650-850 F)						
Gravity, deg-API	15.2	13.1	11.3	11.4	12.3	12.5
Carbon, WZ	89.12	89.38	89.76	89.35	89.82	89.50
Hydrogen, WZ	10.72	10.64	10.13	10.94	10.34	10.18
Sulfur, WZ	0.17	0.043	0.016	0.008	0.008	0.001
Nitrogen, WZ	0.23	0.18	0.21	0.12	0.11	0.22
HVGO (850-975 F)						
Gravity, deg-API	8.4	3.3	1.1	5.1	0.8	0.1
Carbon, WZ	89.12	89.99	90.79	90.14	90.74	90.82
Hydrogen, WZ	10.48	9.57	9.08	9.88	8.94	8.93
Sulfur, WZ	0.17	0.021	0.013	0.015	0.003	0.001
Nitrogen, WZ	0.40	0.38	0.38	0.26	0.30	0.39
RESIDUUM (975 F+)						
Gravity, deg-API	0.4	-5.6	-9.5	-4.6	-9.6	-9.8
Carbon, WZ	88.96	90.13	90.79	90.40	91.71	91.51
Hydrogen, WZ	9.18	8.41	7.27	8.45	7.30	7.23
Sulfur, WZ	0.71	0.091	0.045	0.002	0.012	0.009
Nitrogen, WZ	0.68	0.62	0.73	0.39	0.51	0.63
Cyclohexane Insolubles, WZ	2.58	10.12	25.46	4.35	13.87	13.03
Toluene Insolubles, WZ	0.43	0.79	4.13	0.10	0.70	0.73
Ash, WZ	0.00	0.00	0.03	0.00	0.00	0.00
SOLIDS (THF INSOLUBLE)						
Ash, WZ	16.79	21.00	30.62	36.13	47.20	47.78
Elemental Analyses, Ash-free Basis						
Carbon, WZ	78.69	76.89	78.52	76.67	75.49	75.37
Hydrogen, WZ	4.86	4.56	4.54	4.20	3.75	3.94
Sulfur, WZ	0.67	0.89	1.22	1.43	2.22	2.32
Nitrogen, WZ	1.53	1.47	1.57	1.27	1.04	1.01
Total	85.75	83.81	85.85	84.38	82.50	82.64
Sulfur/Ash	0.033	0.034	0.028	0.025	0.025	0.027
Sulfur In Ash, WZ	2.81	2.53	2.53	2.27	2.36	2.04
SAMPLE FILTRATION						
Filter Cake, Percent of Sample	29.49	39.79	32.73			
THF Insolubles, WZ of Filter Cake	61.70	60.25	61.07			

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TABLE 6

Part 2 of 2

COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES
RUN 227-55

Condition Period Number	First Stage			Second Stage		
	4 16	5 19	6 22	4 16	5 19	6 22
Catalyst Age, Lbs Coal/Lb Catalyst	456	541	660	456	541	660
TOTAL LIQUID						
Gravity, deg-API	2.6	3.5	2.9	7.5	5.3	0.6
Elemental Analyses, WZ						
Carbon, WZ	90.40	89.72	90.27	89.55	89.98	90.23
Hydrogen, WZ	8.85	9.20	9.00	9.45	9.20	8.53
Sulfur, WZ	0.019	0.02	0.04	0.003	0.005	0.04
Nitrogen, WZ	0.41	0.41	0.45	0.37	0.43	0.57
Total	99.68	99.35	99.76	99.37	99.62	99.37
650 F-, WZ	19.9	18.0	7.6	30.2	25.2	8.5
650-850 deg-F, WZ	36.9	38.8	41.6	38.4	40.8	46.8
850-975 deg-F, WZ	14.2	13.1	18.7	11.3	10.7	14.4
975 deg-F+, WZ	28.1	29.4	31.9	19.6	22.7	29.8
Loss, WZ	0.8	0.7	0.2	0.5	0.5	0.6
L60 (IBP-650 F)						
Gravity, deg-API	20.2	18.8	16.6	20.5	19.6	15.9
Carbon, WZ	88.84	88.46	88.46	88.61	88.56	88.56
Hydrogen, WZ	10.76	11.18	10.88	11.22	10.97	10.64
Sulfur, WZ	0.006	0.000	0.005	0.001	0.002	0.010
Nitrogen, WZ	0.21	0.19	0.26	0.20	0.22	0.30
V60 (650-850 F)						
Gravity, deg-API	10.1	11.7	9.9	11.9	9.8	9.6
Carbon, WZ	90.17	89.55	90.02	89.86	89.64	89.66
Hydrogen, WZ	9.79	10.14	9.92	10.13	9.85	9.85
Sulfur, WZ	0.002	0.006	0.013	0.003	0.004	0.005
Nitrogen, WZ	0.26	0.23	0.26	0.24	0.26	0.31
HV60 (850-975 F)						
Gravity, deg-API	-2.0	-0.7	0.5	-1.0	-2.4	-3.1
Carbon, WZ	91.05	90.49	89.94	90.75	91.10	90.74
Hydrogen, WZ	8.37	8.59	8.75	8.58	8.29	8.32
Sulfur, WZ	0.002	0.006	0.009	0.012	0.006	0.045
Nitrogen, WZ	0.46	0.45	0.43	0.42	0.50	0.54
RESIDUUM (975 F+)						
Gravity, deg-API	-12.6	-10.3	-9.1	-11.4	-13.2	-13.0
Carbon, WZ	91.87	90.48	90.79	91.72	92.26	91.21
Hydrogen, WZ	6.42	7.22	7.25	6.89	6.50	6.55
Sulfur, WZ	0.054	0.062	0.054	0.000	0.007	0.036
Nitrogen, WZ	0.81	0.78	0.84	0.66	0.74	0.89
Cyclohexane Insolubles, WZ	38.31	32.17	28.03	20.59	32.55	38.54
Toluene Insolubles, WZ	11.97	6.93	6.80	2.75	6.15	5.43
Ash, WZ	0.02	0.00	0.00	0.02	0.12	0.00
SOLIDS (THE INSOLUBLE)						
Ash, WZ	38.79	19.92	19.64	49.03	46.75	35.90
Elemental Analyses, Ash-free Basis						
Carbon, WZ	77.43	78.68	79.77	75.82	76.54	78.99
Hydrogen, WZ	4.05	4.68	4.89	3.86	4.13	4.49
Sulfur, WZ	1.83	0.73	0.72	2.43	2.23	1.38
Nitrogen, WZ	1.23	1.55	1.51	0.92	1.07	1.37
Total	84.54	85.64	86.59	83.03	83.97	86.23
Sulfur/Ash	0.023	0.029	0.030	0.025	0.026	0.025
Sulfur in Ash, WZ	2.59	2.22	2.35	2.13	2.33	2.13
SAMPLE FILTRATION						
Filter Cake, Percent of Sample	29.02	38.73	56.60			
THE Insolubles, WZ of Filter Cake	53.72	53.25	53.88			

FIRST AND SECOND STAGE FLOWS RUN 227-55

Flows - Percent of Dry Coal Feed	First and Second Stage Vapors Proportional to Coal Reacted					
	1 6	2 10	3 13	4 16	5 19	6 22
Condition Period						
Coal Rate, Lbs/Hr/Ft ³	45.6	44.7	48.0	45.6	44.9	69.6
Recycle TSB, WZ of Dry Coal Feed	0.0	38.1	38.1	38.1	38.1	38.1
Recycle PEL, WZ of Dry Coal Feed	112.5	81.1	81.0	79.9	80.6	75.8
Makeup Oil, WZ of Dry Coal Feed	0.0	0.0	0.0	0.0	0.0	3.1
Catalyst Age, Lb/Lb	204	284	371	456	541	660
First Stage Temperature, F	751	750	796	817	750	752
Second Stage Temperature, F	800	824	795	767	824	826
FIRST STAGE FEED						
650 F-	19.09	35.13	36.37	34.97	29.51	9.73
650-850 F	59.43	50.92	46.99	43.79	46.82	50.30
850-975 F	16.93	12.44	13.51	12.84	12.32	15.46
975 F+ Oil	16.30	14.39	16.36	17.75	17.57	19.69
975 F+ Asphaltene	0.74	2.20	2.31	3.99	6.85	10.61
975 F+ Preasphaltene	0.00	0.12	0.14	0.61	1.63	1.74
Quinoline IDM	93.99	96.28	96.47	96.25	96.22	98.22
Ash	6.01	7.72	7.85	7.89	7.75	8.15
Total	212.50	219.20	219.90	218.10	218.70	213.90
SECOND STAGE BUFFER						
650 F-	0.78	1.16	1.04	0.98	0.85	0.17
650-850 F	2.43	1.68	1.34	1.23	1.35	0.89
850-975 F	0.69	0.41	0.39	0.36	0.35	0.27
975 F+ Oil	0.67	0.47	0.47	0.50	0.51	0.35
975 F+ Asphaltene	0.03	0.07	0.07	0.11	0.20	0.19
975 F+ Preasphaltene	0.00	0.00	0.00	0.02	0.05	0.03
Quinoline IDM	0.00	0.00	0.00	0.00	0.00	0.00
Ash	0.00	0.00	0.00	0.00	0.00	0.00
Total	4.60	3.80	3.30	3.20	3.30	1.90
FIRST STAGE PRODUCT						
650 F-	15.78	30.71	30.93	26.86	24.02	9.62
650-850 F	50.71	57.79	53.14	47.66	49.84	51.29
850-975 F	22.38	17.49	19.35	18.34	16.83	23.05
975 F+ Oil	39.45	24.69	24.48	22.39	25.61	28.31
975 F+ Asphaltene	0.87	2.56	7.00	9.56	9.53	8.35
975 F+ Preasphaltene	0.17	0.22	1.36	4.34	2.62	2.67
Quinoline IDM	32.49	31.55	19.53	13.86	33.44	35.92
Ash	6.01	7.72	7.85	7.89	7.75	8.15
Vapor (estimated)	44.64	50.35	56.25	67.20	49.07	46.55
Total	212.50	219.20	219.90	218.10	218.70	213.90
SECOND STAGE PRODUCT						
650 F-	30.65	42.49	45.06	41.34	35.60	16.86
650-850 F	69.99	60.80	57.49	50.90	55.64	58.29
850-975 F	19.94	14.86	16.53	14.93	14.64	17.92
975 F+ Oil	19.20	17.18	20.02	20.63	20.87	22.81
975 F+ Asphaltene	0.87	2.63	2.83	4.64	8.14	12.29
975 F+ Preasphaltene	0.00	0.14	0.17	0.71	1.93	2.02
Quinoline IDM	10.63	10.33	10.59	9.50	9.94	16.13
Ash	6.01	7.72	7.85	7.89	7.75	8.15
Vapor--	-60.50	66.85	-62.79	70.76	67.43	-61.33
Total	217.10	223.00	223.20	221.30	222.00	215.80

TABLE 8

FIRST AND SECOND STAGE PRODUCT FRACTION FORMATION - RUN 227-55
First and Second Stage Vapors Proportional to Coal Reacted

Condition	1	2	3	4	5	6
Period	6	10	13	16	19	22
Coal Rate, Lbs/Hr/Ft ³ Catalyst	44.9	44.7	48.0	45.6	44.9	69.6
Recycle TSB, WZ of Dry Coal Feed	0.0	38.1	38.1	38.1	38.1	38.1
Recycle PFL, WZ of Dry Coal Feed	112.5	81.1	81.0	79.9	80.6	75.8
Makeup Oil, WZ of Dry Coal Feed	0.0	0.0	0.0	0.0	0.0	3.1
Catalyst Age, Lb/Lb	204	284	371	456	541	660
First Stage Temperature, F	751	750	796	817	750	752
Second Stage Temperature, F	800	824	795	767	824	826

FIRST STAGE FORMATION**WZ of Dry Coal Feed**

Vapors	44.64	50.35	56.25	67.20	49.07	46.55
650 F-	-3.31	-4.42	-5.44	-8.11	-5.49	-0.12
650-850 F	-8.72	2.99	6.15	3.86	3.01	0.98
850-975 F	5.45	5.05	5.84	5.50	4.50	7.59
975 F+ Oil	23.14	10.30	8.11	4.64	8.05	8.62
975 F+ Asphaltene	0.13	0.36	4.69	5.57	2.68	-2.26
975 F+ Preasphaltene	0.17	0.10	1.22	3.73	0.99	0.93
Quinoline IOM	-61.50	-64.73	-76.94	-82.39	-62.78	-62.30
Ash	0.00	0.00	0.00	0.00	0.00	0.00
Total 975 F-	38.05	53.97	76.55	68.45	51.06	55.01
Total 975 F+ Residuum	23.45	10.77	14.02	13.94	11.72	7.29
Coal Converted (WZ of naf Coal)	65.43	68.87	81.86	87.66	66.79	66.29

SECOND STAGE FORMATION**WZ of Dry Coal Feed**

Vapors	15.86	16.50	6.54	3.56	18.36	14.78
650 F-	14.09	10.62	13.10	13.50	10.74	7.07
650-850 F	16.85	5.21	3.01	2.02	4.45	6.11
850-975 F	-3.13	-3.05	-3.21	-3.77	-2.54	-5.41
975 F+ Oil	-20.91	-7.99	-4.93	-2.26	-5.25	-5.84
975 F+ Asphaltene	-0.03	-0.01	-4.24	-5.03	-1.59	3.75
975 F+ Preasphaltene	-0.17	-0.08	-1.19	-3.65	-0.73	-0.69
Quinoline IOM	-21.86	-21.22	-8.94	-4.36	-23.50	-19.79
Ash	0.00	0.00	0.00	0.00	0.00	0.00
Total 975 F-	12.97	29.29	5.67	15.30	31.06	22.56
Total 975 F+ Residuum	-21.12	-8.08	-10.36	-10.94	-7.56	-2.77
Coal Converted (WZ of naf Coal)	23.25	22.57	9.51	4.64	25.00	21.05

TWO STAGE FORMATION**WZ of Dry Coal Feed**

Vapors	60.50	66.85	62.79	70.76	67.43	61.33
650 F-	10.78	6.20	7.66	5.39	5.25	6.95
650-850 F	8.13	8.20	9.16	5.88	7.47	7.10
850-975 F	2.32	2.00	2.63	1.72	1.97	2.18
975 F+ Oil	2.23	2.32	3.19	2.38	2.80	2.78
975 F+ Asphaltene	0.10	0.35	0.45	0.54	1.09	1.50
975 F+ Preasphaltene	0.00	0.02	0.03	0.08	0.26	0.25
Quinoline IOM	-83.36	-85.95	-85.88	-86.76	-86.27	-82.09
Ash	0.00	0.00	0.00	0.00	0.00	0.00
Total 975 F-	37.31	40.83	64.34	75.03	35.13	38.00
Total 975 F+ Residuum	2.33	2.69	3.67	3.00	4.15	4.52
Coal Converted (WZ of naf Coal)	88.69	91.45	91.37	92.30	91.79	87.34

TABLE 9

FEED COAL ANALYSES FOR RUN 227-55
Comparison with Clovis Point Coal Analyses
Run 227-55 Feed: Black Thunder Mine (Wyoming) Coal

FEED DESIGNATION, HRI No.	5630A	5613AA	Mine Analysis	5011AAA	5612
MINE	-----Black Thunder-----			Clovis Point	Coal Creek
TESTS	CTSLA	Micro		CTSLAAA	Micro
REPORTED MINE ANALYSIS					
Moisture, WZ	6.37A		27	31.5	30
Volatile Matter			32	31.0	30.7
Fixed Carbon			35	31.2	32.4
Ash			5	6.3	5.6
Btu/lb			8890	8100	8390
PROXIMATE ANALYSIS, WZ					
Volatile Matter (MAF Basis)	44.2	47.73	(48)	50.3	46.8
Fixed Carbon (MAF Basis)	55.8	52.27	(52)	49.7	53.2
ULTIMATE ANALYSIS					
(WZ, Dry Basis)					
Carbon	67.70	70.50		64.34	68.60
Hydrogen	4.54	4.47		4.44	4.42
Sulfur	0.48	0.46		1.14	0.46
Nitrogen	1.05	0.98		0.92	1.21
Chlorine	0.04	0.03			
Ash	(7.15)	(6.55)	(7)	(10.52)	(7.35)
Sulfur in Ash	(6.35)	(7.56)		(8.43)	(6.11)
Ash (SO ₃ -free)	6.01	5.31		8.30	6.23
Oxygen (By Difference)	20.18	18.15		20.89	19.08
SULFUR FORMS					
(WZ, Dry Basis)					
Sulfate	0.04	0.01		0.02	
Pyrite	0.11	0.06		0.44	
Organic	0.36	0.46		0.61	
HEATING VALUE, Btu/lb(Dry)	11797	12048	(12200)	11408	
Btu/lb MAF	12551	12724	(13100)	12440	
MINE ANALYSIS OF ASH					
(WZ, Ignited)					
Silica, SiO ₂	34.61	27.96		25.40	
Alumina, Al ₂ O ₃	16.98	15.81		11.61	
Titania, TiO ₂	1.30	1.20		0.67	
Ferric Oxide, Fe ₂ O ₃	6.94	5.29		16.11	
Lime, CaO	21.74	26.79		18.47	
Magnesia, MgO	4.40	5.27		3.23	
Potassium Oxide, K ₂ O	0.35	0.37		0.29	
Sodium Oxide, NaO	0.97	1.34		1.52	
Sulfur Trioxide, SO ₃	10.74	13.45		20.76	
Phosphorous Pentoxide, P ₂ O ₅	1.01	0.63		0.67	
Strontium Oxide, SrO	0.29	0.29		0.21	
Barium Oxide, BaO	0.37	0.26		0.31	
Magnesium Oxide, Mn ₃ O ₄	0.00	0.00		0.08	
Undetermined	0.30	1.34		0.67	
MICROAUTOCLAVE RESULTS****					
Thermal Coal Conversion	76.6	84.6		84.9	80.7
Thermal 975 F+ Conversion	44.3	52.0		50.6	51.4
Catalytic Coal Conversion	87.9	94.6		92.9	87.7
Catalytic 975 F+ Conversion	72.9	75.2		75.8	71.4
MACERAL ANALYSIS, WZ					
Reactivities					
Vitrinites					
Exinite					
Resinite					
1/3 Resinite					
Total					
Inerts					
2/3 Semifusinite					
Micrinite					
Fusinite					
Total					
Ash					

* Dried Black Thunder coal feed to Run 227-55.

** Black Thunder coal used in microautoclave tests.

*** Clovis Point coal feed to Runs 227-21 and 227-22.

**** 1989 tests - 800 F, 30 minutes, 2000 psig H₂,

4/1/(1) Solvent/Coal/(Shell S-317 Catalyst)

Solvent - Wilsonville coal liquefaction distillate product.

TABLE 10
INSPECTION OF STARTUP AND MAKEUP OILS
FOR RUN 227-55(CC-1)

Designation	HRI-5443	227-25 SU
Gravity, API	10.2	15.9
Distillation, F		
IBP	205	451
5 V%		500
10 V%	585	510
20 V%	656	527
30 V%	697	536
40 V%	721	550
50 V%	750	572
60 V%	778	594
70 V%	812	623
80 V%	850	666
90 V%	925	727
E.P.	975	884
Recovery, V%	98	98
Residue, W%	4.3	2.4
V% @ 650 F	16	76
V% @ 850 F	80	96
Carbon, W%	88.63	
Hydrogen, W%	10.12	
Sulfur, W%	0.04	
Nitrogen, W%	0.25	
Toluene Insolubles,		
W% of 975 F*	7.98	
Ash, W% of 975 F*	2.36	
Solvent Quality Test*		
Illinois No. 6 Coal	57.7, 69.3	53.4, 55.3
Black Thunder Coal	54.7, 57.4	47.2, 53.0
* Thermal Conversion at 750 F, 30 Minutes, 2/1 solvent/coal		

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TABLE 11

FRESH CATALYST PROPERTIES - RUN 227-55(CC-1)

HRI No.	5394
Designation	Shell S-317
Nominal Size	1/32" Extrudates
CHEMICAL ANALYSIS (W%, DRY BASIS)	
Molybdenum,	11.46
as MoO ₃	17.2
Nickel,	2.27
as NiO	2.89
PHYSICAL PROPERTIES	
Bulk Density, Compacted, Lb/Ft ³	36.7
Particle Density, gm/cc	0.941
Surface Area (Calc.), M ² /gm	267
M ² /cc particle	251
Pore Volume, cc/gm	0.697
cc/cc particle	0.656
Average Crush Strength, Lb/mm	1.94
PORE SIZE DISTRIBUTION, CC/GM	
Diameter > 30 A	0.70
Diameter > 100 A	0.40
Diameter > 250 A	0.15
Diameter > 500 A	0.14
Diameter >1500 A	0.11
Diameter >4000 A	0.03
PENETRATION TEST	
Average Penetration, % of Diameter	34.9

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TABLE 12

**RECOVERED CATALYSTS ANALYSES
RUN 227-55 (CC-1)**

STAGE	First	Second
CATALYST AGE, LB COAL/LB	676	675
CATALYST RECOVERY, VOL%	85.6	89.4
Bulk Density, Gm/cc	0.869	0.903
ANALYSES OF OIL-FREE +20 MESH CATALYST, W%		
Carbon	15.57	18.90
Hydrogen	0.75	0.99
H/C Ratio	0.75	0.63
Sulfur	5.59	5.42
Molybdenum	8.47	8.26
Cobalt		
Nickel	1.66	1.57
Titanium	0.02	0.02
Iron	0.52	0.07
Calcium	0.14	0.20
Sodium	0.81	1.08
Total Metal Contaminants	1.50	1.37
Loss on Ignition, W%	21.78	24.50
Particle Density, Gm/cc	1.387	1.459
particle		
Pore Volume (D>30 A), cc/gm	0.338	0.259
cc/gm	0.469	0.378
cc/cc particle		
Surface Area (calc.), M2/gm	160	101
M2/cc particle	222	148
ANALYSIS OF IGNITED CATALYST		
Particle Density, gm/cc	1.125	1.124
particle		
Pore volume (D>30 A), cc/gm	0.623	0.605
cc/cc particle	0.715	0.680
Surface Area (calc.), M2/gm	288	214
M2/cc particle	245	240
ANALYSES OF 20-100 MESH OIL-FREE SOLIDS		
Weight, Grams	56.4	66.7
Molybdenum, W%	4.93	3.28

In mercury at 10 psia.

Coal Conversion - W% of max Coal

COAL CONVERSION - RUN 227-55

FIGURE 1

975 F+ CONVERSION - RUN 227-55

FIGURE 2

C1-C3 GAS YIELDS - RUN 227-55

FIGURE 3

FIGURE 4

C 4 - 3 9 0 F Y i e l d . W % o f D r y C o a l

IBP-390 F NAPHTHA YIELD - RUN 227-55

FIGURE 5

NAPHTHA VS GAS YIELDS - RUN 227-55

FIGURE 6

390-650 F Yield, W% of Dry Coal

390-650 F LGO YIELD, RUN 227-55

FIGURE 7

650-975 F HGO YIELD - RUN 227-55

FIGURE 8

RESIDUAL OIL YIELDS - RUN 227-55

9 7 5 F + Yield : W % of Dry Coal

FIGURE 9

RESIDUUM CONCENTRATION IN PRODUCT SLURRY

Run 227-55 vs Days

Resid. in Sep. Bottoms, W%

FIGURE 10

FIGURE 11

FIGURE 12

2 of 7

650-850 F MGO YIELD - RUN 227-55

FIGURE 13

850-975 VGO YIELD - RUN 227-55

850-975 Yield, W% of Dry Coal

FIGURE 14

850 F+ RESIDUUM YIELD - RUN 227-55

850 F + Yield, W% of Dry Coal

FIGURE 15

HYDROGEN CONSUMPTION - RUN 227-55

Hydrogen Consumption - W% of Dry Coal

FIGURE 16

HYDROGEN CONTENT OF HEAVY PRODUCTS

Filtered Liquid Product Fractions

FIGURE 17

HYDROGEN CONTENT OF LIGHT PRODUCTS

Contents Adjusted to 420 B. P.

FIGURE 18

HYDROGEN VS NOMINAL MINERAL MATTER

Run 227-55 THF Washed Product Solids

FIGURE 19

NITROGEN VS NOMINAL MINERAL MATTER

Run 227-55 THF Washed Product Solids

FIGURE 20

SULFUR VS NOMINAL MINERAL MATTER

Run 227-55 THF Washed Product Solids

FIGURE 21

HYDROGEN CONTENT CHANGE BETWEEN STAGES

FIGURE 23

NITROGEN CONTENTS OF PRODUCT FRACTIONS

Run 227-55 First and Second Stage

FIGURE 24

PARITY PLOT FOR CORRELATED CONVERSIONS

Overall Two Stage Coal Conversion

PARITY PLOT FOR CORRELATED CONVERSIONS

Conversion in First Stage

SELECTIVITY OF COAL TO RESIDUUM

VS ACTIVATION ENERGY - RUN 227-55

FIGURE 26

FIGURE 27

RESIDUUM REACTION RATE CONSTANTS

43% Prim. Form - Adj. to 750 F, 6 Kcal/m

FIGURE 28

PARITY PLOT FOR RESIDUUM YIELDS

Run 227-55 - Proj. Using Kin. Model

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SECTION II

RUN 227-57(CC-2) - CTSL™ EVALUATION OF BLACK THUNDER MINE COAL WITH REDISTRIBUTED STAGE VOLUMES

INTRODUCTION

Run 227-57(CC-2) was a CTSL™ bench unit evaluation of Black Thunder Mine, Wyodak Anderson Seam (Wyoming), sub-bituminous coal obtained from the Thunder Basin Coal Co. This evaluation was with the first stage volume double that of the second stage, for comparison with Run 227-55(CC-1) with the same coal where the stage volumes were equal.

In general operations indicate a small effect on total distillate yield, reflecting countervailing effects of lower light gas yield and lower residual oil yields against lower coal conversion. The product liquids were of improved quality with lower nitrogen content and higher hydrogen content.

SUMMARY

The Black Thunder Mine Coal was tested in a 14-day run in the CTSL™ Bench Unit. This operation studied three coal space velocities with the first stage volume twice the second stage volume and two different second stage temperatures.

The first condition, a comparison with an equal-stage-volume operation at a common second stage coal space velocity (doubled first stage volume), indicated 1.2% increased coal conversion, 1.1 W% lower residual oil yield, less than 0.5 W% increase in gas yield, and 1.8 W% increase in C₄-975°F distillate yield. Nitrogen contents were about one-half to two-thirds of those of the reference equal-stage-volume operation, while hydrogen contents were slightly higher by 0.04-0.19 W%.

The second condition, a comparison with an equal-stage-volume operations at a common overall coal space velocity (redistributing the stage volumes), indicated 2% lower coal conversions, 1 W% lower residual oil yield, possibly equal gas yields (modelling projects 1 W% lower gas yield, and 1.6 W% lower C₄-975°F distillate yields. Nitrogen contents were lower than in the equal-stage-volume reference operation by a factor of two-thirds to three-fourths, while hydrogen contents were higher by an average of 0.3 W%.

The third condition, a comparison with an equal-stage-volume operation at a higher common overall two-stage coal space velocity, indicated 1.6 W% lower coal conversion, 0.5 W% lower residual oil yield, 0.3 W% lower gas yield, and 1.6 W%

lower C₄-975°F distillate yields. The relative nitrogen contents were lower than in the equal-stage-volume reference operation by the same proportion noted above in the Condition 2 comparisons, while the difference in hydrogen contents was even greater with 0.9 W% higher hydrogen contents than in the reference operation. Another comparison for this condition, with an equal-stage-volume operation at a common first-stage coal space velocity (halving the second stage volume), indicated 5 W% lower coal conversion, 1 W% higher residual oil yield, 1-2 W% lower gas yield, and 3-4 W% lower C₄-975°F distillate yields.

The unit ran smoothly until shortly before the final shutdown which was occasioned by rupture of the diaphragm drive of the first stage internal recycle pump. After repair of the pump internal recycle flow could not be restored because of a plug inlet section of the first stage reactor. Catalysts recovered from the reactors after the run were in good condition and the amount of catalyst recovery was reasonably high.

SCOPE OF WORK

The coal used in Run 227-57(CC-1) was characteristic of commercial shipments from the Black Thunder Mine. The catalyst for both stages was Shell S-317 1/32" nickel molybdate on alumina extrudates, a commercially available catalyst. This catalyst shipment was the same as that used in the CTSLTM demonstration run for Illinois coal, Run 227-47(I-27), and Run 227-55(CC-1).

The operating conditions for the three conditions used during the run are summarized in *Table 1*. The first condition used a coal feed rate and stage temperatures that were the same as the values used in the same stage of Run 227-55(CC-1), so that the difference between the two runs was increased size of the first stage reactor for Run 227-57(CC-2). For Condition 2 of Run 227-57(CC-2) the coal feed rate was increased by 50% so that overall two-stage velocity matched that used in the earlier run. Also, the second stage temperature was increased by 25°F to match that used in Run 227-55(CC-1). For Condition 3 the coal feed rate was increased a further 33%.

Samples of the slurry circulating in the first stage were taken for each of the Conditions for use in evaluating the performance of the individual stages.

PROGRAM RESULTS AND ANALYSES

RUN 227-57(CC-2)

This section discusses the conversions, product yields, process performance and product quality for Run 227-57(CC-2). *Table 2* is the operating summary for the run giving the principal operating conditions for each Period (day), and normalized product distributions for periods which were considered to represent equilibrated results. (Note in this table the ash values are on an SO₃-free basis, for reasons which are discussed below in the section concerning coal analyses.)

Figures 1 to 13 graphically summarize the conversions and yields of the major product fractions against time of stream period, identifying the principal operating conditions for each of the points. These figures also show the yields for a comparable stage of Run 227-55(CC-1), the earlier run with the Black Thunder Mine coal with equal stage volumes. The comparison of the results of the two runs is discussed in greater detail in the section. "Comparison With Operations Having Equal Stage Volumes".

COAL CONVERSION

Figure 1 graphically summarizes the coal conversions against hours of coal operations for the two runs.

Coal conversion ranged from 85.7 to 89.4% of MAF (moisture and ash-free) coal. The highest level of coal conversion was obtained during the Condition 2 operation, with the intermediate space velocity and the higher second stage temperature. The lowest level of coal conversion was obtained during the Condition 3 operation, with the highest space velocity and the higher second stage temperature. The Condition 1 operation, with the lowest space velocity and the lower second stage temperature, had conversions very nearly as great as those of the Condition 2 operation.

Relative to the conversions during Run 227-55(CC-1), where there were equal stage volumes, the conversions of Run 227-57(CC-2) have a reasonable pattern in kinetic terms. Doubling the first stage volume, with a common second stage coal space velocity (2ndSV in the legends of the figures), resulted in higher conversion by about 1.2%. For the second set of operations compared, at a common combined coal space velocity, there was about 2% lower conversion for the Run 227-57(CC-2) operations with the higher proportion of the lower temperature first stage. For the third set of operations compared, having a common first stage space velocity and having twice as great second stage velocity in 227-57(CC-2), the Run 227-57(CC-2) coal conversions were 4-5% lower than those obtained at the same interval of Run 227-55(CC-1).

The pattern of the relative performance of the two runs, in terms of coal conversion, conforms to the kinetic model parameters developed using the Run 227-55(CC-1)

data. However, the magnitude of the differences projected from this model would indicate that the additional first stage reactor volume was less effective in promoting coal conversion than would be expected on the basis of the kinetic model. The modelling is discussed in greater detail in the section below concerning the interpretation of the first stage samples that were obtained.

975°F⁺ CONVERSION

Figure 2 is a summary of the 975°F⁺ Conversions (100 minus unconverted coal minus residual oil yield) through the run, plotted against hours of coal operations with identification of the principal changes in operating conditions.

975°F⁺ conversion ranged from 81.5% to 87.7% of maf coal. For the most part the variations in this performance parameter followed the variations in coal conversions. The highest level of 975°F⁺ conversion was obtained during the Condition 2 operation, with the intermediate space velocity and the higher second stage temperature. The lowest level of 975°F⁺ conversion was obtained during the Condition 3 operation, with the highest space velocity and the higher second stage temperature. The Condition 1 operation, with the lowest space velocity and the lower second stage temperature, reached 975°F⁺ conversions very nearly as great as those of the Condition 2 operation.

Relative to the performance during Run 227-55(CC-1), where there were equal stage volumes, the 975°F⁺ conversions of Run 227-57(CC-2) indicate somewhat greater contribution of the added first stage volume than indicated by the relative coal conversions of the two runs. The addition of first stage volume, with a common second stage coal space velocity (2ndSV in the legends of the figures), resulted in higher 975°F⁺ conversion by up to 2.4%, for the first operations compared. For the second set of operations compared, at a common combined coal space velocity, there was about 1.2% lower 975°F⁺ conversion for the Run 227-57(CC-2) operations with the higher proportion of the lower temperature first stage. For the third set of operations compared in *Figure 2*, having in effect a common first stage space velocity with Run 227-57(CC-2) and having twice as great second stage velocity, the Run 227-57(CC-2) 975°F⁺ conversions were 6-7% lower than those obtained at the same interval of Run 227-55(CC-1). In Condition 3 at intermediate space velocity, higher than expected 975°F⁺ conversions were obtained.

The comparison of the results for Condition 3 of Run 227-57(CC-2) is complicated by the differing overall two space velocities involved. A more detailed comparison of the results of the two runs is given below, in the section which makes a comparison with the results of an operation later in Run 227-55(CC-1) which had the same overall space velocity as that of Condition 3 of Run 227-57(CC-2). That operation in Run 227-55(CC-1) had 975°F⁺ conversions in the same general range as that obtained in Condition 3 of Run 227-57(CC-2).

NORMALIZED PRODUCT DISTRIBUTION

Normalized product distributions for periods of equilibrated operations are included in *Table 2*. Yields, as a percentage of dry coal fed, are plotted against hours of coal operations *Figures 3 through 13*.

C₁-C₃ Gas Yields

Figure 3 summarizes the normalized yield of C₁-C₃ hydrocarbon gases through the run, which ranged from 6.5 to 8.7 W% of dry coal. The gas yields were erratic in the current run and in the reference run, Run 227-55(CC-1), but have a pattern that corresponds to the expected differences between the two runs.

Gas yields for Run CC-2, at 7.4 W% of dry coal, averaged 0.3 W% more than projected from correlation of the gas yields during Run CC-1, allowing for the redistribution of reactor volumes. This discrepancy cannot be considered significant in view of the scatter of the data.

For Condition 1 of Run CC-2, doubling the volume of the lower temperature first stage (compared to Run CC-1), the average gas yield was 1.1 W% higher than in the earlier run. Because of the scatter of the gas yield data for the two runs, this difference would not be considered significant. However, kinetic correlation of the results of the two runs (see below) projects a 1.1 W% difference in this yield for the two runs.

For Condition 2 of Run CC-2, with increased feed rate and increased second stage temperature, the gas yields averaged 0.9 W% less than that for Condition 1 of the run. This yield in Run CC-2 averaged 1.0 W% lower than in the reference run (Run CC-1) with equal stage volumes at the same overall two stage space velocity and the same first and second stage temperatures. Again, the scatter of the data might make the significance of these differences doubtful. However, kinetic correlation of the gas yields largely supports the apparent impact of these changes. The correlation of gas yields projected 1.8 W% lower gas yield for Run CC-2 configuration with the higher proportion of lower temperature first stage reactor volume.

For Condition 3 of Run CC-2, with space velocities increased by 50%, gas yields averaged 0.4 W% lower than for Condition 2 of the run. Compared to the reference run, with equal stage volumes and half as great second stage space velocity, the gas yield of Run CC-2 was lower by about 2.0 W%. The difference for the two reactor configurations projected from the kinetic correlations was also about 2.0 W%.

The pooled data for gas yields from Runs CC-1 and CC-2 were correlated by the kinetic model previously developed for these yields for Clovis Point (Wyoming) and

Illinois No. 6 coal. The resulting least-squares values of the correlating parameters were the following:

Primary yield - 2.8 W% of converted coal

Secondary formation from slurry phase reactions

Rate Constant @ 810°F - 0.905 lbs/hr/ft³(reactor)

Temperature Dependence

Arrhenius Activation Energy - 68,000 Btu/lb mole

The correlation has a high statistical confidence level, 99.99%, with an R-squared value of 0.495, and a standard error of 1.15 W%. The low value of R-squared (the deviation from the means values removed by the correlation) is for the most part due to the poor replication of results at a given set of conditions, since an analysis of variance indicates that the experimental standard error is about 1.07 W% only slightly less than the standard error of the correlation.

There appears to be no strong evidence on any synergistic effect upon gas yield of the redistribution of reactor volumes, beyond that projected considering the severity of conditions in each of the two stages.

C₄-390°F Naphtha Yields

Figure 4 summarizes the normalized yield of C₄-390°F Naphtha through the run, which ranged from 14.0 to 20.1 W% of dry coal. The highest yields were obtained during the Condition 1 and Condition 2 operations, while the lowest yields were obtained during the Condition 3 operations.

Naphtha yields for Run CC-2, at 17.7 W% of dry coal, averaged within 0.1 W% of the projected values (considering the differing proportions of volumes of the two stages) based upon the kinetic correlation of the naphtha yields during Run CC-1. However, re-correlation of the pooled naphtha yield data for the two runs gave a improved fit to the correlation, with an increase in the R-squared value from 0.647 to 0.806, and lowering the mean residual error from 1.53 W% to 1.13 W%. The fit of the revised correlation of the data was good for both of the two runs as indicated in *Figure 5*, the parity plot for the correlated naphtha yields. The principal changes in the correlation were lowering the temperature dependence of the secondary reaction of liquid components of the reactor slurry, from an activation energy of 83,000 Btu/lb mole to 65,100 Btu/lb mole, and lowering the proportion of naphtha derived from the primary conversion of the coal from 12.7% to 7.5% of reacted coal. The apparent rate of secondary reaction of slurry liquid phase components was 2.22 lbs/hr/ft³ (reactor). The R-squared value of the kinetic correlation was 0.806, and the statistical confidence level of the correlation was over 99.99%.

For Condition 1 of Run CC-2, doubling the volume of the lower temperature first stage (compared to Run CC-1) apparently caused some increase in naphtha yield, by about 2.0 W% compared to this yield in Run CC-1 (the correlated values project an increase of 2.6%).

For Condition 2 of Run CC-2, redistributing the reactor volumes to a higher proportion of low temperature first stage reactor volume, the naphtha yield was 0.0-2.9 W% lower than in Run CC-1, although the fact of any difference is uncertain because of the scatter of the Run CC-2 naphtha yield. The correlated values project 3.9 W% lower yield for the Run CC-2 reactor configuration, indicating that the lower experimental value of this yield in Run CC-2 is probably the more representative value.

For Condition 3 of Run CC-2, with space velocity increased by 33%, naphtha yields were sharply lower, by about 4.5 W%, than in the previous operations of the same run. The correlation projects a decrease of 2.8 W% in yield for this change in conditions. The comparison offered in *Figure 4*, with the operation in Run CC-1 at the same catalyst age, reflects the impact of halving the second stage volume at the same first space velocity, showing a naphtha yield lower by 5.8 W% for the Run CC-2 configuration (the correlated difference in naphtha yield is 3.9 W%). A comparison for the configurations at a nearly common overall-two-stage space velocity can be made with a later operation of Run CC-1, as follows:

Run	Periods	-----Conditions-----				Naphtha Yield W%	
		No.	1st Temp.	2nd Temp.	Sp. Vel.*	Experi.	Proj.
CC-1	21-22	6	752	824	34.6	15.3	15.1
CC-2	12-14	3	749	823	30.2	14.4	15.3
CC-2**	21-22**	3	749	823	30.2		14.4
CC-2**	21-22**	3	749	823	34.6		13.4

* Overall two-stage space velocity, Lb/Hr/Ft³(Catalysts)

** Projection only

This comparison indicates that the configuration of Run CC-2, with the higher proportion of first stage reactor volume, probably results in a lower naphtha yield up to 2 W% of dry coal.

390-650°F Light Distillate Yield

Figure 6 summarizes the yield of 390-650°F light distillate through Run 227-57(CC-2), with a comparison with the results of Run CC-1. The 390-650°F light distillate yield in Run CC-2 ranged from 24.3 to 29.1 W% of dry coal. The highest yield was obtained during the Condition 2 operations of the run, with only slightly lower yields during the Condition 1 operation, and the lowest yield during the Condition 3 operations of the run.

For Condition 1 of Run CC-2, the yield of 390-650°F distillate appeared to be very nearly the same as that obtained in Run CC-1. This pattern would suggest that the kinetic factors involved in the generation and the secondary reaction of this component were essentially balanced by the additional first stage volume in Run CC-2.

For Condition 2 of Run CC-2, the yield of 390-650°F distillate again appeared to be very nearly the same as that obtained in Run CC-1. However, evaluation of this pattern should consider a difference in recycle oil composition (reflecting a similar difference in liquid phase compositions in the reactor) for the two runs at this stage of operations. In Run CC-1, with a temperature of the atmospheric still removing light distillates from the recycle solvent (PFL) at only 300°F, there was about 30 W% of 390-650°F distillate in the recycle solvent, while in Run CC-2 this temperature was 525°F so that there was only about 22 W% of this fraction in the recycle solvent. This difference would tend to conserve this fraction (i.e. decrease the potential for secondary reaction) in the mode of atmospheric still operation in Run CC-2. The kinetics of the secondary conversion of this fraction are not well defined by the CTSLTM operating results, but the results of microautoclave experiments on relatively narrow boiling range gas oil components of the CTSLTM product have been used to estimate the impact of this difference in recycle solvent composition. These calculations indicate, as operated with the difference in recycle oil compositions, the expected yields of this product fraction would be fairly close, within 1-2 W%, for the two reactor configurations. However, had recycle oil compositions been the same for the two runs, with the Run CC-2 configuration the yield of this fraction would be expected to be up to 3-4 W% lower than with the Run CC-1 configuration. This increment would apparently be principally in increased yield of the higher boiling gas oil components, although some increase in naphtha yield would be expected.

Incidentally, in the comparison of the Condition 1 operations for the two runs, the atmospheric still was at 525°F in both runs, so that an allowance for differences in recycle composition is not necessary in comparing the results of the two runs. A kinetic projection of the impact of the additional first stage volume during the Condition 1 operations indicates that there would be a 1-2 W% higher yield of the 390-650°F gas oil with the additional first stage volume as in Run CC-2, while the experimental results indicate essentially no impact upon this yield, during the Condition 1 operations.

For Condition 3 of Run CC-2, the yield of 390-650°F distillate was about 3.5 W% lower than had been obtained in the earlier operations of the run, and 2 W% lower than obtained at the comparable stage of Run CC-1. This latter difference, the apparent impact of halving the second stage volume (at a common first stage space velocity) also should consider the differences of recycle solvent composition which was the same as noted above in the discussion of the Condition 2 results. Ostensibly, the difference in this result at this stage of the two runs would have been even greater had the recycle solvent contained the same proportion of 390-650°F oil in the two runs.

650-975°F Heavy Distillate Yield

Figure 7 summarizes the yield of 650-975°F heavy distillate through Run 227-57(CC-2), with a comparison with the results of Run CC-1. The 650-975°F heavy distillate yield in Run CC-2 ranged from 11.4 to 19.5 W% of dry coal. The highest yield was obtained during the Condition 3 operations of the run (average 17.6 W%), with the lowest level of yields holding for the Condition 1 and Condition 2 operations (average 13.3 W%).

For Condition 1 of Run CC-2, the average yield of 650-975°F distillate was very nearly the same as that obtained in Run CC-1. This pattern would suggest that the kinetic factors involved in the generation (from the 2.4 W% additional 975°F⁺ conversion in the Run CC-2 operation) and the secondary reaction of this component were essentially balanced by the additional first stage volume in Run CC-2. However, such a small change indicates a very low secondary reaction rate for the 650-975°F⁺ oil at the first stage temperature, corresponding to a first order reaction rate constant of less than 2.5 lbs/hr/(ft³ catalyst). Microautoclave tests on distillate components from CTSLTM Run CC-1 products have indicated reaction rates about twice as great. It can be concluded that the additional hydrogenation afforded by the additional first stage volume in Run CC-2 (see below) did not appreciably increase the rate of reaction of this fraction to lighter products.

For Condition 2 of Run CC-2, the yield of 650-975°F distillate averaged 1.1 W% below this yield at the same stage of Run CC-1. The differences in recycle solvent composition noted above in the above discussion of the 390-650°F yields is also a factor in considering these results. In the Run CC-2 operation the concentration of 650-975°F gas oils in the recycle solvent was 62.5 W%, while it was 55 W% in the Run CC-1 operation, so that there was probably somewhat greater potential for secondary reaction of this component during the Run CC-2 operation, and that its yield would have been relatively higher during Run CC-2 had the recycle composition been the same as in the earlier run. The kinetic parameters developed from the microautoclave results indicate that the 650-975°F yields would be virtually the same for Condition 2 of the two runs, as operated, and that for the Run CC-2 reactor configuration this yield would have been as much a 4 W% higher had the recycle solvent composition been the same as during Run CC-1.

For Condition 3 of Run CC-2, the yield of 650-975°F distillate averaged 3.7 W% higher than this yield at the same stage of Run CC-1. This difference reflects the difference in the higher second stage space velocity for Run CC-2 operation, and a difference in recycle oil content of this fraction (52% in Run CC-1, and 62 W% in Run CC-2), and this degree of change is consistent with the kinetic parameters indicated by the microautoclave experiments.

To estimate the kinetic impact of the doubled first stage volume for Run CC-2, the kinetic parameters, indicated by microautoclave tests, for the secondary reaction of the gas oil fractions from Run CC-1 were applied to the results of both Run CC-1 and CC-2. With a first order reaction rate for the 650-975°F fraction to lighter products of 0.22 Hr^{-1} at 825°F, and an activation energy of 78,000 Btu/lb mole, the indicate primary formation of this fraction averaged 56.5% of converted coal and residual oil for Run CC-1, and 55.5% for Run CC-2. This small difference indicates that there was little kinetic impact, besides the additional reaction volume, that could be ascribed to the higher degree of hydrogenation of this product fraction with the Run CC-2 reactor configuration.

With this average indicated primary yield of this fraction, and cited kinetic parameters, the correspondence of experimental and kinetically projected yields is mediocre, with a standard error of 2.5 W% for projected yields of this fraction for the Run CC-1 and CC-2 operations, which compares to a standard deviation 1.7 W% for the average of the uncorrelated data.

975°F+ Residuum Yield

The yield of 975°F+ Residuum oil in Run 227-57(CC-2), summarized in *Figure 8*, ranged from 0.8 to 4.3 W% of dry coal. The lowest yields were in the initial operation with the lowest space velocity, and the highest yields in the final operations at the highest space velocity.

Compared to Run 227-55(CC-1), this yield during the Condition 1 operation of Run 227-57(CC-2) averaged about two-thirds that during the comparable stage of the earlier run, representing the impact of additional first stage volume at a common coal feed rate to the system. During the Condition 2 operations of these runs, with a common two-stage coal space velocity, the relative yields were similar, reflecting the combined effects of the higher proportion of first stage volume and the higher boiling recycle during Run 227-57(CC-2). During the Condition 3 operations of the runs compared in *Figure 8*, this yield in Run 227-57(CC-2) was about 1.25 times that during the earlier run.

Figure 9 compares the residual oil concentrations in the recycle PFL solvent, reflecting the concentration in the reactor slurry and the kinetic impact of the additional first stage volume during Run 227-57(CC-2), during these two runs. For the Condition 1 operations, the residual oil concentration averaged 0.64 times as

great in Run 227-57(CC-2) as in Run 227-55(CC-1). For Condition 2 operations this ratio reached a value of about 1.04, and for Condition 3 operations it was 1.15. The pattern of these relative values are not appreciably different from those projected from the correlation of residual oil yields of Run 227-55(CC-1), which assumes an activation energy of 11,000 Btu/Lb Mole, as follows:

Condition	Ratio of Residual Oil Concentrations	
	Experimental	Projected
1	0.64	0.65
2	1.04	1.12
3	1.15	1.43

The relatively more moderate upward trend of the experimental results than the project trend indicates a possibly lower rate of catalyst deactivation for residual oil conversion during Run 227-57(CC-2) because of the higher proportion of the catalyst in the lower temperature first stage. The trends of Run 227-57(CC-2) relative to those of Run 227-55(CC-1) indicate that the rate of deactivation of the later run would appear to be two-thirds of that of the earlier run.

C₄-975°F Distillate Yield

Figure 10 summarizes the yield of C₄-975°F distillate during Run 227-57(CC-2). The C₄-975°F distillate yield ranged from 61.4 to 65.4 W% of dry coal. The highest yields were obtained during the Condition 1 and 2, where the effect of the 50% increase in space velocity of the Condition 2 operation was compensated for by its 25°F higher second stage temperature. The lowest yield was obtained in the Condition 3 operations after an additional 33% increase in space velocity.

Comparison with the results of Run 227-55(CC-1), included in *Figure 10*, indicate the following relative C₄-975°F distillate yields:

- A) For the Condition 1 operations, while the scatter in the experimental yields is of the order of the apparent difference in performance of the two runs, it is judged the additional first stage volume increased the yield of C₄-975°F distillate by about 1-2 W%, with the small increase in light gas yield being compensated for by larger increases in coal conversion and decrease in residual oil yield;
- B) For the Condition 2 operations, the increased proportion of first stage volume in Run 227-57(CC-2), with a common overall space velocity, caused a decrease in the yield of C₄-975°F Distillate by about 2 W%, principally because of lower coal conversion with that reactor configuration;
- C) For the Condition 3 operations compared in *Figure 10*, with a common first stage space velocity and a higher second stage velocity in

Run 227-57(CC-2), the yield of C₄-975°F Distillate was lower by 3-4 W% in that run, with the decrease in coal conversion, and increase in residual oil yield being more than the decrease in light gas yield.

Water and Carbon Oxides Yields

Figure 11 summarizes the water formation through Run 227-57(CC-2). Water formation ranged from 15.1 W% to 19.7 W% of dry coal. The average water formation during Condition 3 operations of the run, at the highest space velocity operations, was 2.6 W% lower than the average yield for Condition 1 and 2, with no definite difference in the results for the Condition 1 and Condition 2 operations.

The difference of the Condition 3 yields from those of the other two conditions is larger than can be accounted for by the apparent oxygen retention in the other products and unreacted coal. Direct analyses for oxygen contents are not available, but the "oxygen by difference" values for the various liquid products and product fractions are not appreciably different (0.3 W% or less) for the 3 conditions. The low coal conversion of the Condition 3 operation would account for an increase in oxygen retention, with about 17% "oxygen by difference" in the unreacted coal and a 3-4 W% increase in the amount of unconverted coal corresponding to 0.6-0.8 W% lower water formation. In addition, the higher carbon oxides yields in the latter stages of the run (see below) corresponds to a reduction in prospective water yield of about 0.8 W% of dry coal.

Comparing Run 227-55(CC-1) and Run 227-57(CC-2) for Conditions 1 and 2, there was essentially no difference in water yields which would correspond to the small differences in coal conversion for these operations. For the Condition 3 Operations of Run 227-57(CC-2) the water yield was about 3.5 W% below that for the corresponding stage of Run 227-55(CC-1). A difference of 1.2 W% would be expected because of the difference in coal conversions (6%) for these two operations. In addition, there were appreciably more carbon oxides formed in the latter stages of Run 227-57(CC-2) than in Run 227-55(CC-1) (see below), which would account for a difference in water yields of about 0.8 W%, for a total of 2.0 W%.

Carbon oxide yields during Run 227-57(CC-2), see *Figures 12 and 13*, increased progressively, as the space velocity was increased through the run, from about 0.7 W% of dry coal to 1.9 W% of dry coal. This pattern is in contrast to that of Run 227-55(CC-1), operating at constant space velocity, where the carbon oxides yield remained at a low level, 0.3-0.7 W%, over the same interval of the run. For the Condition 1 operations, the carbon oxides yields for the two runs were virtually the same, indicating that additional first stage volume in itself had little impact on this yield. For the Condition 2 operations, in Run 227-57(CC-2) the carbon oxides yields averaged 0.8 W% higher than during the corresponding stage of the earlier run, the nominal impact of a higher proportion of low-temperature first stage volume at a

common over-all space velocity. For the Condition 3 operations, in Run 227-57(CC-2) the carbon oxides yields averaged 1.3 W% higher than during the corresponding stage of the earlier run, the apparent impact of halving the second stage volume at a common first stage space velocity. This pattern follows a model where the carbon oxides are generated in the first stage, and are reacted in the second stage. Consequently, there may be a small advantage in terms of hydrogen "efficiency", with lower wastage of hydrogen in the formation of by-product water, with a higher proportion of first stage volume.

HYDROGEN CONSUMPTION

Hydrogen consumption during Run 227-57(CC-2) ranged from 6.7 to 8.0 W% of dry coal. The highest hydrogen consumptions were during the initial operations at the lowest space velocity, and the lowest hydrogen consumption was during the final operations at the highest space velocity. These differences are associated with lower hydrogen contents of the product liquids for the final operations, and a higher proportion of higher boiling liquids, which have relatively low hydrogen contents.

PRODUCT QUALITY

The elemental analyses of the net product fractions were made only on the gas oil and residual oil constituents of the filtered liquid produced in excess of solvent recycle requirements. These analyses for Run 227-57(CC-2) product fractions are summarized in *Table 3*. In addition, *Table 4* summarizes the analyses that were obtained for the lower boiling product streams, namely the Separator Overhead Product of about 130°F to 700°F boiling range, and the Atmospheric Still Overhead product of about 250°F to 675°F boiling range.

Hydrogen Contents - The average of the measured hydrogen contents was lower by 0.4 W% in the Condition 2 operation than in the Condition 1 operation. There was further decrease of 0.2 W% in this average for the Condition 3 operation. These changes are slightly greater than occurred over the same interval of Run 227-55(CC-1), 0.4 W% between Conditions 1 and 3. The Run 227-57(CC-2) hydrogen contents averaged 0.4-0.6 W% higher than in the earlier run.

Nitrogen Contents - Nitrogen contents increased progressively during Run 227-57(CC-2), being about twice as great in the Condition 2 operation as in the Condition 1 operation, with a comparable rise in the Condition 3 operation, but were all lower than in equal volume operations.

Sulfur Contents - Sulfur contents of the distillate products were generally in the range of 0.01-0.02 W%. The sulfur content of the residual oil product were 0.03-0.16 W%, with the highest sulfur content reported for the Condition 1 operation.

COMPARISON WITH OPERATIONS HAVING EQUAL STAGE VOLUMES

Table 5 compares the product distribution for the three Conditions of Run 227-57(CC-2), having two-thirds of the reactor volume in first stage, with those comparable operations in Run 227-55(CC-1) which processed the Black Thunder Mine coal with equal stage volumes. *Table 6* compares product stream analyses for the two runs and *Table 7* compares product fraction analyses for the two runs. *Figure 3* through *13* include comparisons of the yields of various product fractions for the two runs.

Condition 1 Results - The comparison of the Condition 1 results with those of the first operation of Run 227-55(CC-1) is, in effect, the impact of the halving the space velocity of the first stage while having equal second stage space velocities. In Run 227-57(CC-2), with the higher proportion of first stage volume, the yield of C₄-975°F distillate product was higher by 1.8 W% of dry coal (*Figure 10*), which reflected a higher coal conversion by 1.2 W% of maf coal (*Figure 1*), a lower residual oil yield by 1.1 W% (*Figure 8*). There was only a small impact on light gas yield (*Figure 3*), possibly an increase of the order of one-half of one percent, as expected from modelling the earlier operation. The incremental distillate yield was principally in the naphtha boiling range (*Figure 4*), with little difference in light and heavy gas oil yields (*Figures 6 and 7*).

A notable difference in the analyses of the products from the two modes of operation was lower nitrogen contents, for the operations with increased first stage volume. This difference occurred for the product streams (*Table 6*) and for the product fractions of the recycle solvent (*Table 7*), but the pattern of the difference in nitrogen contents was somewhat erratic, with perhaps greater difference for the higher boiling products fraction, by a factor of one-half to two-thirds.

Each of the three collected product streams had higher hydrogen contents with the increased first stage volume, although the difference was fairly narrow, by 0.04 to 0.19 W%, of the order of the precision of the analytical method.

Condition 2 Results - Comparison of the results for Condition 2 of Run 227-57(CC-2) with those of Run 227-55(CC-1) shows the impact of different proportions of first stage and second stage reactor volumes with a common overall two-stage space velocity.

The yield of C₄-975°F distillates for the Run 227-57(CC-2) operations, with the higher proportion of first stage volume, was 1.6 W% lower than that for the Run 227-55(CC-1). This difference was because of lower coal conversion by 2% for the Run 227-57(CC-2) operation, despite lower residual yield, by about 1.0 W% for that operation, with little difference in light gas yield for the two operations. The equivalence of the gas yields was inconsistent with the model based on earlier operations which projected about 1.1 W% lower gas yield with the higher proportion of the reactor volumes in the first stage. Some of the data for the two operations

supports this pattern of relative gas yields (see *Figure 3*). In that case, total distillate yields would for the two cases would be within 1 W%.

The distribution of the of distillate products between naphtha, light gas oil, and heavy gas oil was very nearly the same for the two modes of operation under the Condition 2 comparison.

Here again, the nitrogen contents of the product streams and product fractions were all lower for the products from the operation with the higher proportion of first stage volume. Perhaps there was slightly narrower difference than in the comparison of the Condition 1 results, but still of the order of two-thirds to three-fourths for the relative nitrogen contents.

Hydrogen contents of the product streams and product fractions were slightly higher for the operation with the higher proportion of first stage volume, after consideration of the differences in boiling ranges for the various streams involved. The average of the differences was about 0.3 W% hydrogen.

Condition 3 Results - Here the comparison in the *Table 5* is with an operation with a common combined overall two-stage space velocity in Run 227-55(CC-1), at 50% higher space velocity than the above comparison for Condition 2. The relative results are very nearly the same as noted for the Condition 2 comparison, with, for operation with the higher proportion of first stage volume, 1.6 W% lower C_4 -975°F distillate yield, 1.6 W% lower coal conversion, 0.5 W% lower residual oil yield, and 0.3 W% lower gas yield.

Here again, the nitrogen contents of the product streams and product fractions were all lower for the products from the operation with the higher proportion of first stage volume. The relative nitrogen contents for the two modes of operation were about the same as noted above in the Condition 2 discussion, although at a higher level of nitrogen contents, which were due in part because of the higher space velocity and in part because of the higher catalyst ages involved.

Hydrogen contents of the product streams and product fractions were likewise considerably higher for the operation with the higher proportion of first stage volume. The average of the differences was about 0.9 W% hydrogen, with a more pronounced difference in the higher boiling products. This pattern suggests a larger effect of catalyst age changes for the run with equal first and second stage reactor volumes.

The figures comparing the Run 227-57(CC-2) product structure with those of a comparable stage of Run 227-55(CC-1), in effect compare the Condition 3 operation of Run 227-57(CC-2) with a reference operation of Run 227-55(CC-1) having a common first stage space velocity and half as great a second stage space velocity. In effect, this comparison reflects halving the second stage reactor size for the Run 227- 57(CC-2) test. This change lowered C_4 -975°F distillate yield by 3-4 W%, with

5% lower coal conversion, about 1 W% higher residual oil yield, and 2-3 W% lower gas yield. The distribution of distillate products reflect lower naphtha yield, by about 6 W%, lower light gas oil yield, by about 1-2 W%, and increased heavy gas oil yield by about 4 W%.

FIRST STAGE SLURRY ANALYSES AND INTERPRETATION

Samples of the first stage slurry were obtained during each of the Conditions in Run 227-57(CC-2). The analyses of the samples that were obtained were used in conjunction with the second stage net product and recycle solvent analyses to characterize the performance of the individual stages. The analyses were conventional D-1160 distillation characterization of the filterable portion, and solvent fractionation of the 975°F⁺ residuum as 975°F⁺ Oil (cyclohexane soluble), 975°F⁺ Asphaltenes (toluene soluble, cyclohexane insoluble), and 975°F⁺ Pre-asphaltenes (toluene insoluble). The THF insoluble solids were characterized as ASTM ash and unconverted coal (the balance of the quinoline insoluble portion). Elemental analyses were obtained on the THF washed solids, the total filtered portion, and product fractions obtained in a D-1160 distillation.

Table 8 summarizes the distillation characterization of the first and second stage slurry phase liquids, and the elemental analyses that were obtained on these liquids, some product fractions, and on the oil-free solids obtained.

Table 9 interprets the distillations and solids content analyses in terms of first and second stage product fraction flows relative to the amount of coal feed to the operating system.

Table 10 interprets the flows of *Table 9* as individual stage performances in terms of apparent formation or reaction of the product fractions as a percentage of the coal fed to the operation. It should be noted that the quantities given in *Tables 9 and 10* are only for the slurry phase, and that any vapor phase content, particularly significant for the lighter distillate fractions, is not included.

An estimated vapor phase flow for the first stage is included in *Table 9*, the value used is based on the experimental vapor flow from the second stage, by assuming that the vapor generation in each stage was proportional to the amount of coal reacted in that stage. This value differs from the values used in the interpretation of the stage performances of the previous runs of the CTSLTM program, where it was assumed the first stage vapor equal the second stage vapor. The current procedure attempts to deal with the considerable variations in the first stage severity in Run 227-55(CC-1). The alternative of basing the first stage slurry phase flow (and apparent vapor flow) on the apparent ash content of the first stage sample and an ash balance, gave very erratic results for Run 227-55 (CC-1) corresponding to apparent vapor flows ranging from 15.6 to 91.6% of feed flow, with no clear relation to first stage severity.

Hydrogenation and Heteroatom Removal

Hydrogenation - The hydrogen contents of each of the second stage product fractions were generally lower than those of the corresponding first stage products.

This stage-to-stage decrease in hydrogen content averaged 0.37 W% for Condition 1 operations, 0.15 W% for Condition 2 operations, and 0.35 W% for Condition 3 operations. These values are in the range experienced in Run 227-55(CC-1), where this average decrease was 0.33-0.63 W% when the stage temperatures configuration was the same as used in Run 227-57(CC-2).

Denitrogenation - For the Condition 1 operations of Run 227-57(CC-2), the nitrogen content of the second stage liquids averaged 0.04 W% lower than that of the first stage liquids. In Condition 2, this difference was also a decrease of 0.04 W%, while for the Condition 3 operations the second stage nitrogen contents averaged 0.10 W% higher than those of the first stage. This pattern is similar to that noted in Run 227-55(CC-1) where there was nitrogen reduction in the second stage during the initial operations and a nitrogen increase in that stage in the final operations. However, in Run 227-55(CC-1) this switch-over was not apparent until the nineteenth day of operations, while in Run 227-57(CC-2) it occurred by the thirteenth day. Ostensibly, the deactivation of the second stage catalyst was more severe than that of the first stage catalyst.

Sulfur Contents - Sulfur contents were generally higher in the first stage liquids than in the second stage liquids, although there is no clear relationship of this pattern to the operating conditions.

Coal Conversion

The conversion in the first stage during Run 227-57(CC-2) range from 66.7 to 76.4 W% of maf coal, compared to the two stage conversions of 85.7 to 89.4 W%. First stage conversion was directly related to first stage space velocity, moderated by the recycling of some solids in the TSB recycle stream of Conditions 2 and 3. The pattern of first stage conversions in this run, and comparable operations of Run 227-55(CC-1), corresponds fairly closely to that projected by the coal conversion model developed from the results of the earlier run, as follows:

	Projected Conversion	Experimental Conversion
Run 227-57 (CC-2)		
Condition 1	75.8	76.4
Condition 2	71.9	72.3
Condition 3	66.8	68.3
Run 227-55 (CC-1)		
Condition 1	68.1	65.4
Condition 2	68.8	68.9
Condition 6	64.4	66.3

The projected impact upon first stage conversion (7.7 %) of the addition of first stage volume (compare Condition 1 of the two runs) was slightly lower than the difference in experimental results for the two operations (11.0%). The project impact of redistribution of stage volumes at a common two-stage space velocity (compare Condition 2 results and compare Condition 3 with Condition 6) was an increase of 2.3-3.1 W% with the higher proportion of first stage volume, compared to experimental differences of 2.0-3.4 W%.

The projections of two stage coal conversions for Run 227-57(CC-2) did not match experimental results as well, with an apparent bias of about 1.4 W% (high), as follows:

	Projected Conversion	Experimental Conversion
Run 227-57 (CC-2)		
Condition 1	89.5	88.4
Condition 2	90.6	89.4
Condition 3	87.8	85.7
Run 227-55 (CC-1)		
Condition 1	86.8	87.2
Condition 2	91.5	91.4
Condition 6	88.5	87.3

The projected additional conversion with additional first stage volume was 2.7 W%, compared to an experimental impact of 1.2 W% (Condition 1 results). The redistribution of stage volumes was projected to cause 0.7-0.9 W% lower coal conversion while the experimental impact was 1.6-2.0 W% (Condition 2 results, and Condition 3 compared to Condition 6).

The correlating parameters which were developed from the results of Run 227-55(CC-1), with reference to the previous work on Clovis Point Mine (Wyoming) coal were the following:

	Black Thunder	Clovis Point
Coal Distribution, W%		
High Reactivity	55	60
Low Reactivity	42	40
Unreactive	3	0
Kinetic Parameters		
Low Reactivity Constant		
Lbs/hr/ft ³ @ 750°F	17.1	18.5
Act. Energy, Kcal Mole	38.5	38.5
High Rate/Low Rate	56.7	56.7

The model assumed three coal species of different reactivity as in the above tabulation.

Residual Oil Formation

During Run 227-57(CC-2), the formation of 975°F+ residual oil in each of the stages, as summarized in *Table 10*, followed a pattern, common to such analyses in previous runs of the CTS^L™ program, of a moderate formation in the first stage, and net reaction in the second stage. In this run, first stage net residual oil formation was at a level of 6.2 to 8.7 W% of dry coal, slightly lower than at a corresponding stage of Run 227-55(CC-1), 10.8 to 14.0 W%. This difference indicates that the additional first stage volume of Run 227-57(CC-2) promoted the secondary reaction of residual oil to a greater degree than its additional generation as a primary product of the additional first stage coal conversion noted above.

Figure 14 compares for the two runs the apparent reaction rate constants for the secondary conversion of residual oil using the correlating parameters developed from the Run 227-55(CC-1) results (namely, 43% primary formation from the conversion coal, and temperature dependence corresponding to an Arrhenius Equation activation energy of 6 Kcal/gm mole). The apparent rate constants for the two runs are in the same general range, although the results of Run 227-57(CC-2) are considerably more scattered. For the Run 227-57(CC-2), there is no definite downward trend with increasing catalyst age of the rate constants corresponding to that in the Run 227-55(CC-1) results, although the scatter of the results weakens this conclusion. Other factors indicate some decline in performance as the catalyst aged in Run 227-57(CC-2), i.e. increasing asphaltenes (cyclohexane insoluble-toluene soluble) and preasphaltenes (toluene insoluble) contents, increasing nitrogen contents, and decreasing hydrogen contents. These latter trends might be

associated to a degree with the progressively increasing space velocity during Run 227-57(CC-2), although it is probable even after this consideration, some catalyst deactivation is indicated.

DETAILS OF OPERATIONS

This report summarizes the operations of Run 227-57(CC-2) in the CTSL™ bench unit using Black Thunder Mine Wyoming Coal in a reactor configuration with a first stage volume twice that of the second stage. Using three identical three identical 2,000 cc reactors, this reactor volume configuration was accomplished by returning the ebullating flow from the top outlet of the first-stage second reactor to the bottom of the first-stage first reactor. The net product from the first-stage second reactor flowed to the third reactor (second stage). The catalyst used in this run was Shell S-317 1/32" extrudate nickel molybdate. Shell S-317 catalyst had also been used in the earlier run with the Black Thunder Mine coal, and in earlier operations with Illinois No. 6 and Ohio 5/6 coals.

Run 227-57(CC-2) completed 347 hours of operations with coal feed while processing 280 lbs coal/lb first stage catalyst inventory (560 lbs/lb second stage inventory). Operations were with minimal problems until a shut-down was forced when the diaphragm of the first stage internal recycle pump failed, depressuring the system so that feed flow could not be resumed when the system was repressured. Operations with coal feed started on June 11, 1989, and the shutdown occurred on June 25, 1989. The completion of the intended Condition 4 operation, with bottoms oil extinction, was precluded because of the internal recycle pump failure.

Preoperational Procedures - Operations were started using HRI 5648 catalytic distillate produced using Illinois No. 6 coal at the Wilsonville coal liquefaction facility. This feed was used with dimethyl disulfide added in the catalyst presulfiding operation summarized below in the section covering the fresh catalyst. At the time of coal introduction the slurring oil was recycle material recovered during the heatup/presulfiding operations.

Operating Summary - A summary of the three sets of conditions used during the run is given in *Table 1*, along with the intended fourth condition to be started at the time of the shutdown. The final eight hours at each condition (an "A" period) was used to obtain a sample of slurry from the internal recycle line of the first stage as characteristic of material circulating through the first stage reactor.

Condition 1 (Periods 1A-7A) - The operating conditions were similar to those used in the similar stage of the previous run, Run 227-55(CC-1), excepting that the first stage space velocity was half of that during that run, because of the greater stage volume in Run 227-57(CC-2). The first and second stage temperatures were 750 and 800°F, respectively. The coal feed rate was 22 lbs/hr/ft³ (first stage catalyst), or 44 lbs/hr/ft³ (second stage catalyst). The solvent recycle was 1.0 lbs/lb coal consisting of pressure filter liquid obtained by filtration of reactor product slurry which had been topped of light distillate in the atmospheric still which was held at 525°F. During the first day the check valves on the internal recycle pump required

flushing several times to establish a steady internal recycle flow. There were no other operating problems during this interval of the run.

Condition 2 (Period 7B-11A) - For this condition the coal feed rate was increased by 50% so that the space velocities increased by a corresponding amount. The solvent recycle was changed to two-thirds pressure filter liquid, and one-third topped separator bottoms (unfiltered reactor product slurry that had been topped in the atmospheric still). The second stage temperature was increased to 825°F. This Condition corresponded to the Condition 2 of Run 227-55(CC-1), with common stage temperature, solvent recycle characteristics, and overall two-stage space velocity (with the difference that two-thirds of the reactor volumes was in the first stage of Run 227-57(CC-2)).

The unit ran smoothly during this interval of the run.

Condition 3 (Period 11B-15A) - For this condition the coal feed rate was increased by another 33%. Reactor temperatures and solvent recycle ratios were unchanged.

In the latter part of Period 14 there was an interval of about nine hours during which full flow of the second stage internal recycle stream could not be maintained, although there was sufficient flow to maintain some degree of catalyst bed expansion so that pressure drops were in the normal range throughout the system. Normal internal recycle flows had been restored by the end of Period 14 by flushing the checks valves.

In Period 15A, over the interval during which the first stage slurry sample was being obtained, slurry feed flow was erratic with no actual feed for about two hours. At this time a substantial increase in pressure drop, to 300 psi, developed, principally over the second stage. The pressure drop was about 100 psi before the final shutdown.

Condition 4 (Period 15B-) - This operation had been intended to be a bottoms oil "extinction" operation, where, by raising the atmospheric still temperature, middle oil would be removed from the recycle solvent to a degree that would raise the concentration of heavy gas oil and residual oil in the recycle solvent promoting additional secondary reaction resulting in their elimination from the product slate.

However, about two hours into this operation the diaphragm of the first stage internal recycle pump failed, depressuring the system. When the normal system back-pressure was restored, slurry feed flow could not be established before the pump discharge pressure reached the design limit. The reactors were cooled and a wash flow was attempted, although there was very little flow through the first stage reactors.

Post Run Inspection - The catalyst in the upstream reactor of the first stage appeared to be in a settled position in the reactor with the top of the bed in a

position corresponding to an 8% greater volume than the volume charged. It was necessary to drill out some material from the bottom of the reactor before free-flowing catalyst could be removed from the reactor. Some oil was trapped above the catalyst.

The catalyst in the downstream reactor of the first stage was in settled position in the reactor with the top of the bed in a position corresponding to 19% loss of catalyst volume. Free-flowing catalyst was recovered from the reactor with no difficulties.

The catalyst in the second stage reactor was found lifted towards the outlet screen of the reactor, in a position about 3-1/2 feet above its charged settled level, but still about 1-3/4 feet below the top screen in the reactor. The top screen was clear. About 1/3 of the catalyst fell from the reactor free-flowing and the rest had to be flushed from the reactor with wash oil.

There were no appreciable deposits in the other high-pressure vessels or lines.

The focus of the final high pressure drop was apparently the bottom section of the upstream reactor of the first stage.

Coal Feed

The coal feed for Run 227-57(CC-2) was obtained from the Black Thunder Mine (Wright, Wyoming) of the Thunder Basin Coal Company. The material used in the run, designated HRI 5630, was part of a three ton shipment received in drums about six months before the start of the run. A smaller, five-gallon, sample, designated HRI 5613, had been received earlier for preliminary evaluation in the HRI microautoclave. Thunder Basin Coal also provided a five-gallon sample from a second mine in the Wright Area, the Coal Creek Mine, which gave results in the microautoclave very similar to those of the Black Thunder Mine coal.

The HRI 5630 shipment was crushed to -1/2 inch, and ground to pass a 70 mesh screen in micropulverizer. Before the start of Run 227-57(CC-2) the ground coal was dried in a nitrogen swept tray oven at 200 F to an average moisture content of 6.8 W% (from about 27 W%), requiring 8-10 hours. The dried coal was stored in drums under nitrogen blanket until fed to the bench unit. The range of moisture contents for material actually fed to the CTSL™ operation was 6.3-7.5 W%.

Table 11 summarizes the analyses obtained on the dried, ground HRI 5630 coal feed to Run 227-57(CC-2) as well as the feed to Run 227-55(CC-1) and Run-238-04, a Co-processing run using the Black Thunder coal. A factor to be noted in this table is the expression of the ash content on an SO₃-free basis. The feed coal ash and the ash obtained from the CTSL™ product solids differ markedly in sulfur contents (6.35 W% sulfur and 2.1-2.9 W%, respectively) so that they are not truly equivalent materials in considering the ash (mineral matter) balance of the

CTSL™ operations. The apparent reason for the anomaly is that in the combustion during ash analysis the sulfur oxides formed from organic sulfur and pyritic/pyrrhotite sulfur react with alkali metal oxides and are retained in the ash, apparently over 90% of the available sulfur in both types of samples. Since there is less sulfur available in the product solids because of desulfurization/conversion reactions, less sulfur is retained in those products. It is considered that a reasonable estimate of "true" mineral matter is on this SO₃-free ash basis, and this is the best basis for comparing equivalent materials when calculating yields from the ash (mineral matter) balance.

The characteristics of the Black Thunder Mine coal relative to those of the Clovis Point Mine Wyoming coal that had been tested in earlier CTSL™ operations are discussed in some detail in the report of Run 227-55(CC-1). In summary, the two coals gave comparable CTSL™ performance, with the Black Thunder Mine coal having a probable processing advantage in having about 3 W% lower ash content.

Start-up Oil

The start-up oil for Run 227-57(CC-2) was a heavy distillate, HRI 5648, produced during operations using Illinois No. 6 coal at the Wilsonville Coal Liquefaction facility. It was used to provide the initial inventory of the system, and as the carrier oil during the presulfiding operations prior to the start of the coal feed. The HRI 5648 shipment is a new shipment of this type of oil from Wilsonville, and Run 227-57(CC-2) was the first run in which it was used. *Table 12* summarizes the inspections made on this oil, and compares them with those for the HRI 5443 shipment of oil from Wilsonville which was used as start-up oil for Run 227-55(CC-1). This table also contains the inspections on the PFL recovered by toluene extraction of the oil from the product filter cakes of Run 227-55(CC-1), designated L-741, which was intended as a makeup oil during the "extinction" operations of Condition 4 of Run 227-57(CC-2). Even though the Condition 4 operation was not actually attempted, the analysis of L-741 is included here as a matter of record.

The HRI 5648 oil is a heavy vacuum distillate, of somewhat higher boiling range than the oils that have been used previously as CTSL™ start-up materials. The following tabulation compares its properties with the HRI 5443 oil and other oils used for this purpose:

Oil Identif.	-----Inspections-----						Solvent Ill. No. 6	- Quality Black Thunder
	Source	Start-up Use	IBP	% @ 650	% @ 850	Endpt.		
HRI 4907	Catlettsburg	Clovis Pt.	486	75			58.0	65.3
L-721	Wilsonville	Ill. No. 6	492	32		800	60.8	63.7
HRI 5443	Wilsonville	Bl. Thunder	205	18	80	975	57.7	54.7
HRI 5648	Wilsonville						69.3	57.4
		Bl. Thunder	735	0	47	1008	78.4	61.1

Thermal Conversion at 750°F, 30 Minutes, 4/1 solvent/coal - 1989 Tests

The HRI 5648 oil had an average boiling point about 100°F higher than that of the HRI 5443 oil. Consideration of the boiling range, gravity, and hydrogen content indicate that the two oils were of about the same aromaticity. The microautoclave solvent quality tests summarized in *Table 12* indicate that the HRI 5648 oil was possibly a better solvent for coal conversion.

Fresh Catalyst

The catalyst used in both stages for Run 227-57(CC-2) was Shell S-317, 1/32" extrudate, nickel-molybdate on alumina. The designation was HRI No. 5394, the same lot that had been used for Illinois Coal and Ohio Coals in previous CTSL™ operations, as well as the previous run with the Black Thunder Mine coal, Run-227-55(cc-1). The inspections on the fresh catalyst are presented in *Table 13*.

The catalyst charged to the reactors was presulfided during the run start-up by treating with start-up oil spiked with 1.4 W% dimethyldisulfide. As product oil at the time of the presulfiding became available, it was spiked and recycled as the presulfiding solvent. The presulfiding operation consisted of two 6-hour holding periods with the reactors at 450°F, and at 550°F, and a 4-hour holding period at 650°F while feeding the spiked oil at about 1.0 V/Hr/V(total catalyst). The first and second stage reactor temperatures were then increased to 700 and 750°F, respectively, before coal feed was started. The first and second stage temperatures were then increased to the specified initial condition temperatures over a 48 hour period.

Recovered Catalyst

Analyses of the catalysts recovered from the two stages after Runs 227-55(CC-1) are given in *Table 14*.

The catalyst recovery from the upstream reactor of the first stage was 87% based on the relative volumes of charged and recovered +20 mesh oil-free catalysts, and 94% based on the reported molybdenum contents for the charged and recovered catalyst. There was also some catalyst in the 20/100 mesh material recovered, with the molybdenum content corresponding to 4.0% of the amount of molybdenum in the catalyst charged. The 20 mesh classification is close the diameter of the 1/32" diameter extrudates, so that some of the extrudates may have passed the screen. The catalyst recovery from the downstream reactor of the first stage was 94% based on the relative volumes of charged and recovered +20 mesh oil-free catalysts, and 104% based on the reported molybdenum contents for the charged and recovered catalyst. There was also some catalyst in the 20/100 mesh material recovered, with the molybdenum content corresponding to 1.5% of the amount of molybdenum in the catalyst charged. The carbon accumulation on the catalysts in the first stage reactors, 11.4 and 8.7 W%, was in the range experienced after Clovis Point Wyoming CTSL™ coal operations using Amocat 1C NiMo catalyst, 8.5 - 10.0 W% carbon on the recovered first stage catalyst. The principal metals accumulation were iron, 0.26 and 0.51 W%, and sodium, 0.33 and 0.50 W%. The total analyzed metals contamination, 0.67 and 1.04 W%, was moderate compared to that after Clovis Point Operations, which ranged from 1.3 to 4.1 W%, and that after Illinois Coal operations, which has been over 7 W% in some cases. The total of the analyzed contaminants on the Run 227-55(CC-1) catalyst was 19.1 and 16.7 W%, compared to values of 19 and 15 W% indicated by the reported molybdenum contents of the charged and recovered catalysts. The particle densities of the first stage recovered catalysts indicated 26 and 30 W% total contaminants. The pore volumes of the recovered catalysts were about 83 and 90% of that of fresh catalyst, when compared on a common catalyst content basis, which is higher the range of the pore volume retentions experienced in other runs. Ignition of the recovered first stage catalysts increased the pore volumes to about 92 and 107% of that of fresh catalyst, when compared on a common catalyst content basis, and the calculated surface area of the ignited catalyst was 98% of that of fresh catalyst. The catalyst recovery from the second stage was 89% based on the relative volumes of charged and recovered +20 mesh oil-free catalysts, and 99% based on the reported molybdenum contents of the charged and recovered catalysts. The molybdenum content of the 20/100 mesh recovered material corresponded to 3.0% of the amount in the catalyst charged.

The carbon accumulation on the second stage catalyst was 13.1 W%, lower than the range experienced after CTSL™ operations with Illinois coal, 13.8-19.6 W%, and also lower than the range of values after Clovis Point coal operations, 15.3-19.3 W%. The principal metallic contaminant was sodium at 1.31 W%, while iron accumulation was very low, 0.08 W%. The metallic contamination totalling

1.5 W% was again moderate compared to that after Clovis Point Coal operations and also after Illinois Coal operations. The total of the analyzed contaminants of the second stage catalyst was 20.8 W%, while the total contaminants estimated on the basis of the molybdenum content was 19 W%. The total contaminants estimated on the basis of the particle density was 35 W%. The pore volume of the recovered second stage catalyst was 89% of that of fresh catalyst when compared on a common catalyst content basis, a very high pore volume retention. Ignition of the recovered second stage catalyst increased the pore volume approximately to the degree that was experienced with the first stage catalysts.

The principal difference in the analyses of the recovered catalysts compared to those of the catalysts after Run 227-55 (CC-1) was the lower carbon contents of the Run 227-57(CC-2) recovered catalysts, 8.7 and 11.4 W% compared to 15.6 W% on the first stage catalysts, and 13.1 W% compared to 18.9 W% on the second stage catalysts. The difference in first stage catalyst carbon contents is possibly because of the lower first stage temperature used in Run 227-57(CC-2), 750°F throughout compared to temperatures up to 817°F during Run 227-55(CC-1). The second stage temperatures were generally in the same range for the two runs, 800 to 825°F, although there was 3 day interval at 767°F in run 227-55(CC-1). The difference in second stage carbon contents between the two runs is possibly associated with shorter run length of Run 227-57(CC-2), 337 hours compared to 526 hours, and second stage catalyst ages of 560 lbs coal/lb catalyst compared to 676. The pattern of metals contamination of the recovered catalysts for the two runs was very similar, with appreciable sodium accumulation in both stages, although slightly higher in the second stage, and considerably greater iron accumulation in the first stage than in the second stage..

TABLE 1**RUN 227-55 OPERATING CONDITIONS**

Catalyst - Shell S-317 (HRI 5394) in Both Stages
 Coal Feed-Black Thunder Mine (Wyoming) Coal,
 Thunder Basin Coal Co.

	1	2	3	4 ⁽¹⁾
CONDITION NUMBER				
PERIOD (DAYS)	<u>1A-7A</u>	<u>7B-11A</u>	<u>11B-15A</u>	<u>15B-19A</u>
Nominal Conditions				
Unit Pressure, Psig	2500	2500	2500	2500
Coal, Lb (dry)/hr/ft ³ (catalyst)				
First Stage	22	33	44	44
Second Stage	44	67	88	88
Solvent Recycle, lb/lb Coal				
Filtered Liquid	1.1	0.76	0.76	0.76
Topped Separator Bottoms	0.0	0.38	0.38	0.38
Oil/Solids in Feed	1.1	1.1	1.1	1.1
Atmos. Still Btms. Temp., °F	525	525	525	⁽²⁾
Reactor Temperatures, °F				
First Stage	750	750	750	750
Second Stage	800	825	825	825

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⁽¹⁾ Condition 4 operation was not actually attempted after the system depressured during Period 15B because of a diaphragm failure on the first stage internal recycle pump, so that feed flow could not be re-established when the system was repressured.

⁽²⁾ Temperature of atmospheric still to be raised to demonstrate bottoms extinction. PFL recovered from filter cake products produced during Run 227-55 to be used to maintain PFL recycle rate. Probable atmospheric still temperature about 700°F.

TABLE 2
BENCH-SCALE TWO STAGE COAL LIQUEFACTION
Coal: Black Thunder Mine (HRI-5630)
Catalyst: Both Stages: Shell NiMo $\frac{1}{2}$ (HRI-5394)

PERIOD NUMBER	1	2	3	4	5	6	7	8
Date (Start of Period)	6/11/89	6/12/89	6/13/89	6/14/89	6/15/89	6/16/89	6/17/89	6/18/89
Hours of Run (End of Period)	15.	39.	63.	87.	111.	135.	159.	183.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	8.	23.	37.	51.	66.	80.	96.	119.
Stg 2 Catalyst Age, Lb Dry Coal/Lb Cat	16.	46.	73.	103.	131.	159.	192.	238.
TEMPERATURES, °F								
First Stage Reaction	705.	724.	747.	749.	750.	750.	747.	750.
Second Stage Reaction	760.	778.	799.	803.	800.	801.	808.	826.
Slurry Mix Tank	258.	259.	268.	271.	289.	293.	234.	203.
Atmospheric Still	518.	525.	525.	526.	526.	526.	526.	524.
PRESSURES, PSIG								
Unit Back Pressure	2498.	2493.	2490.	2498.	2502.	2495.	2500.	2498.
Overall DP	46.0	24.6	14.8	14.2	15.0	15.2	14.7	14.5
SPACE VELOCITIES								
Dry Coal Sp. Vel.-Stg. 1, Lb/Hr/Ft ³ (cat.)	20.2	24.0	22.2	23.8	23.1	22.4	26.4	36.9
Dry Coal Sp. Vel.-Stg. 2, Lb/Hr/Ft ³ (cat.)	40.7	48.2	44.4	47.3	46.2	45.1	53.1	73.6
Dry Coal Sp. Vel.-2-Stg. Lb/Hr/Ft ³ (cat.)	13.6	16.0	14.9	15.8	15.3	15.1	17.8	24.4
RECYCLES, W% OF DRY COAL								
Pressure Filter Liquid	123.1	105.7	108.6	109.5	109.5	109.4	95.9	72.1
PFL to Buffer - Stage 1	12.0	4.7	5.7	5.7	5.0	5.5	5.9	3.2
PFL to Buffer - Stage 2	5.0	4.2	4.2	3.8	3.8	3.7	4.5	2.6
Topped Separator Bottoms	0.0	0.0	0.0	0.0	0.0	0.0	28.7	35.6
Make-up Oil (HRI 5648)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.8
Total Material Recovery (Gross)	88.83	91.53	94.88	100.88	95.90	101.91	97.75	92.93
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED								
C ₁ -C ₃ in Gases				8.73	7.98	7.49		
C ₄ -C ₇ in Gases				6.10	6.29	7.13		
IBP-390°F in Liquids				12.81	13.85	12.80		
390-500°F in Liquids				10.96	11.60	10.62		
500-650°F in Liquids				16.37	16.44	16.32		
650-850°F in Liquids				12.37	10.04	12.73		
850-975°F in Liquids				1.97	1.32	1.98		
Toluene Soluble 975°F Oil				1.11	0.75	1.41		
Toluene Insoluble 975°F Oil				0.00	0.01	0.00		
Unconverted Coal				13.12	12.75	10.95		
Ash (SO ₃ -free)				6.01	6.01	5.80		
Water				16.73	18.67	18.42		
CO				0.09	0.38	0.35		
CO ₂				0.20	0.40	0.35		
NH ₃				1.12	1.12	1.12		
H ₂ S				0.34	0.34	0.33		
Total (100 + H₂ Reacted)				108.02	107.94	107.82		
PROCESS PERFORMANCE								
C ₄ -975°F Distillates, W% of MAF Coal				64.5	63.4	65.4		
975°F Conversion, W% MAF				84.9	85.6	86.9		
Coal Conversion, W% MAF		74.2	84.2	86.6	86.9	88.4		89.2
HDS, W%				66.1	66.1	65.5		
HDN, W%				87.5	87.8	87.5		

Normalization for Periods 6, 11, and 14 actual elemental analyses.
Other periods borrow such analyses from similar operations.

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TABLE 2
BENCH-SCALE TWO STAGE COAL LIQUEFACTION - FIRST VOLUME TWICE SECOND VOLUME

Coal: Black Thunder Mine (HRI-5630)
 Catalyst: Both Stages: Shell NiMo $\frac{1}{32}$ " (HRI-5394)

PERIOD NUMBER	9	10	11	12	13	14	15
Date (Start of Period)	6/11/89	6/12/89	6/13/89	6/14/89	6/15/89	6/16/89	6/17/89
Hours of Run (End of Period)	207.	231.	255.	279.	303.	327.	337.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	140.	161.	184.	212.	240.	268.	280.
Stg 2 Catalyst Age, Lb Dry Coal/Lb Cat	280.	322.	368.	424.	481.	536.	560.
TEMPERATURES, °F							
First Stage Reaction	748.	749.	750.	750.	749.	750.	750.
Second Stage Reaction	814.	823.	826.	827.	827.	828.	828.
Slurry Mix Tank	215.	235.	232.	227.	252.	251.	259.
Atmospheric Still	522.	521.	522.	521.	526.	527.	527.
PRESSURES, PSIG							
Unit Back Pressure	2489.	2493.	2489.	2477.	2500.	2508.	2507.
Overall DP	15.3	15.0.	15.8	16.7	17.5	18.3	24.4
SPACE VELOCITIES							
Dry Coal Sp. Vel.-Stg. 1, Lb/Hr/Ft ³ (cat.)	33.8	34.4	36.9	45.1	45.8	44.9	45
Dry Coal Sp. Vel.-Stg. 2, Lb/Hr/Ft ³ (cat.)	67.6	68.8	73.8	90.0	91.8	89.8	90
Dry Coal Sp. Vel.-2-Stg. Lb/Hr/Ft ³ (cat.)	22.4	22.9	24.7	30.0	30.7	30.0	30
RECYCLES, W% OF DRY COAL							
Pressure Filter Liquid	76.5	76.8	85.6	76.4	76.6	76.8	77.
PFL to Buffer - Stage 1	3.5	3.3	3.2	2.7	2.2	4.0	3.
PFL to Buffer - Stage 2	2.7	2.8	2.5	2.0	2.0	1.9	2.
Topped Separator Bottoms	38.2	38.0	43.2	38.2	38.3	38.4	38.
Make-up Oil (HRI 5648)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Material Recovery (Gross)	96.54	97.40	95.69	93.93	98.64	95.05	

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	6.58	7.72		6.82	6.48	7.35
C ₄ -C ₇ in Gases	6.35	7.87		9.52	7.74	7.83
IBP-390°F in Liquids	12.21	12.58		5.55	6.27	6.47
390-500°F in Liquids	10.86	11.17		7.66	8.27	8.58
500-650°F in Liquids	17.56	17.95		16.69	17.70	17.50
650-850°F in Liquids	11.82	11.31		16.13	15.53	14.85
850-975°F in Liquids	1.62	1.34		3.36	3.30	2.64
Toluene Soluble 975°F Oil	1.65	1.60		4.25	4.19	3.93
Toluene Insoluble 975°F Oil	0.01	0.01		0.03	0.03	0.02
Unconverted Coal	10.82	9.95		11.50	12.63	13.43
Ash (SO ₃ -free)	5.80	5.80		5.80	5.80	5.80
Water	19.70	17.94		16.32	15.66	15.13
CO	0.43	0.54		0.82	0.79	0.87
CO ₂	0.64	0.61		1.11	0.89	1.15
NH ₃	1.04	1.06		0.91	0.33	0.90
H ₂ S	0.35	0.35		0.34	0.34	0.33
Total (100 + H₂ Reacted)	107.45	107.80		106.83	106.67	106.79

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal	64.1	66.1		62.5	62.4	61.4
975°F Conversion, W% MAF	86.8	87.7		83.2	82.1	81.5
Coal Conversion, W% MAF	88.5	89.4		87.8	86.6	85.7
HDS, W%	69.4	67.9		67.0	64.6	64.8
HDN, W%	81.8	83.4		71.5	70.1	70.4

Normalization for Periods 6, 11 and 14 use actual elemental analyses.
 Other periods borrow such analyses from similar operations.

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TABLE 3**Operations With Black Thunder Mine Coal - Shell S-317 Catalyst**

Period Number	6	10	14
Catalyst Age, (1st Stg/2nd Stg), Lb Coal/Lb Cat.	80/159	161/322	268/327
LGO (IBP-650°F)			
IBP (D-1160 of Solvent	485	508	474
Gravity, °API	20.3	18.4	18.4
Carbon, W%	87.57	88.74	88.99
Hydrogen, W%	11.29	11.26	11.22
Sulfur, W%	0.004	0.001	0.037
Nitrogen	0.12	0.11	0.21
H/C Ratio	1.57	1.51	1.50
VGO (650-850°F)			
Gravity, °API	14.6	13.3	12.5
Carbon, W%	87.60	89.10	89.30
Hydrogen, W%	10.72	10.64	10.44
Sulfur, W%	0.027	0.019	0.001
Nitrogen, W%	0.07	0.07	0.18
H/C Ratio	1.46	1.43	1.39
HVGO (850-975°F)			
Gravity, °API	5.8	2.5	0.6
Carbon, W%	89.68	90.46	90.64
Hydrogen, W%	10.20	9.79	9.16
Sulfur, W%	0.055	0.008	0.008
Nitrogen, W%	0.6	0.22	0.35
H/C Ratio	1.36	1.29	1.29
RESIDUUM (975°F*)			
Gravity, °API	-3.8	-9.0	-8.8
Carbon, W%	90.32	91.05	91.90
Hydrogen, W%	8.63	7.53	7.52
Sulfur, W%	0.156	0.060	0.032
Nitrogen, W%	0.20	0.42	0.59
Cyclohexane Insolubles, W%	1.80	10.27	11.16
Ash, W%	0.32	0.64	0.57
H/C Ratio	1.14	0.99	0.97

Nitrogen analyses all by Perkin-Elmer 240B Elemental Analyzer

TABLE 4

Operations With Black Thunder Mine Coal - Shell S-317 Catalyst

PERIOD NUMBER	6	10	14
Catalyst Age, Lbs Coal/Lb Catalyst	80/159	161/322	268/327
SEPARATOR OVERHEAD			
Volume Average Boiling Point, F	445	470	512
Gravity, °API	33.00	30.30	25.00
Watson Characterization Factor	11.06	10.99	10.84
Carbon, W%	87.90	86.87	87.71
Hydrogen, W%	12.65	12.28	11.70
Sulfur, W%	0.01	0.01	0.00
Nitrogen (Perkin-Elmer), W%	0.00	0.11	0.33
Total	100.56	99.27	99.83
Nitrogen (Kjeldahl), W%	0.04	0.08	0.18
H/C Ratio	1.71	1.68	1.60
ATMOSPHERIC OVERHEAD			
Volume Average Boiling Point, F Gravity, °API	473	460	442
Watson Characterization Factor	28.90	28.00	29.10
Carbon, W%	11.03	10.90	10.91
Hydrogen, W%	87.35	87.05	87.18
Sulfur, W%	12.32	11.95	12.27
Nitrogen (Perkin-Elmer), W%	0.01	0.00	0.01
Total	0.00	0.12	0.27
Nitrogen (Kjeldahl), W%	99.74	99.22	99.70
H/C Ratio	0.06	0.22	0.24
	1.68	1.64	1.68
PRESSURE FILTER LIQUID (Recycle Solvent)			
Gravity, °API	12.80	9.70	7.10
Composition			
IBP-650 F, W%	20.48	22.45	18.92
650-850 F, W%	55.56	50.10	49.07
850-975 F, W%	13.97	12.48	12.83
975 Deg.F+, W%	9.99	14.97	19.20
Carbon, W%	88.49	89.62	89.56
Hydrogen, W%	10.53	10.15	9.84
Sulfur, W%	0.01	0.02	0.02
Nitrogen (Perkin-Elmer), W%	0.09	0.16	0.27
H/C Ratio	1.42	1.35	1.31

Nitrogen (Perkin-Elmer) -

Nitrogen (Kjeldahl) -

Analysis with Perkin-Elmer 240B Elemental Analyzer
Wet Chemical determination

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TABLE 5

COMPARISON OF CTSL RESULTS WITH REDISTRIBUTED STAGE VOLUMES

Run-Period, Unit 227	57-6	55-6	57-10	55-10	57-14	55-22
Run 227-57 Condition	1		2		3	
Percent of Combined Volume in first Stage	66.7	50.0	66.7	50.0	66.7	50.0
Hours of Run (End of Period)	135.	144.	231.	240.	327.	528.
Stg 1 Catalyst Age,Lb Dry Coal/Lb Cat	80.	170.	161.	284.	268.	660.
Stg 2 Catalyst Age,Lb Dry Coal/Lb Cat	159.	170.	322.	284.	536.	660.
TEMPERATURES, F						
First Stage Reaction	759.	751.	749.	750.	750.	752.
Second Stage Reaction	801.	800.	823.	824.	828.	826.
Atmospheric Still	526.	523	521.	294	536.	551
PRESSURES, PSIG						
Unit Back Pressure	2495.	2500.	2493.	2499.	2508.	2498.
SPACE VELOCITIES						
Stg. 1, Lb Dry Coal/Hr/Ft3(Catalyst)	22.4	44.9	34.4	44.7	44.9	68.9
Stg. 1, Lb Dry Coal/Hr/Ft3(Catalyst)	45.1	44.9	68.8	44.7	89.8	68.9
Combined Stages, Lb Dry Coal/Hr/Ft3(Catalysts)	15.1	22.4	22.9	22.3	30.0	34.4
RECYCLES, W% OF DRY COAL						
Pressure Filter Liquid	109.4	110.0	76.8	76.3	76.8	73.0
PFL to Buffer - Stage 1	5.5	4.2	3.3	4.8	4.0	2.8
PFL to Buffer - Stage 2	3.7	4.6	2.8	3.8	1.9	1.9
Separator Bottoms	0.0	0.0	38.0	38.1	38.4	38.1
Make-up Oil	0.0	0.0	0.0	0.0	0.0	3.1
TOTAL MATERIAL RECOVERY (GROSS)	101.91	97.83	97.40	97.77	95.05	97.74
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED						
C1-C3 in Gases	7.49	7.22	7.72	7.74	7.35	7.67
C4-C7 in Gases	7.13	4.28	7.87	4.06	7.83	4.53
1BP-390 deg-f in Liquids	12.80	12.44	12.58	15.96	6.47	11.05
359-500 deg-f in Liquids	10.62	9.67	11.17	10.62	8.58	8.87
500-650 deg-f in Liquids	16.32	17.90	17.95	19.12	17.50	17.88
650-850 deg-f in Liquids	12.73	13.07	11.31	12.03	14.85	12.24
850-975 deg-f in Liquids	1.98	2.48	1.34	2.00	2.64	1.61
Toluene Soluble 975F+ Oil	1.41	2.49	1.60	2.67	3.93	4.14
Toluene Insoluble 975F+ Oil	0.00	0.00	0.01	0.02	0.02	0.25
Unconverted Coal	10.95	12.04	9.95	8.04	13.43	11.90
Ash (SO3-free)	5.80	6.01	5.80	6.01	5.80	6.01
Water	18.42	18.01	17.94	17.79	15.13	18.41
CO	0.35	0.28	0.54	0.20	0.87	0.21
CO2	0.35	0.18	0.61	0.08	1.15	0.72
NH3	1.12	1.01	1.06	0.96	0.90	0.83
H2S	0.33	0.36	0.35	0.36	0.33	0.35
Total (100 + H2 Reacted)	107.82	107.44	107.80	107.66	106.79	106.66
PROCESS PERFORMANCE						
C4-975 deg-f Distillates, W% Dry Coal	61.6	59.8	62.2	63.8	57.8	56.2
C4-975 deg-f Distillates, W% MAF Coal	65.4	63.7	66.1	67.9	61.4	59.8
975F+ Conversion, W% MAF Coal	86.9	84.5	87.7	88.6	81.5	82.7
Coal Conversion, W% MAF Coal	88.4	87.2	89.4	91.4	85.7	87.3
HDS, W%	65.5	69.9	67.9	71.0	64.8	69.2
HDN, W%	87.5	79.3	83.4	75.4	70.4	65.4

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TABLE 6

COMPARISON OF PRODUCT STREAM ANALYSES WITH REDISTRIBUTED STAGE VOLUMES

Run-Period, Unit 227	57-6	55-6	57-10	55-10	57-14	55-22
Percent of Combined Volume in first Stage	66.7	50.0	66.7	50.0	66.7	50.0
Hours of Run (End of Period)	135.	144.	231.	240.	327.	528.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	80.	170.	161.	284.	268.	660.
Stg 2 Catalyst Age, Lb Dry Coal/Lb Cat	159.	170.	322.	284.	536.	660.
TEMPERATURES, F						
First Stage Reaction	759.	751.	749.	750.	750.	752.
Second Stage Reaction	801.	800.	823.	824.	828.	826.
Atmospheric Still	526.	523.	521.	294.	536.	551.
SPACE VELOCITY						
Combined Stages, Lb Dry Coal/Hr/Ft ³ (Catalysts)	15.1	22.4	22.9	22.3	30.0	34.4
RECYCLES, W% OF DRY COAL						
Pressure Filter Liquid, Total	118.6	118.8	83.1	84.9	82.7	77.7
Separator Bottoms	0.0	0.0	38.0	38.1	38.4	38.1
Make-up Oil	0.0	0.0	0.0	0.0	0.0	3.1
SEPARATOR OVERHEAD						
Volume Average Boiling Point, F	445	449	470	423	512	480
Gravity, deg-API	33.00	32.90	30.30	33.90	25.00	27.80
Watson Characterization Factor	11.06	11.06	10.59	11.03	10.84	10.85
Carbon, W%	87.90	86.77	86.87	86.73	87.71	87.60
Hydrogen, W%	12.65	12.46	12.28	12.31	11.79	11.68
Sulfur, W%	0.01	0.00	0.01	0.01	0.00	0.01
Nitrogen (Perkin-Elmer), W%	0.00	0.24	0.11	0.26	0.33	0.30
Total	100.56	99.47	99.27	99.32	99.83	99.59
Nitrogen (Kjeldahl), W%	0.04	0.043	0.08		0.18	0.31
H/C Ratio	1.71	1.71	1.68	1.69	1.60	1.59
ATMOSPHERIC OVERHEAD						
Volume Average Boiling Point, F	473	482	460	363	442	495
Gravity, deg-API	28.90	28.10	28.00	37.80	29.10	24.10
Watson Characterization Factor	11.03	11.00	10.90	11.18	10.91	10.77
Carbon, W%	87.35	87.66	87.05	87.21	87.18	87.04
Hydrogen, W%	12.32	12.28	11.95	12.89	12.27	11.38
Sulfur, W%	0.01	0.01	0.00	0.00	0.01	0.00
Nitrogen (Perkin-Elmer), W%	0.00	0.19	0.12	0.20	0.27	0.38
Total	99.74	100.14	99.22	100.30	99.70	98.80
Nitrogen (Kjeldahl), W%	0.06	0.054	0.22		0.24	0.32
H/C Ratio	1.68	1.67	1.64	1.76	1.68	1.56
PRESSURE FILTER LIQUID						
Gravity, deg-API	12.80	12.10	9.70	10.40	7.10	0.60
Composition						
IBP-650 F, W%	20.48	16.77	22.45	30.00	18.92	8.49
650-850 F, W%	55.56	52.83	50.10	44.20	49.07	46.78
850-975 F, W%	13.97	15.05	12.48	10.80	12.83	14.38
975 DEG-F+, W%	9.99	15.15	14.97	14.50	19.20	29.79
Carbon, W%	88.49	89.09	89.62	88.89	89.56	90.23
Hydrogen, W%	10.53	10.38	10.15	10.06	9.84	8.53
Sulfur, W%	0.01	0.01	0.02	0.01	0.02	0.04
Nitrogen (Perkin-Elmer), W%	0.09	0.18	0.16	0.29	0.27	0.57
Total	99.12	99.66	99.95	99.25	99.69	99.37
H/C Ratio	1.42	1.39	1.35	1.35	1.31	1.13

Nitrogen (Perkin-Elmer) - Analysis with Perkin-Elmer 240B Elemental Analyzer

Nitrogen (Kjeldahl) - Wet chemical determination

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TABLE 7

COMPARISON OF PRODUCT FRACTION ANALYSES WITH REDISTRIBUTED STAGE VOLUMES

Run-Period, Unit 227	57-6	55-6	57-10	55-10	57-14	55-22
Percent of Combined Volume in first Stage	66.7	50.0	66.7	50.0	66.7	50.0
Hours of Run (End of Period)	135.	144.	231.	240.	327.	528.
Stg 1 Catalyst Age,Lb Dry Coal/Lb Cat	80.	170.	161.	284.	268.	660.
Stg 2 Catalyst Age,Lb Dry Coal/Lb Cat	159.	170.	322.	284.	536.	660.
TEMPERATURES, F						
First Stage Reaction	759.	751.	749.	750.	750.	752.
Second Stage Reaction	801.	800.	823.	824.	828.	826.
Atmospheric Still	526.	523	521.	294	536.	551
SPACE VELOCITY						
Combined Stages, Lb Dry Coal/Hr/Ft ³ (Catalysts)	15.1	22.4	22.9	22.3	30.0	34.4
RECYCLES, W% OF DRY COAL						
Pressure Filter Liquid, Total	118.6	118.8	83.1	84.9	82.7	77.7
Separator Bottoms	0.0	0.0	38.0	38.1	38.4	38.1
Make-up Oil	0.0	0.0	0.0	0.0	0.0	3.1
LGO (IBP-650 F)						
IBP (D-1160 of Solvent)	485	505	508	450	474	525
Gravity, deg-API	20.3	19.5	18.4	21.4	18.2	15.9
Carbon, W%	87.57	88.47	88.74	88.32	88.99	88.56
Hydrogen, W%	11.29	11.58	11.26	11.10	11.22	10.64
Sulfur, W%	0.004	0.008	0.001	0.001	0.037	0.010
Nitrogen, W%	0.12	0.18	0.11	0.13	0.21	0.30
H/C Ratio	1.57	1.54	1.51	1.50	1.50	1.43
VGO (650-850 F)						
Gravity, deg-API	14.6	11.4	13.3	12.3	12.5	9.6
Carbon, W%	87.60	89.35	89.10	89.82	89.30	89.66
Hydrogen, W%	10.72	10.94	10.64	10.34	10.44	9.85
Sulfur, W%	0.027	0.008	0.019	0.008	0.001	0.005
Nitrogen, W%	0.07	0.12	0.07	0.11	0.18	0.31
H/C Ratio	1.46	1.46	1.43	1.37	1.39	1.31
HVGO (850-975 F)						
Gravity, deg-API	5.8	5.1	2.5	0.8	0.6	-3.1
Carbon, W%	89.68	90.14	90.46	90.74	90.64	90.74
Hydrogen, W%	10.20	9.08	9.79	8.94	9.16	8.32
Sulfur, W%	0.055	0.015	0.008	0.003	0.008	0.045
Nitrogen, W%	0.06	0.26	0.22	0.30	0.35	0.54
H/C Ratio	1.36	1.20	1.29	1.17	1.29	1.09
RESIDUUM (975 F+)						
Gravity, deg-API	-3.8	-4.6	-9.0	-9.6	-8.8	-13.0
Carbon, W%	90.32	90.40	91.05	91.71	91.90	91.21
Hydrogen, W%	8.63	8.45	7.53	7.30	7.52	6.55
Sulfur, W%	0.156	0.002	0.060	0.012	0.032	0.036
Nitrogen, W%	0.20	0.39	0.42	0.51	0.59	0.89
Cyclohexane Insolubles, W%	1.80	4.35	10.27	13.87	11.16	38.54
Toluene Insolubles, W%	0.32	0.10	0.64	0.70	0.57	5.43
H/C Ratio	1.14	1.11	0.99	0.95	0.97	0.86

Nitrogen analyses all by Perkin-Elmer 240B Elemental Analyzer.

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TABLE 8

COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES
RUN 227-57

	-----First Stage-----			-----Second Stage-----		
Condition	1	2	3	1	2	3
Period Number	6	10	14	6	10	14
Catalyst Age, Lbs Coal/Lb Catalyst						
Total Liquid						
Gravity, deg-API	12.8	9.7	6.8	12.8	9.7	7.1
Elemental Analyses, W%						
Carbon, W%	89.13	89.04	89.91	88.49	89.62	89.56
Hydrogen, W%	10.76	10.35	9.75	10.53	10.15	9.84
Sulfur, W%	0.007	0.009	0.003	0.004	0.017	0.016
Nitrogen, W%	0.08	0.16	0.20	0.09	0.16	0.27
Total	99.72	99.65	99.42	99.66	99.25	99.41
650 F-, W%	18.9	17.9	15.7	19.5	21.5	17.9
650-850 deg-F, W%	50.2	44.8	44.9	55.6	50.1	49.1
850-975 deg-F, W%	15.7	16.0	16.6	14.0	12.5	12.8
975 deg-F+, W%	14.1	20.1	21.0	10.0	15.0	19.2
Loss, W%	1.2	1.3	1.9	1.0	1.0	1.0
LGO (IBP-650 F)						
Gravity, deg-API	19.9	19.1	18.0	20.3	18.4	18.2
Carbon, W%	88.03	88.51	88.42	87.57	88.74	88.99
Hydrogen, W%	11.50	11.28	11.30	11.29	11.26	11.22
Sulfur, W%	0.009	0.016	0.000	0.004	0.001	0.037
Nitrogen, W%	0.06	0.15	0.13	0.12	0.11	0.21
VGO (650-850 F)						
Gravity, deg-API	14.8	13.4	12.6	14.6	13.3	12.5
Carbon, W%	89.35	89.51	89.70	87.60	89.10	89.30
Hydrogen, W%	11.14	10.49	10.69	10.72	10.64	10.44
Sulfur, W%	0.036	0.026	0.021	0.027	0.019	0.001
Nitrogen, W%	0.07	0.11	0.07	0.07	0.07	0.18
HVGO (850-975 F)						
Gravity, deg-API	7.3	3.7	3.0	5.8	2.5	0.6
Carbon, W%	89.66	90.52	90.17	89.68	90.46	90.64
Hydrogen, W%	10.44	9.67	9.51	10.20	9.79	9.16
Sulfur, W%	0.059	0.023	0.057	0.055	0.008	0.008
Nitrogen, W%	0.14	0.25	0.27	0.06	0.22	0.35
RESIDUUM (975 F+)						
Gravity, deg-API	-1.7	-5.4	-6.4	-3.8	-9.0	-8.8
Carbon, W%	89.60	89.91	89.67	90.32	91.05	91.90
Hydrogen, W%	9.24	8.34	8.26	8.63	7.53	7.52
Sulfur, W%	0.146	0.038	0.114	0.156	0.060	0.032
Nitrogen, W%	0.33	0.43	0.51	0.20	0.42	0.59
Cyclohexane Insolubles, W%	1.67	3.98	4.79	1.80	10.27	11.16
Toluene Insolubles, W%	0.00	0.00	0.06	0.32	0.64	0.57
Ash, W%						
SOLIDS (THF INSOLUBLE)						
Ash, W%	20.67	20.66	17.59	35.83	39.80	32.11
Elemental Analyses, Ash-free Basis						
Carbon, W%	74.54	73.68	74.53	75.50	75.34	75.93
Hydrogen, W%	4.71	4.66	4.71	4.58	4.47	4.82
Sulfur, W%	0.83	0.76	0.76	1.47	1.71	
Nitrogen, W%	1.47	1.42	1.40	1.22	1.15	1.30
Total	81.55	80.52	81.40	82.77	82.67	
Sulfur/Ash	0.0320	0.0292	0.0358	0.0264	0.0260	
Sulfur In Ash, W%	2.56	2.19	3.50			
SAMPLE FILTRATION						
Filter Cake, Percent of Sample	44.59	48.33	42.43			
THF Insolubles, W% of Filter Cake	57.06	54.63	55.95			

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TABLE 9

FIRST AND SECOND STAGE FLOWS RUN 227-57

Flows - Percent of Dry Coal Feed		First and Second Stage Vapors Proportional to Coal Reacted		
CONDITION PERIOD	1 6	2 10	3 14	
Coal Rate, Lbs/Hr/Ft3(Catalyst)	22.4/45.1	34.4/68.8	44.9/89.8	
Recycle TSB, W% of Dry Coal Feed	0.0	38.0	38.4	
Recycle PFL, W% of Dry Coal Feed	114.9	80.1	80.8	
Makeup Oil, W% of Dry Coal Feed	0.0	0.0	0.0	
Catalyst Age, Lb/Lb	80/159	161/322	268/536	
First Stage Temperature, F	750	749	750	
Second Stage Temperature, F	801	823	828	
FIRST STAGE FEED				
650 F-	23.53	25.41	21.44	
650-850 F	63.84	56.71	55.60	
850-975 F	16.05	14.13	14.54	
975 F+ Oil	11.27	15.20	19.33	
975 F+ Asphaltene	0.17	1.63	2.30	
975 F+ Preasphaltene	0.04	0.11	0.12	
Quinoline IOM	94.20	97.30	98.32	
Ash	5.80	7.61	7.58	
TOTAL	214.90	218.10	219.20	
SECOND STAGE BUFFER				
650 F-	0.76	0.63	0.36	
650-850 F	2.06	1.40	0.93	
850-975 F	0.52	0.35	0.24	
975 F+ Oil	0.36	0.38	0.32	
975 F+ Asphaltene	0.01	0.04	0.04	
975 F+ Preasphaltene	0.00	0.00	0.00	
Quinoline IOM	0.00	0.00	0.00	
Ash	0.00	0.00	0.00	
TOTAL	3.70	2.80	1.90	
FIRST STAGE PRODUCT				
650 F-	26.77	24.48	23.44	
650-850 F	66.87	57.12	59.79	
850-975 F	20.91	20.40	22.10	
975 F+ Oil	18.47	24.61	26.62	
975 F+ Asphaltene	0.31	1.02	1.32	
975 F+ Preasphaltene	0.00	0.00	0.02	
Quinoline IOM	22.26	29.22	35.52	
Ash	5.80	7.61	7.58	
Vapor (estimated)	53.64	53.77	42.94	
TOTAL	214.90	218.10	219.20	
SECOND STAGE PRODUCT				
650 F-	34.19	34.92	30.48	
650-850 F	73.77	63.99	70.78	
850-975 F	18.55	15.82	17.42	
975 F+ Oil	13.03	17.02	23.16	
975 F+ Asphaltene	0.20	1.83	2.76	
975 F+ Preasphaltene	0.04	0.12	0.15	
Quinoline IOM	10.95	13.05	17.56	
Ash	5.80	7.61	7.58	
Vapor	62.07	66.54	55.22	
TOTAL	218.60	220.90	221.10	

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TABLE 10

FIRST AND SECOND STAGE PRODUCT FRACTION FORMATION - RUN 227-57

First and Second Stage Vapors Proportional to Coal Reacted

CONDITION PERIOD	1 6	2 10	3 14
Coal Rate, Lbs/Hr/Ft3(Catalyst)	22.4/45.1	34.4/68.8	44.9/89.8
Recycle TSB, W% of Dry Coal Feed	0.0	38.0	38.4
Recycle PFL, W% of Dry Coal Feed	114.9	80.1	80.8
Makeup Oil, W% of Dry Coal Feed	0.0	0.0	0.0
Catalyst Age, Lb/Lb	80/159	161/322	268/536
First Stage Temperature, F	750	749	750
Second Stage Temperature, F	801	823	828
FIRST STAGE FORMATION			
W% of Dry Coal Feed			
Vapors	53.64	53.77	42.94
650 F-	3.24	-0.93	2.00
650-850 F	3.03	0.41	4.19
850-975 F	4.86	6.27	7.57
975 F+ Oil	7.20	9.40	7.30
975 F+ Asphaltene	0.14	-0.61	-0.98
975 F+ Preasphaltene	-0.04	-0.11	-0.11
Quinoline IOM	-71.94	-68.08	62.80
Ash	0.00	0.00	0.00
Total 975 F-	64.64	59.39	56.59
Total 975 F+ Residuum	7.30	8.68	6.21
Coal Converted (W% of maf Coal)	76.37	72.27	66.67
SECOND STAGE FORMATION			
W% of Dry Coal Feed			
Vapors	8.43	12.77	12.28
650 F-	6.66	9.81	6.68
650-850 F	4.85	5.47	10.06
850-975 F	-2.88	-4.93	-4.92
975 F+ Oil	-5.81	-7.96	-3.78
975 F+ Asphaltene	-0.12	0.77	1.40
975 F+ Preasphaltene	0.04	0.12	0.13
Quinoline IOM	-11.31	-16.17	17.96
Ash	0.00	0.00	0.00
Total 975 F-	17.20	23.25	20.22
Total 975 F+ Residuum	-5.89	-7.08	-2.25
Coal Converted (W% of maf Coal)	12.01	17.17	19.07
TWO STAGE FORMATION			
W% of Dry Coal Feed			
Vapors	62.07	66.54	55.22
650 F-	9.90	8.88	8.68
650-850 F	7.88	5.88	14.25
850-975 F	1.98	1.34	2.64
975 F+ Oil	1.39	1.44	3.52
975 F+ Asphaltene	0.02	0.15	0.42
975 F+ Preasphaltene	0.00	0.01	0.02
Quinoline IOM	-83.25	-84.25	80.76
Ash	0.00	0.00	0.00
Total 975 F-	59.21	50.30	40.88
Total 975 F+ Residuum	1.42	1.61	3.96
Coal Converted (W% of maf Coal)	88.38	89.44	85.74

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TABLE 11

FEED COAL ANALYSES FOR RUN 227-57(CC-2)

Run 227-57 Feed: Black Thunder Mine (Wyoming) Coal

FEED DESIGNATION, HRI No.	5630*	5630**	5630***	5613****	Mine Analysis
MINE	-----Black Thunder-----				
TESTS	227-57	227-55	238-04	Micro	
REPORTED MINE ANALYSIS					
Moisture, W%	6.84*	6.37**			27
Volatile Matter					32
Fixed Carbon					35
Ash					5
Btu/lb					8890
PROXIMATE ANALYSIS, W%					
Volatile Matter (MAF Basis)		44.2		47.73	(48)
Fixed Carbon (MAF Basis)		55.8		52.27	(52)
ULTIMATE ANALYSIS					
(W%, Dry Basis)					
Carbon		67.70		68.92	70.50
Hydrogen		4.54		4.15	4.47
Sulfur		0.48		0.51	0.46
Nitrogen		1.05		0.95	0.98
Chlorine		0.04		0.03	
Ash	6.90	(7.15)		6.91	(6.55) (7)
Sulfur in Ash	6.35	(6.35)		5.64	(7.56)
Ash (SO ₃ -free)	6.01	6.01		5.94	5.31
Oxygen (By Difference)		20.18		19.53	18.15
SULFUR FORMS					
(W%, Dry Basis)					
Sulfate		0.04		0.01	
Pyrite		0.11		0.06	
Organic		0.36		0.46	
HEATING VALUE, Btu/lb(Dry)		11797		12048	(12200)
Btu/Lb MAF		12551		12724	(13100)
MINERAL ANALYSIS OF ASH					
(W%, Ignited)					
Silica, SiO ₂		34.61		27.96	
Alumina, Al ₂ O ₃		16.98		15.81	
Titania, TiO ₂		1.30		1.20	
Ferric Oxide, Fe ₂ O ₃		6.94		5.29	
Lime, CaO		21.74		26.79	
Magnesia, MgO		4.40		5.27	
Potassium Oxide, K ₂ O		0.35		0.37	
Sodium Oxide, NaO		0.97		1.34	
Sulfur Trioxide, SO ₃		10.74		13.45	
Phosphorous Pentoxide, P ₂ O ₅		1.01		0.63	
Strontium Oxide, SrO		0.29		0.29	
Barium Oxide, BaO		0.37		0.26	
Magnesium Oxide, Mn ₃ O ₄		0.00		0.00	
Undetermined		0.30		1.34	

(continued)

TABLE 11 (cont'd)

FEED COAL ANALYSES FOR RUN 227-57(CC-2)

Run 227-57 Feed: Black Thunder Mine (Wyoming) Coal

FEED DESIGNATION, HRI No.	5630*	5630**	5630***	5613****	Mine Analysis
MINE	-----Black Thunder-----				
TESTS	227-57	227-55	238-04	Micro	
MICROAUTOCLAVE RESULTS *****					
Thermal Coal Conversion		76.6		84.6	
Thermal 975 F+ Conversion		44.3		52.0	
Catalytic Coal Conversion		87.9		94.6	
Catalytic 975 F+ Conversion		72.9		75.2	
MACERAL ANALYSIS, V%					
Reactives					
Vitrinites		73.4			
Exinite		3.6			
Resinite		---			
1/3 Semifusinite		4.1			
Total		81.1			
Inerts					
2/3 Semifusinite		8.4			
Micrinite		8.5			
Fusinite		2.0			
Total		18.9			
Ash		----			

* Dried Black Thunder coal feed to Run 227-57.

** Dried Black Thunder coal feed to Run 227-55.

*** Dried Black Thunder coal feed to Run 238-04.

**** Black Thunder coal used in microautoclave tests.

***** 1989 tests - 800 F, 30 minutes, 2000 psig H₂,
4/1/(1) Solvent/Coal/(Shell S-317 Catalyst)
Solvent - Wilsonville coal liquefaction distillate product.

TABLE 12

INSPECTION OF START-UP AND MAKEUP OILS FOR RUN 227-57 (CC-2)

Designation	HRI-5443	HRI-5648	L-541
Gravity, °API	10.2	5.7	6.8
Distillation, °F			
IBP	205	735	473
5 V%		776	553
10 V%	585	798	591
20 V%	656	810	637
30 V%	697	830	697
40 V%	721	841	739
50 V%	750	858	773
60 V%	778	876	820
70 V%	812	888	892
80 V%	850	902	975
90 V%	925	930	
E.P.	975	1008	975
Recovery, V%	98	98	80
Residue, W%	4.3	3.2	20.8
V% @ 650°F	16	0	24
V% @ 850°F	80	47	66
Carbon, W%	88.63	90.14	88.25
Hydrogen, W%	10.12	9.85	9.25
Sulfur, W%	0.04	0.06	0.07
Nitrogen, W%	0.25	0.37	0.34
Toluene Insolubles,			
W% of 975°F	7.98		2.65
Ash, W% of 975°F	2.36		0.28
Solvent Quality Test			
Illinois No. 6 Coal	57.7, 69.3	78.4	
Black Thunder Coal	54.7, 57.4	61.1	

Thermal Conversion at 750°F, 30 Minutes, 4/1 solvent/coal

TABLE 13

FRESH CATALYST PROPERTIES - RUN 227-57 (CC-2)

HRI NO.	5394
Designation	Shell S-317
Nominal Size	1/32" Extrudates
CHEMICAL ANALYSIS (W%, DRY BASIS)	
Molybdenum, HRI Analyses	10.76, 11.02, 11.58, 12.26
Vendor Specification	12.0
Nickel, HRI Analyses	2.00, 2.00, 2.25, 2.60
Vendor Specification	2.5
PHYSICAL PROPERTIES	
Bulk Density, Compacted, Lb/Ft ³	36.7
Particle Density, gm/cc	0.941
Surface Area (Calc.), M ² /gm	267
M ² /cc particle	251
Pore Volume, cc/gm	0.697
cc/cc particle	0.656
Average Crush Strength, Lb/mm	1.94
PORE SIZE DISTRIBUTION, CC/GM	
Diameter > 30 Å	0.70
Diameter > 100 Å	0.40
Diameter > 250 Å	0.15
Diameter > 500 Å	0.14
Diameter > 1500 Å	0.11
Diameter > 4000 Å	0.03
PENETRATION TEST	
Average Penetration, % of Diameter	34.9

TABLE 14
RECOVERED CATALYSTS ANALYSES - RUN 227-57 (CC-2)

STAGE	First 1st Reactor	First 2nd Reactor	Second
CATALYST AGE, LB COAL/LB	280	280	560
CATALYST RECOVERY, VOL %	86.7	94.4	88.9
Bulk Density, Gm/cc	0.836	0.800	0.851
ANALYSES OF OIL-FREE +20 Mesh Catalyst, W%			
Carbon	11.38	8.69	13.15
Hydrogen	1.12	0.90	1.01
H/C Ration	1.18	1.24	0.92
Nitrogen	0.29	0.20	0.14
Sulfur	5.60	5.90	5.95
Molybdenum	9.16	9.72	9.23
Nickel	1.62	1.94	1.64
Titanium	0.014	0.017	0.017
Iron	0.26	0.51	0.08
Calcium	0.07	0.02	0.12
Sodium	0.33	0.50	1.31
	0.67	1.04	1.53
Total Metal Contaminants			
Loss on Ignition, W%	21.5	17.8	
Particle Density, Gm/cc particle*	1.272	1.338	1.446
Pore Volume (D>30*A), cc/gm	0.427	0.442	0.405
cc/cc particle	0.543	0.591	0.585
Surface Area (calc.), M ² /gm	174	182	176
Ms/cc particle	221	221	254
ANALYSES OF IGNITED CATALYST			
Particle Density, Gm/cc particle*			
Pore Volume (D>30*A), cc/gm	0.606	0.640	0.616
cc/cc particle			
Surface Area (calc.), M ² /gm	227	221	213
Ms/cc particle			
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS			
Weights, Grams	43.7	19.2	25.3
Molybdenum, W%	7.14	5.21	7.57

*In mercury at 24 psia.

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COAL CONVERSION

Comparison of Runs 227-55 and 227-57

FIGURE 1

975 F+ CONVERSION

Comparison of Runs 227-55 and 227-57

FIGURE 2

C1-C3 GAS YIELDS

Comparison of Runs 227-55 and 227-57

FIGURE 3

C4-390 F NAPHTHA YIELDS

Comparison of Runs 227-55 and 227-57

FIGURE 4

FIGURE 5

PARITY PLOT FOR CORRELATED NAPHTHA YIELD

Runs 227-55(CC-1) and 227-57(CC-2)

390-650 F LGO YIELDS

Comparison of Runs 227-55 and 227-57

FIGURE 6

650-975 HGO YIELDS

Comparison of Runs 227-55 and 227-57

FIGURE 7

975 F+ RESIDUUM YIELDS

Comparison of Runs 227-55 and 227-57

FIGURE 8

FIGURE 9

RESIDUUM CONC. IN RECYCLED PFL

Comparison of Runs 227-55 and 227-57

YIELD OF C4-975 F DISTILLATES

Comparison of Runs 227-55 and 227-57

FIGURE 10

NORMALIZED WATER YIELDS

Comparison of Runs 227-55 and 227-57

FIGURE 11

CARBON OXIDES YIELDS - RUN 227-57

FIGURE 12

FIGURE 13

CARBON OXIDES YIELDS

Comparison of Runs 227-55 and 227-57

FIGURE 14

RESID. REACT. RATE CONST. - RUNS CC-1 AND CC-2

43% Prim. Form - Adj. to 750 F, 6 Kcal/mole Act. Eng.

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Section III

Run 227-58

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SECTION III

RUN 227-58 (CC-3) CTSL™ EVALUATION OF IRON-MOLYBDENUM CATALYST WITH BLACK THUNDER MINE COAL

SUMMARY

Black Thunder mine coal, a Wyodak seam sub-bituminous coal, was processed in a nominal 50 lb/day bench unit using the HRI Catalytic Two-Stage Liquefaction (CTSL™) process. A developmental catalyst from UOP, RCM-1-123, Fe-Mo supported on alumina, was used in both stages. This catalyst offers the possibility of lower catalyst replacement costs because it would be less expensive than a nickel-based catalyst. The test was conducted over 12 days, using a space velocity of 44 lb coal/ft³ of catalyst. The liquefaction performance was evaluated at two temperature conditions, 750°F/800°F and 750°F/825°F.

The overall conversion to 975°F distillate was 82.5-87.3 W%. Compared to Shell S-317 NiMo catalyst, the 975°F conversion and the C₄-975°F yield were only slightly lower with FeMo catalyst. However, considering the much lower catalyst charge weight (due to the lower bulk density), the difference was not very large. The quality of the product obtained with the FeMo catalyst was significantly lower.

SCOPE OF WORK

The run plan for the bench test is shown in *Table 1*. The test duration was 12 days plus one eight-hour period. The feed space velocity was maintained at 44 lbs of dry coal/ft³ of catalyst (packed) volume. In the first condition, which lasted for six days plus one eight hour period, the first and the second stage temperatures were maintained at 750°F and 800°F respectively. Pressure Filter Liquid (PFL) was used to slurry coal using a PFL/Coal ratio of 1.1. In the second condition, the second stage temperature was increased to 825°F. PFL as well as Topped Separator Bottoms (TSB's) were used as recycle in the amount shown in *Table 1*. These two conditions were similar to those used in the baseline run 227-55(CC-1) using Shell S-317 NiMo catalyst.

PROGRAM RESULTS AND ANALYSES - RUN 227-58 (CC-3)

Table 2 is the Operating Summary for the run, giving the principal operating conditions for each Period (day), and normalized product distributions for periods which were considered to represent equilibrated results. *Table 3* shows the yields and process performance for the two conditions, using averages of Period 5 and 6 results for Condition 1 and Period 11 and 12 results for Condition 2.

COAL AND 975°F CONVERSION

Coal conversion increased from 86.8 W% (MAF) in the first condition (750°F/800°F) to 91.8 W% in the second condition (750°F/825°F). During the early part of the run, the coal conversions were lower, starting at 77.7% in Period 2 and increasing to 85.1 % in Period 4 as the reactor temperatures were increased and the solvent and reactor compositions equilibrated. After the transition Periods 7 and 8, the coal conversion became very steady in Periods 9 through 12, remaining between 91.6 and 92.0 W%. The 975°F conversion increased from an average of 82.5 W% of MAF coal in Condition 1 (750°F/800°F) to 87.3 W% in Condition 2 (750°F/825°F). The similar 5 W% differences between the coal conversions in the two conditions and between the 975°F conversions in the two conditions indicate that the increased rate of resid formation from coal in Condition 2 was matched by an increased rate of resid reaction to lighter products.

NORMALIZED PRODUCT DISTRIBUTION

As indicated in *Table 3*, the C₄-975°F distillate yield increased from an average of 61.4 W% (MAF) in Condition 1 (750°F/800°F) to an average of 63.3 W% in Condition 2 (750°F/825°F). This increased distillate yield was due to a 4.6 W% (of dry coal) decreased unconverted coal yield offset by a 2.7 W% DC increased C₁-C₃ gas yield. The distillate product distribution was shifted to the lighter fractions in Condition 2, but the yields of 975°F residual oil only increased from 4.0 W% DC for Condition 1 to 4.2 W% DC for Condition 2. The normalized product distributions are discussed further below with respect to the comparison of the performance of this catalyst with the Shell S-317 NiMo catalyst.

HETEROATOM REMOVAL

Hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) did not change appreciably when the second stage reactor temperature was increased to 825°F in Condition 2. HDN, the most accurate of these measures, only increased from 62.7 W% in Condition 1 to 64.7 W% in Condition 2. Probably the higher temperature in the second condition was counteracted by the decreased catalyst activity. HDS and HDN were calculated from the sulfur and nitrogen contents of the products after normalization. HDO was calculated from the normalized yields of water, CO, and CO₂. Although the level of HDS appears only moderate (69.5 W% average), the sulfur content of the distillate was very low. Almost all of the remaining sulfur was in the coal solids.

PRODUCT QUALITY

Table 4 shows the analyses of the product streams removed from the unit. The Separator Overhead (SOH) and Atmospheric Still Overhead (ASOH) became only slightly more aromatic, as indicated by the lower Watson Characterization Factor, in Condition 2 of the Run 227-58 (CC-3). This small change was not confirmed by the hydrogen/carbon ratio of these products, which showed no discernable trend. The sulfur contents remained low for both conditions, but the nitrogen content increased, due to increased catalyst age, from an average of 0.35 W% to 0.41 W% for the SOH and from an average of 0.42 W% to 0.57 W% for the ASOH.

Table 5 shows the analyses of the first-stage and second-stage (PFL) liquid products, distillation fractions, and THF-washed solids. The first-stage samples were withdrawn at the conclusion of each condition. The following discussion refers to the analyses of the three defined distillation fractions, 650-850°F, 850-975°F, and 975°F in *Table 5*, averaged where two analyses were available for the second stage fractions. API gravities were lower for the Condition 2 operations by 1.8 to 6.7 API, and the hydrogen contents were lower by 0.59 to 1.16 W%. The nitrogen contents were slightly higher in the Condition 2 operations (0.07 to 0.25 W%, probably due to the lower catalyst activity at about twice the catalyst age).

The differences between the first and second stage analyses depended on the condition and the distillation fraction. The API gravities were similar for the two stages in Condition 1 operations, but consistently lower in the second stage in Condition 2 (0.9 to 4.5 API). The hydrogen contents actually increased in the second stage for the heavier fractions of Condition 1, but in Condition 2, with the equilibrium shifted toward dehydrogenation in the 825°F second stage, the hydrogen contents decreased by 0.01 W% for the 650-850°F fraction to 0.75 W% for the 975°F fraction. The nitrogen contents were lower in the second stage in Condition 1 (by 0.09 to 0.19 W%), but the nitrogen-content differences between the two stages were mixed in Condition 2. The sulfur contents of the three liquid fractions generally declined from about 0.10 W% in the first stage to about 0.01 W% in the second stage. The hydrogen/carbon ratios of the THF-washed solids remained about the same in the two stages during Condition 1, but decreased from 0.77 to 0.69 with the higher coal conversion in Condition 2.

Tables 6 and *7* show the same analyses as discussed above for the TBP cuts of the full-range liquid product.

PERFORMANCE COMPARISON - FEMO AND NIMO CATALYST

Tables 8 and 9 show comparisons between the performance of FeMo and NiMo catalysts for Condition 1 and Condition 2, respectively. Note that the age of FeMo catalyst (measured as lb feed/lb cat) is higher than the age of NiMo catalyst at the corresponding condition of Run 227-55 (CC-1) due to the low bulk density of FeMo catalyst. In both conditions, NiMo gave higher hydrogen consumption, 7.6 W% DC vs. 6.0 W% DC and 7.7 W% DC vs. 6.5 W% DC. There was no effect of catalyst type on coal conversion. NiMo catalyst gave higher 975°F+ conversion: 84.5 W% with NiMo versus 82.5 W% with FeMo in Condition 1, 88.6 W% with NiMo versus 87.3 w% with FeMo in Condition 2. The yield of C₄-975°F distillate was similarly higher with NiMo catalyst. There was no significant difference in HDS and in HDO obtained with NiMo and FeMo catalysts; however, HDN was significantly lower with FeMo catalyst. The indicated difference between the carbon oxide yields for the two catalysts is not considered real because the carbon oxide yields in subsequent operations with NiMo catalyst were similar to these yields with FeMo catalyst. The product slate obtained with NiMo catalyst was lighter than that obtained with FeMo catalyst. Figures 1 and 2 show the selectivity for more naphtha and less vacuum gas oil for the NiMo catalyst.

Table 10 compares the amount of resid (975°F+ material including coal) converted to 975°F+ product for the NiMo and FeMo catalysts. The calculations are based on the analyses of the first stage samples. In the first condition, the first stage data is not available due to a poor sample in Run 227-75 (CC-1), but the overall resid conversion (the sum of first and second stage resid conversion) was 3.4 W% DC higher with the NiMo catalyst. In Condition 2, the overall resid conversion with NiMo catalyst is marginally better than with FeMo catalyst, and the conversions are distributed similarly between the two stages.

Higher activity of NiMo catalyst is not surprising in view of the intrinsically higher hydrogenation activity of nickel relative to that of iron. The UOP FeMo catalyst had much lower bulk density than the Shell 317 NiMo catalyst. The weight of the NiMo catalyst charged to the reactors in CC-1 was approximately 1.6 times the weight of FeMo catalyst charge in CC-3. It is rather surprising that the performance of FeMo catalyst was not poorer in view of its lower weight.

The different pore structures of the two catalysts makes it impossible to make unqualified determination of the differences between the activities of the promoter metals. The pore-size differences are discussed in the Details of Operation "Fresh Catalyst" below. Microautoclave tests comparing similar macroporous NiMo and FeMo catalysts indicated similar activity for resid conversion on a per weight basis, and did not indicate any definitive advantage of the macroporous catalyst (See "tests of Alternative Supported Catalysts" in the concurrently published Report #3). Thus the bench run comparisons are essentially valid, and

the FeMo catalyst is a fairly effective catalyst, and in view of its lower cost, it should be given further consideration.

There was a pronounced difference in product quality of the first and second stage liquid products obtained with FeMo and NiMo catalysts. As indicated in *Tables 11 and 12*, products from operations with FeMo catalyst had lower API gravities, lower hydrogen contents, and higher nitrogen contents. The differences were quite large, more than could be explained by the lower catalyst ages (on a per weight basis) of the Run 227-55 operations with NiMo catalyst. Typically, the second-stage product fractions for operations with the NiMo catalyst had API gravities lower by 5°API, hydrogen contents lower by 1.0 W%, and nitrogen contents higher by a factor of two.

DETAILS OF OPERATIONS

The test operations were smooth with no major problems experienced during the run. Several problems were experienced during the start-up period. The run start-up commenced on 7/1/89 after charging 345 g and 346 g of catalyst to first and second stage reactors respectively. The start-up was terminated on 7/2/89 following a very high pressure drop in the unit. The bubble cap on the first reactor was found to be frozen and the top of the riser plugged. The catalyst was washed and recharged. The start-up was re-started on 7/4/89. However, the unit was shut down on 7/5/89 when high pressure drop was noticed. An inspection revealed that the first stage bubble cap had frozen again. The catalyst was washed and sieved and recharged after adding fresh catalyst to make up 900 cc of each charge. The weights of catalyst charges to the first and second stages at this point were 398 g and 397 g respectively. The start-up was re-initiated on 7/8/89 and coal was cut-in at 2200 hours on 7/9/89. The period 1A commenced at 0400 on 7/10/89. The operations were fairly smooth from this point onwards except for a few failures of the charge pumps and the Tuthill circulating pump during the course of the run. The run was concluded at 1200 hours on 7/21/89. The first-stage samples were withdrawn at the end of each condition.

COAL FEED

The bench test was conducted using Black Thunder mine coal from Wyoming. The coal analyses are shown in *Table 13*. This is the same shipment of coal (HRI No. 5630) used in bench runs 227-55(CC-1) and 227-57(CC-2), and comparisons of these analyses with previous Wyoming coals are included in those sections of this report. The feed coal, screened to obtain -70 mesh size, contained 6-9 W% moisture after drying at 200°F under nitrogen flow.

START-UP OIL

The bench test was started using HRI-5648, a Wilsonville heavy distillate derived from Illinois No. 6 coal, as start-up oil. *Table 14* shows the analyses of this oil. This start-up oil had also been used in Run 227-57(CC-2), and its analyses are compared with previously used start-up oils in *Table 12* of that section of this report.

FRESH CATALYST

The catalyst was RCM-1-123 (HRI No. 5677), a developmental catalyst from UOP. The catalyst was available in spherical form and contained Fe and Mo oxides supported on alumina. The catalyst analyses are shown in *Table 15*. *Figures 3-5* show the catalyst pore volume distribution and a comparison with Shell S-317 NiMo catalyst. The UOP catalyst has a very high pore volume. The catalyst bulk density was consequently quite low, 0.382 g/cc vs. 0.617 g/cc for Shell S-317 catalyst. Shell S-317 catalyst is bimodal, with pore volume predominantly distributed around 100-120 Å and 1000-1500 Å. The UOP catalyst has pore volume primarily in 700-800 Å range.

The catalyst was presulfided in situ using dimethyl disulfide (DMDS) as a sulfiding agent. The start-up oil was doped with 1.4 W% DMDS. The presulfiding was done by holding temperatures at 450°F, 550°F, and 650°F at six hours each during start-up.

RECOVERED CATALYST

Table 16 shows the analyses of the recovered catalysts. The carbon accumulation on the first stage catalyst was not much different than had been experienced in previous operations with Wyoming coal, but the 10.9 W% second-stage catalyst carbon content was lower than the range of 13.1 to 19.3 W% experienced previously in this higher temperature reactor. The calcium contaminations on both catalysts (0.60 and 0.51 W%) were significantly higher than had been experienced in the two previous runs.

The pore volumes of the two recovered catalysts were 71% and 74% of their original value, and the surface areas decreased from 145 m²/g to 119 and 117 m²/g. *Figure 6* shows a comparison of the pore size distribution of the fresh and the recovered catalyst. The volume of the smaller-diameter pores is almost eliminated due to carbon deposition. The distribution curve of the used catalyst has shifted indicating decreased pore diameter due to carbon deposition.

TABLE 1

Run 227-58 Run Plan

Condition	1	2
Periods	1A-7A	7B-13A
<u>Nominal Conditions</u>		
Space Velocity		
Lbs Coal/Hr/Ft ³ Catalyst	44	44
<u>Recycle Rate</u>		
PFL/Fresh Feed	1.1	0.8
TSB/Fresh Feed	0.0	0.4
<u>Temperatures, °F</u>		
Reactor 1	750	750
Reactor 2	800	825
Slurry Mix Tank	190	190
Hot Separator	610	610
CAS	525	525
<u>Hydrogen Feed, SCFH</u>		
First Stage	45	45
Second Stage	20	20
Back Pressure, PSIG	2,500	2,500

TABLE 2
Run 227-58 (CC-3) Operating Summary

Part 1 of 3

Bench-Scale CTSL™ with FeMo Catalyst

Coal: Black Thunder (HRI-5630)
 Catalyst: Both Stages: UOP FeMo (HRI-5677) Spherical Catalyst

Period No.	1	2	3	4
Date (Start of Period)	07/09/89	07/10/89	07/11/89	07/12/89
Hours of Run (End of Period)	24.	48.	72.	96.
Stg. 1 Catalyst Age, lb dry feed/lb cat	44.	88.	132.	177.

Temperatures, °F

First Stage Reaction	711.	735.	751.	749.
Second Stage Reaction	756.	779.	797.	797.
Slurry Mix Tank	158.	213.	241.	264.
Hot Separator Liquid	611.	603.	587.	575.

Pressures, PSIG

Unit Back Pressure	2,469.	2,461.	2,365.	2,469.
Overall DP	10.6	10.4	9.7	9.5

Space Velocities

Dry Fresh Feed - Stg. 1 Lb/Hr/Ft ³ (catalyst)	44.0	44.0	44.4	44.2
Dry Fresh Feed - Two Stg. Lb/Hr/Ft ³ (catalyst)	22.0	22.0	22.2	22.1

Recycles, W% Dry Fresh Feed

PFL to Buffer - Stage 1	4.0	4.4	6.2	4.3
PFL to Buffer - Stage 2	5.2	6.6	5.5	3.5
Separator Bottoms	0.0	0.0	0.0	0.0
Total Material Recovery (Gross)	94.37	93.92	91.58	98.49

Estimated Normalized Yields,

W% Dry Fresh Feed

C ₁ -C ₃ in Gases	
C ₄ -C ₇ in Gases	
IBP-390°F in Liquids	
390-500°F in Liquids	
500-650°F in Liquids	
650-850°F in Liquids	
850-975°F in Liquids	
Toluene Soluble 975°F+ C.I	
Toluene Insoluble 975°F+ Oil	
Unconverted Coal	
Ash (SO ₃ -Free)	
Water	
CO	
CO ₂	
NH ₃	
H ₂ S	
Total (100+H ₂ Reacted)	

Continued...

TABLE 2 (continued)
Run 227-58 (CC-3) Operating Summary
Bench-Scale CTSL™ with FeMo Catalyst

Period No.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Process Performance</u>				
C ₄ -975°F Distillates, W% MAF				
975°F Conversion, W% MAF				
Conversion, W% MAF		77.74	82.91	85.10
Desulfurization, W%				
Denitrogenation, W%				

TABLE 2
Run 227-58 (CC-3) Operating Summary

Part 2 of 3

CTSL™
Alternative Catalyst Run

Coal: Black Thunder (HRI-5630)
 Catalyst: Both Stages: UOP FeMo (HRI-5677) Spherical Catalyst

Period No.	5	6	7	8
Date (Start of Period)	07/13/89	07/14/89	07/15/89	07/16/89
Hours of Run (End of Period)	120.	144.	168.	192.
Stg. 1 Catalyst Age, lb dry feed/lb cat	220.	263.	306.	349.

Temperatures, °F				
First Stage Reaction	749.	753.	751.	751.
Second Stage Reaction	799.	802.	813.	824.
Slurry Mix Tank	272.	270.	265.	263.
Hot Separator Liquid	568.	573.	570.	569.

Pressures, PSIG				
Unit Back Pressure	2,470.	2,497.	2,502.	2,494.
Overall DP	9.1	9.5	8.6	8.6

Space Velocities				
Dry Fresh Feed - Stg. 1 Lb/Hr/Ft ³ (catalyst)	43.1	43.1	43.1	43.6
Dry Fresh Feed - Two Stg. Lb/Hr/Ft ³ (catalyst)	21.6	21.6	21.6	21.8

Recycles, W% Dry Fresh Feed				
PFL to Buffer - Stage 1	5.0	6.0	3.8	4.7
PFL to Buffer - Stage 2	4.1	4.5	3.6	4.7
Topped Separator Bottoms	0.0	0.0	25.3	40.1
Total Material Recovery (Gross)	95.93	93.93	100.20	96.21

Estimated Normalized Yields, W% Dry Fresh Feed		
C ₁ -C ₃ in Gases	5.82	6.25
C ₄ -C ₇ in Gases	3.05	3.14
IBP-390°F in Liquids	9.79	9.51
390-500°F in Liquids	10.37	10.19
500-650°F in Liquids	15.46	13.98
650-850°F in Liquids	16.55	16.52
850-975°F in Liquids	3.55	3.35
Toluene Soluble 975°F+ Oil	3.87	4.13
Toluene Insoluble 975°F+ Oil	0.02	0.00
Unconverted Coal	13.01	11.84
Ash (SO ₃ -Free)	6.01	6.01
Water	15.14	16.91
CO	1.11	1.14
CO ₂	1.18	1.66
NH ₃	0.78	0.82
H ₂ S	0.37	0.37
Total (100+H ₂ Reacted)	106.09	105.81

Continued...

TABLE 2

Run 227-58 (CC-3) Operating Summary

CTSL™ Alternative Catalyst Run

Period No.	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
Process Performance				
C ₄ -975°F Distillates, W% MAF	62.25	60.3		
975°F+ Conversion, W% MAF	82.02	83.01		
Conversion, W% MAF	86.15	87.40		89.79
Desulfurization, W%	72.01	71.76		
Denitrogenation, W%	61.54	63.95		

TABLE 2
Run 227-58 (CC-3) Operating Summary

Part 3 of 3

CTSL™
Alternative Catalyst Run

Coal: Black Thunder (HRI-5630)
Catalyst: Both Stages: UOP FeMo (HRI-5677) Spherical Catalyst

Period No.	9	10	11	12
Date (Start of Period)	07/17/89	07/18/89	07/19/89	07/20/89
Hours of Run (End of Period)	216.	240.	264.	288.
Stg. 1 Catalyst Age, lb dry feed/lb cat	394.	437.	481.	524.

<u>Temperatures, °F</u>				
First Stage Reaction	752.	753.	751.	752.
Second Stage Reaction	826.	826.	826.	827.
Slurry Mix Tank	265.	268.	268.	268.
Hot Separator Liquid	573.	573.	576.	576.

<u>Pressures, PSIG</u>				
Unit Back Pressure	2,503.	2,508.	2,508.	2,507.
Overall DP	8.4	8.8	8.7	8.9

<u>Space Velocities</u>				
Dry Fresh Feed - Stg. 1 Lb/Hr/Ft ³ (catalyst)	44.2	43.7	44.2	42.9
Dry Fresh Feed - Two Stg. Lb/Hr/Ft ³ (catalyst)	22.1	21.8	22.1	21.4

<u>Recycles, W% Dry Fresh Feed</u>				
PFL to Buffer - Stage 1	3.1	3.7	4.3	3.9
PFL to Buffer - Stage 2	4.4	3.5	4.6	3.7
Topped Separator Bottoms	39.8	39.8	39.9	40.1
Total Material Recovery (Gross)	97.27	94.82	100.08	98.08

<u>Estimated Normalized Yields, W% Dry Fresh Feed</u>			
C ₁ -C ₃ in Gases	8.22	9.14	
C ₄ -C ₇ in Gases	4.36	4.87	
IBP-390°F in Liquids	11.50	10.71	
390-500°F in Liquids	12.49	12.34	
500-650°F in Liquids	16.75	16.48	
650-850°F in Liquids	12.16	12.35	
850-975°F in Liquids	2.36	2.45	
Toluene Soluble 975°F+ Oil	3.96	3.93	
Toluene Insoluble 975°F+ Oil	0.17	0.33	
Unconverted Coal	8.03	7.51	
Ash (SO ₃ -Free)	6.01	6.01	
Water	17.01	17.24	
CO	1.29	1.38	
CO ₂	0.90	0.58	
NH ₃	0.82	0.83	
H ₂ S	0.36	0.35	
Total (100+H ₂ Reacted)	106.40	106.50	

Continued...

TABLE 2

Run 227-58 (CC-3) Operating Summary

CTSL™ Alternative Catalyst Run

Period No.	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
Process Performance				
C ₄ -975°F Distillates, W% MAF			87.07	87.48
Coal Conversion, W% MAF	91.60	91.57		
Desulfurization, W%			69.61	67.87
Denitrogenation, W%			64.55	64.84

TABLE 3**Summary of Results
Run 227-58 (CC-3)**

	Condition 1 (Avg. Per 5 & 6)	Condition 2 Avg. Per 11 & 12
1st Stage Temperature (°F)	751	751
2nd Stage Temperature (°F)	800	827
<u>Space Velocity Per Stage</u>		
Lb/Hr/Ft ³ of Catalyst	43.1	43.6
Catalyst Age (Lb Coal/Lb Cat)	242	503
<u>Recycle (% of Dry Coal Feed)</u>		
PFL	125	88
TSB	0	40
<u>Yields (% of Dry Feed)</u>		
C ₁ -C ₃	6.0	8.7
C ₄ -390°F	12.7	15.7
390-500°F	10.3	12.4
500-650°F	14.7	16.6
650-850°F	16.5	12.3
850-975°F	3.5	2.4
975°F+ Liquid	4.0	4.2
Unconverted Coal + Ash	18.4	13.8
Water	16.0	17.1
CO + CO ₂	2.5	2.1
H ₂ S + NH ₃	1.2	1.2
Total (100 + H ₂ Consumption)	106.0	106.5
Coal Conversion (W% MAF)	86.8	91.8
975°F+ Conversion (W% MAF)	82.5	87.3
C ₄ -975°F Yield (W% MAF)	61.4	63.3
HDS	71.9	67.2
HDN	62.7	64.7
HDO	83.4	87.3

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TABLE 4**Analyses of Products
Run 227-58 (CC-3)**

Condition	<u>1</u>	<u>1</u>	<u>2</u>	<u>2</u>
Period	5	6	11	12
Catalyst Age	220	263	481	524
<u>Separator Overhead</u>				
Vol. Avg. BP, °F	451	423	420	423
API Gravity	25.7	26.6	25.8	25.3
Watson Char Factor	10.77	10.72	10.65	10.63
Carbon, W%	86.58	86.49	85.73	86.05
Hydrogen, W%	11.37	11.06	11.01	11.08
Nitrogen, W%	0.38	0.32	0.41	0.41
Sulfur, W%	0.03	0.00	0.02	0.04
H/C Ratio	1.58	1.53	1.54	1.55
<u>Atmospheric Overhead</u>				
Vol. Avg. BP, °F	515	N/A	460	463
API Gravity	17.9	15.2	20.3	19.6
Watson Char Factor	10.47	N/A	10.43	10.40
Carbon, W%	86.46	86.59	86.35	85.74
Hydrogen, W%	10.51	10.20	10.52	10.44
Nitrogen, W%	0.42	0.42	0.58	0.56
Sulfur, W%	0.04	0.04	0.01	0.01
H/C Ratio	1.46	1.41	1.46	1.46
<u>Calculated CAS</u>				
<u>Bottoms</u>				
IBP-975°F, W%	71.63	69.82	68.36	67.69
975°F+ Toluene Sol Oil	17.00	18.56	19.84	19.41
975°F+ Toluene Insol. Oil	0.08	0.00	0.85	1.65
IOM	6.50	6.24	6.24	6.22
Ash	3.00	3.17	4.68	4.99

TABLE 5

**Analyses of First and Second Stage Liquids/Solids
Run 227-58 (CC-3)**

	1st Stage		2nd Stage			
	1	2	1	1	2	2
Condition	6	12	5	6	11	12
Period	263	524	220	263	481	524
Catalyst Age						
THF-Insols, W%	24.70	21.65	10.15	10.15	10.92	11.21
API	5.1	3.0	4.6	3.7	1.7	1.4
Carbon, W%	89.68	89.52	89.75	89.50	89.98	90.48
Hydrogen, W%	8.77	8.94	9.34	9.24	8.56	8.37
Nitrogen, W%	0.51	0.56	0.39	0.38	0.53	0.58
Sulfur, W%	0.05	0.09	0.01	0.02	0.01	0.02
IBP-650°F, W%	13.71	11.78	10.38	12.19	17.04	16.70
650-850°F, W%	40.35	43.25	50.77	47.43	46.42	45.92
850-975°F, W%	18.24	18.54	18.56	18.09	13.28	13.62
975°F*, W%	27.70	26.43	20.29	22.29	23.26	23.76
<u>IBP-650°F Cut</u>						
API	20.0	16.7	15.0	14.4	12.7	12.5
Carbon, W%	86.77	87.71	87.94	88.28	88.57	88.72
Hydrogen, W%	10.68	10.17	10.35	10.41	9.97	9.86
Nitrogen, W%	0.27	0.35	0.37	0.43	0.49	0.58
Sulfur, W%	0.04	0.06	0.01	0.01	0.02	0.02
<u>650-850°F Cut</u>						
API	10.7	8.7	10.0	10.2	8.2	7.4
Carbon, W%	89.26	89.34	89.36	89.47	89.71	90.23
Hydrogen, W%	9.97	9.28	9.80	9.91	9.31	9.22
Nitrogen, W%	0.33	0.40	0.22	0.25	0.37	0.42
Sulfur, W%	0.10	0.09	0.01	0.01	0.02	0.02
<u>850-975°F Cut</u>						
API	1.4	-0.6	1.4	1.8	-4.8	-5.4
Carbon, W%	89.81	89.88	90.30	90.34	91.15	90.89
Hydrogen, W%	9.00	8.30	9.11	8.96	7.88	7.74
Nitrogen, W%	0.49	0.56	0.35	0.36	0.61	0.60
Sulfur, W%	0.11	0.13	0.01	0.02	0.03	0.01
<u>975°F* Cut</u>						
API	-7.8	-10.3	-8.3	-8.3	-14.9	-13.3
Carbon, W%	89.19	89.59	90.54	90.63	91.63	91.51
Hydrogen, W%	7.20	7.03	7.52	7.35	6.32	6.23
Nitrogen, W%	0.84	0.99	0.63	0.67	0.82	0.85
Sulfur, W%	0.12	0.08	0.01	0.03	0.03	0.02
<u>Solids (THF Washed)</u>						
Carbon, W%	58.78	61.32	49.52	48.06	43.00	42.01
Hydrogen, W%	3.50	3.97	2.93	2.89	2.44	2.52
Nitrogen, W%	1.12	1.10	0.87	0.83	0.64	0.580.65
Sulfur, W%	0.58	0.45	0.77	0.81	1.02	1.03
Ash, W%	19.74	19.25	32.26	34.89	42.96	44.52

TABLE 6**Analyses of TBP Cuts
Run 227-58 (CC-3)****Condition 1 (Period 5)**

BP Range	API Gravity	Carbon	Hydrogen	Nitrogen	Sulfur
IBP-180°F	58.6	85.04	14.46	0.04	0.00
180-390°F	36.6	85.54	12.32	0.19	0.00
390-500°F	21.4	86.72	10.96	0.39	0.00
500-650°F	16.5	88.36	10.60	0.39	0.00
650-850°F	8.4	89.35	9.77	0.38	0.00
850-975°F	1.4	90.30	9.11	0.35	0.01
975°F+	-8.3	90.54	7.52	0.62	0.01

TABLE 7**Analyses of TBP Cuts
Run 227-58 (CC-3)****Condition 2 (Period 12)**

BP Range	API Gravity	Carbon	Hydrogen	Nitrogen	Sulfur
IBP-180°F	57.8	85.97	14.07	0.03	0.00
180-390°F	38.2	84.97	12.30	0.20	0.00
390-500°F	20.3	85.81	10.40	0.53	0.01
500-650°F	14.8	88.41	10.19	0.54	0.01
650-850°F	8.3	89.26	9.23	0.57	0.01
850-975°F	-5.4	90.54	7.74	0.60	0.01
975°F+	-13.3	91.51	6.23	0.85	0.01

TABLE 8

**Comparison Between Fe-Mo and Ni-Mo Catalysts
Condition 1**

	Run 227-55 NiMo Catalyst Period 5/6	Run 227-58 FeMo Catalyst Period 5/6
1st Stage Temperature (°F)	751	751
2nd Stage Temperature (°F)	701	827
<u>Space Velocity Per Stage</u>		
Lb/Hr/Ft ³ of Catalyst	44.7	43.1
Catalyst Age (Lb Coal/Lb Cat)	154	242
<u>Recycle (% of Dry Coal Feed)</u>		
PFL	121	125
TSB	0	0
<u>Yields (% of Dry Feed)</u>		
C ₁ -C ₃	7.6	6.0
C ₄ -390°F	17.6	12.7
390-500°F	10.0	10.3
500-650°F	18.0	14.7
650-850°F	11.8	16.5
850-975°F	2.1	3.5
975°F+ Liquid	2.1	4.0
Unconverted Coal + Ash	18.3	18.4
Water	18.3	16.0
CO + CO ₂	0.5	2.5
H ₂ S + NH ₃	1.3	1.2
Total (100 + H ₂ Consumption)	107.6	106.0
Coal Conversion (W% MAF)	86.8	86.8
975°F+ Conversion (W% MAF)	84.5	82.5
C ₄ -975°F Yield (W% MAF)	63.2	61.4
HDS	70.0	71.9
HDN	72.1	62.7
HDO	86.7	83.4

TABLE 9

**Comparison Between Fe-Mo and Ni-Mo Catalysts
Condition 2**

	Run 227-55 NiMo Catalyst Period 9/10	Run 227-58 FeMo Catalyst Period 11/12
1st Stage Temperature (°F)	750	751
2nd Stage Temperature (°F)	825	827
<u>Space Velocity Per Stage</u>		
Lb/Hr/Ft ³ of Catalyst	45.2	43.6
Catalyst Age (Lb Coal/Lb Cat)	270	503
<u>Recycle (% of Dry Coal Feed)</u>		
PFL	84	88
TSB	38	40
<u>Yields (% of Dry Feed)</u>		
C ₁ -C ₃	8.2	8.7
C ₄ -390°F	20.1	15.7
390-500°F	10.4	12.4
500-650°F	18.8	16.6
650-850°F	12.1	12.3
850-975°F	2.1	2.4
975°F+ Liquid	2.6	4.2
Unconverted Coal + Ash	14.2	13.8
Water	17.7	17.1
CO + CO ₂	0.3	2.1
H ₂ S + NH ₃	1.3	1.2
Total (100 + H ₂ Consumption)	107.7	106.5
Coal Conversion (W% MAF)	91.3	91.8
975°F+ Conversion (W% MAF)	88.6	87.3
C ₄ -975°F Yield (W% MAF)	67.6	63.3
HDS	71.6	67.2
HDN	75.7	64.7
HDO	84.9	87.3

TABLE 10**Comparison Between NiMo and FeMo Catalysts****Resid Conversion**

Resid Converted (W% Dry Fresh Feed)				
Condition	Stage 1		Stage 2	
	227-55 (NiMo)	227-58 (FeMo)	227-55 (NiMo)	227-58 (FeMo)
1 750/800°F		67.37	*	11.28
2 750/825°F	53.97	53.42	29.29	28.80

- * Condition 1 resid conversion is not listed because 1st stage sample was not good.
See CC-1 "First Stage Slurry Analyses and Interpretation".

TABLE 11

**Comparison Between FeMo and NiMo Catalysts
Analyses of First Stage Liquids/Solids**

Catalyst Run	FeMo 227-58	NiMo 227-55	FeMo 227-58	FeMo 227-55
Condition	1	1	2	2
Period	6	6	12	10
Catalyst Age	263	204	524	284
<u>Total Liquid</u>				
API	5.1	10.4	3.0	10.3
Carbon, W%	89.68	88.74	89.52	89.16
Hydrogen, W%	8.77	10.38	8.94	10.20
Nitrogen, W%	0.51	0.37	0.56	0.28
Sulfur, W%	0.05	0.23	0.09	0.01
IBP-650°F, W%	13.71	12.20	11.78	23.70
650-850°F, W%	40.35	39.20	43.25	41.60
850-975°F, W%	18.24	17.30	18.54	13.50
975°F+, W%	27.70	31.30	26.43	21.20
<u>IBP-650°F Cut</u>				
API	20.0	20.9	16.7	20.1
Carbon, W%	86.77	88.16	87.71	88.52
Hydrogen, W%	10.68	11.79	10.17	11.65
Nitrogen, W%	0.27	0.19	0.35	0.13
Sulfur, W%	0.04	0.01	0.06	0.01
<u>650-850°F Cut</u>				
API	10.7	15.2	8.7	13.1
Carbon, W%	89.26	89.12	89.34	89.38
Hydrogen, W%	9.97	10.72	9.28	10.64
Nitrogen, W%	0.33	0.23	0.40	0.18
Sulfur, W%	0.10	0.06	0.09	0.04
<u>850-975°F Cut</u>				
API	1.4	8.14	-0.6	3.3
Carbon, W%	89.81	89.12	89.88	89.99
Hydrogen, W%	9.00	10.48	8.30	9.57
Nitrogen, W%	0.49	0.40	0.56	0.36
Sulfur, W%	0.11	0.17	0.13	0.02
<u>975°F+ Cut</u>				
API	-7.8	0.4	-10.3	-5.6
Carbon, W%	89.19	88.96	89.59	90.13
Hydrogen, W%	7.20	9.18	7.03	8.41
Nitrogen, W%	0.84	0.68	0.99	0.62
Sulfur, W%	0.12	0.71	0.08	0.09
<u>Solids (THF Washed)</u>				
Carbon, W%	58.78	65.48	61.32	60.74
Hydrogen, W%	3.50	3.97	3.97	3.60
Nitrogen, W%	1.12	1.27	1.10	1.16
Sulfur, W%	0.58	0.56	0.45	0.70
Ash, W%	19.74	16.79	19.25	21.00

TABLE 12

**Comparison Between FeMo and NiMo Catalysts
Analyses of Second Stage Liquids/Solids**

Catalyst Run	FeMo 227-58	NiMo 227-55	FeMo 227-58	FeMo 227-55
Condition	1	1	2	2
Period	6	6	12	10
Catalyst Age	263	204	524	284
<u>Total Liquid</u>				
API	3.7	12.1	1.4	10.4
Carbon, W%	89.50	89.09	90.48	88.89
Hydrogen, W%	9.24	10.38	8.37	10.06
Nitrogen, W%	0.38	0.18	0.58	0.29
Sulfur, W%	0.02	0.01	0.02	0.01
IBP-650°F, W%	12.19	16.97	16.70	30.50
650-850°F, W%	47.43	52.83	45.92	44.20
850-975°F, W%	18.09	15.05	13.62	10.80
975°F+, W%	22.29	15.15	23.76	14.50
<u>IBP-650°F Cut</u>				
API	14.4	19.5	12.5	21.4
Carbon, W%	88.28	88.47	88.72	88.32
Hydrogen, W%	10.41	11.58	9.86	11.10
Nitrogen, W%	0.43	0.20	0.58	0.13
Sulfur, W%	0.01	0.01	0.02	0.00
<u>650-850°F Cut</u>				
API	10.2	14.4	7.4	12.3
Carbon, W%	89.47	89.35	90.23	89.82
Hydrogen, W%	9.91	10.94	9.22	10.34
Nitrogen, W%	0.25	0.12	0.42	0.11
Sulfur, W%	0.01	0.01	0.02	0.01
<u>850-975°F Cut</u>				
API	1.8	5.1	-5.4	0.8
Carbon, W%	90.34	90.14	90.89	90.74
Hydrogen, W%	8.96	9.88	7.74	8.94
Nitrogen, W%	0.36	0.26	0.60	0.30
Sulfur, W%	0.02	0.02	0.01	0.00
<u>975°F+ Cut</u>				
API	-8.3	-4.6	-13.3	-9.6
Carbon, W%	90.63	90.40	91.51	91.71
Hydrogen, W%	7.35	8.45	6.23	7.30
Nitrogen, W%	0.67	0.39	0.85	0.51
Sulfur, W%	0.03	0.01	0.02	0.01
<u>Solids (THF Washed)</u>				
Carbon, W%	48.06	48.97	42.01	39.86
Hydrogen, W%	2.89	2.68	2.52	1.98
Nitrogen, W%	0.83	0.81	0.65	0.55
Sulfur, W%	0.81	0.91	1.03	1.17
Ash, W%	34.89	36.13	44.52	47.20

TABLE 13**Feed Coal Analyses for Runs 227-58 (CC-3)****Analyses of Black Thunder Mine (Wyoming) Coal - HRI-5630****Proximate Analysis (W%)**

Moisture	7.79
Volatile Matter	40.76
Fixed Carbon	44.86
Ash	6.59

Ultimate Analysis (W%, Dry)

Carbon	67.70
Hydrogen	4.54
Nitrogen	1.05
Sulfur	0.48
Ash (ASTM)	7.15
(SO ₃ Free)	6.01

Mineral Analysis (W%, Ash)

Silica	34.61
Alumina	16.98
Titanium Oxide	1.30
Ferric Oxide	6.94
Calcium Oxide	21.74
Magnesium Oxide	4.40
Potassium Oxide	0.35
Sodium Oxide	0.97
Sulfur Trioxide	10.74
Phosphorous Pentoxide	1.10
Strontium Oxide	0.29
Barium Oxide	0.37
Manganese Oxide	0.00
Undetermined	0.30

Maceral Analysis (V%)

Vitrinite	73.4
Exinite	3.6
Semifusinite	12.5
Micrinite	8.5
Fusinite	2.0

TABLE 14

Analyses of Start-Up Oil Run 227-58 (CC-3)

HRI Number	5648
API Gravity	5.7

Elemental Analysis (W%)

Carbon	90.14
Hydrogen	9.85
Nitrogen	0.37
Sulfur	0.13

ASTM D-1160 Distillation

IBP	735°F
5 V%	776°F
10 V%	798°F
20 V%	810°F
30 V%	830°F
40 V%	842°F
50 V%	858°F
60 V%	876°F
70 V%	888°F
80 V%	902°F
90 V%	930°F
95 V%	952°F
FBP	1008°F

TABLE 15

Fresh Catalyst Analyses Run 227-58 (CC-3)

Catalyst Type:	UOP RCM-1-123 FeMo Catalyst
HRI Number:	5677
Iron:	2.38 W%
Molybdenum:	9.35 W%
Crush Strength:	1.76 lb/mm
Compacted Bulk Density:	0.382 g/cc 23.87 lb/ft ³
Particle (Bead) Density:	0.617 g/cc
Substrate Density:	3.25 g/cc

Pore Volume in Pores > 4000 Å Diameter = 0.0002 cc/g
Pore Volume in Pores > 1500 Å Diameter = 0.0005 cc/g
Pore Volume in Pores > 500 Å Diameter = 0.9354 cc/g
Pore Volume in Pores > 250 Å Diameter = 1.1192 cc/g
Pore Volume in Pores > 100 Å Diameter = 1.2573 cc/g
Pore Volume in Pores > 50 Å Diameter = 1.2972 cc/g
Total Pore Volume (D > 29.4 Å) = 1.3120 cc/g

Calculated Surface Area (Porosimetry) = 145 m²/g

TABLE 16**Recovered Catalyst Analyses
Run 227-58 (CC-3)**

	1st Stage	2nd Stage
Age (lb coal/lb cat)	524	524
Carbon, W%	11.3	10.9
Hydrogen, W%	0.94	0.81
H/C Ratio	1.00	0.89
Nitrogen, W%	0.23	0.15
Sulfur, W%	3.78	3.79
Molybdenum, W%	6.70	6.73
Iron, W%	2.11	1.57
Titanium, W%	0.13	0.04
Calcium, W%	0.60	0.51
Sodium, W%	0.11	0.89
Compacted Bulk Density (g/cc)	0.520	0.495
Pore Volume (cc/g) in Pores with		
Diameter > 4000 Å	0.0001	0.0001
Diameter > 1500 Å	0.0003	0.0004
Diameter > 500 Å	0.5714	0.6139
Diameter > 250 Å	0.7707	0.8194
Diameter > 100 Å	0.8777	0.9255
Diameter > 50 Å	0.9133	0.9605
Total Pore Volume (cc/g)	0.9297	0.9738
Calculated Surface Area (m ² /g)	119	117

COMPOSITION OF C4-975 F DISTILLATE

Condition 1 (750 F/800 F)

NiMo
Run 227-55

FeMo
Run 227-58

COMPOSITION OF C4-975 F DISTILLATE

Condition 2 (750 F/825 F)

FeMo
Run 227-58

NiMo
Run 227-55

PORE SIZE DISTRIBUTION

PORE VOLUME (CC/G)
RUN 227-58

PORE SIZE DISTRIBUTION

$dV/d(\log D)$ (cc/g)

RUN 227-58

PORE SIZE DISTRIBUTION

 $dV/d(\log D)$ (CC/G)

RUN 227-58

FIGURE 6

PORE SIZE DISTRIBUTION

$dV/d(\log D)$ (CC/G)

RUN 227-58

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SECTION IV

RUN 227-61 (CC-4) CTSL™ EVALUATION OF IRON-BASED DISPERSED CATALYSTS WITH BLACK THUNDER MINE COAL

SUMMARY

The objective of this run was to investigate the performance of iron-based additives (dispersed catalyst) for liquefaction of sub-bituminous coal in the presence of supported catalyst.

Two dispersed catalysts were tested. The first additive was an iron oxide magnetic pigment. The second additive was a pyrrhotite concentrate. These additives were added at the rate of 5 W% (equivalent FeS) of coal rate. Hydrogen sulfide was injected continuously to provide sulfur at S/Fe atomic ratio of two. The test was conducted using Black Thunder mine sub-bituminous coal. Partially deactivated supported catalyst (Shell S-317 NiMo) recovered from the previous runs was used. The test was conducted using constant conditions of space velocity (67 lb coal per hour per ft³ of supported catalyst per stage) and reactor temperatures (750°F in the first stage and 825 F in the second stage).

The process performance was marginally better with the iron oxide additive than with no additive. Coal conversion was higher by about 1.5 W% (MAF) and 975°F+ conversion and C₄-975°F yield were higher by about 2 W% (MAF). With pyrrhotite additive, coal and resid conversions were higher by less than 1 W%, and the distillate yield was lower due to significantly higher gas yield.

SCOPE OF WORK

Use of fine dispersed catalyst in coal liquefaction has an appeal because through effective interactions with both hydrogen donor solvent and large fragment of coal derived resid molecules, these catalyst can enhance the stability of these large molecules that cannot easily access active sites on supported catalysts. On the other hand, the supported catalysts can be designed for superior performance with reactions involving smaller molecules. Using dispersed catalyst along with supported catalyst could provide an optimum environment.

Run 227-61(CC-4) tested two additives. One was an oxide catalyst magnetic pigment. The other was a pyrrhotite concentrate obtained from a nickel refining facility. These additives were added at 5 W% (FeS equivalent) of coal rate. Hydrogen sulfide was injected continuously to provide a sulfiding atmosphere at S/Fe atomic ratio of two, but it was also injected in Condition 1 with no additive.

Lesser amount of H_2S was needed with pyrrhotite because it contained sulfur itself.

The run conditions, as planned, are shown in *Table 1*. The plan called for three operating conditions; Condition 1 without any additive, Condition 2 using iron oxide additive, and Condition 3 using pyrrhotite additive. Operational problems during Condition 2 led to a shutdown. The plan was then modified. The revised plan, as executed, is shown in *Table 2*.

The space velocity was kept constant at 67 lb coal per hour per cubic foot of compacted catalyst (per stage). The first and the second stage temperatures were also held constant at 750°F and 825°F, respectively. The supported catalyst in both reactors was partially deactivated Shell S-317 recovered from the previous runs.

PROGRAM RESULTS AND ANALYSES - RUN 227-61 (CC-4)

Table 3 is the Operating Summary for the run, giving the principal operating conditions for each Period (day), and normalized product distributions for periods which were considered to represent equilibrated results. *Table 4* shows the yields and process performance for the three conditions using averages of the results from the last periods of each condition.

COAL CONVERSION

Coal conversion is normally calculated from the ash-to-solids (quinoline insoluble) ratio of the product and by comparing it with the feed coal. This assumes that the non-ash portion of the product is organic unconverted coal. This simple calculation is not entirely rigorous because ashing transforms mineral matter into other inorganic forms. In dealing with sub-bituminous coal, HRI usually considers ash on a SO_3 -free basis to discount the sulfur capture by lime that might occur during ashing. When additives are added, calculation of true coal conversion can be uncertain and imprecise. If the additive contains iron (as is the case here), it captures sulfur during the liquefaction process either from coal or coal-derived liquid or from H_2S . If the liquefaction product containing this sulfided iron species is ashed, the organic material undergoes transformation. For example, if the product contains FeS , it could be oxidized to Fe_2O_3 or some other oxide. If it is converted to Fe_2O_3 , it would lose weight during ashing. As a result, the amount of the mineral matter in the product would be underestimated and that of the organic matter overestimated. Calculated coal conversion would then be lower than the real conversion.

A true or more accurate value of coal conversion could be arrived at if the chemical nature of the iron species in the product and in the ashed form is known. As this information was lacking, it was assumed here that the iron species in the liquefaction product was present as pyrrhotite $\text{Fe}(1-x)\text{S}$ with x of 0.15 and that it was converted to Fe_2O_3 during ashing.

The coal conversions for the three conditions are included in *Figure 1*. The coal conversion for the baseline (no dispersed catalyst) Condition 1 was 86.6 W% (MAF). It increased by 1.5 W% to 88.1 W% during Condition 2 operations with the iron oxide additive and by 1.9 W% to 88.5 W% during Condition 3 operations with the pyrrhotite additive. The accuracy of these comparisons is dependent on the accuracy of the assumption of the change of the additive species during ashing.

975°F⁺ CONVERSION

The 975°F⁺ conversions for the three conditions are included in *Figure 1*. The 975°F⁺ conversion was 85.6 W% (MAF) for Condition 1 (no dispersed catalyst), 87.5 W% for Condition 2 (with iron oxide additive), and 86.3 W% for Condition 3 (with pyrrhotite additive). By this measure of process performance, there was some advantage to the iron additives, especially the iron oxide additive.

The 975°F⁺ oil yields, the differences between the coal conversion and 975°F⁺ conversion, were only 1.0 W% (MAF), 0.6 W%, and 2.2 W% for the three conditions. The 1.0 W% 975°F⁺ oil yield for the base case, Condition 1, was lower than expected, considering that an aged catalyst was being used; however, hydrogen sulfide was being injected continuously, and it might have contributed to or restored catalytic activity. Even with this low residual oil yield for the base condition, it decreased even further to 0.6 W% in operations with the iron oxide catalyst, indicating the increased reactivity of this fraction with this dispersed catalyst. The 975°F⁺ oil yield was a higher 2.2 W% in operations with the pyrrhotite catalyst, indicating no definitive additional catalyst activity. The increase in 975°F⁺ oil yield was mostly due to the increased catalyst age in Condition 3.

NORMALIZED PRODUCT DISTRIBUTION

The normalized yields of the gas and C₄-975°F distillate liquid are included in *Figures 1* and *2*. The C₄-975°F distillate yield was highest for operations with the iron oxide dispersed catalyst (64.6 W% MAF) compared to 61.9 W% for the base condition). Operations with the pyrrhotite dispersed catalyst had 60.0 W% C₄-975°F distillate yield. This distillate yield was lower primarily because of the higher gas yield, which was 11.1 W% (dry coal) compared to 7.4 W% in Condition 1 and 8.3 W% in Condition 2. Correspondingly, the hydrogen consumption was higher for the operations with the dispersed catalysts.

Figures 3 and *4* show distillate yields and selectivity obtained in Run 227-61(CC-4). Compared to Condition 1 with no additive, the yields of the lighter distillate cuts were slightly higher in Condition with the oxide additive. The pyrrhotite additive had a higher selectivity for 650°F⁺ distillate formation.

HETEROATOM REMOVAL

As shown in *Table 4*, the yield of H_2S was negative when using additives. The net negative yield was due to H_2S consumption by additive sulfidation. As expected, pyrrhotite, which was already partially sulfided, consumed less H_2S than did the oxide additive. Hydrodenitrogenation (HDN) was slightly better with the iron oxide catalyst.

PRODUCT QUALITY

Table 5 shows analyses of the product streams removed from the unit. The quality of the Separator Overhead and Atmospheric Still Overhead did not change appreciably during the run.

Table 6 shows the analyses of the first-stage and second-stage (PFL) liquid products, distillation fractions, and THF-washed solids. The first-stage samples were withdrawn at the conclusion of each condition. The quality of these fractions also did not change appreciably during the run. The small differences are more likely due to the small amount of additional catalyst deactivation and the inclusion of variable amounts of makeup oil than due to the presence of dispersed iron catalyst. The only consistent trend was the higher hydrogen content of the Condition 2 second-stage liquid fractions. Compared to the Condition 1 and Condition 3 liquid fractions, they averaged 0.53 W% higher hydrogen. Possibly the iron oxide dispersed catalyst is active at the higher temperature of the second stage in a way that does not cause as much dehydrogenation.

DETAILS OF OPERATION

Run CC-4 was started as Run 227-59. The start-up commenced August 16, 1989. Soon into Condition 1, a shutdown was caused by a power failure. The run was aborted when two additional start-ups proved unsuccessful due to high pressure drops at the reactors.

The catalyst from 227-59 was recovered and used later as the run restarted as 227-61 October 12, 1989. Catalyst was not held at intermediate temperatures for sulfiding during the start-up although H_2S was injected continuously. Condition 1 commenced October 14. In Period 8 (Condition 2), the level control on the hot separator failed and the unit had to be shut down. It was restarted with Period 9 commencing October 29. The run went smoothly after this point and completed successfully.

Three high-pressure first-stage samples were withdrawn during the run, once after the end of each condition.

COAL FEED

The bench run was conducted using Black Thunder mine sub-bituminous coal. This is the same shipment of coal (HRI No. 5630) used in the previous bench runs in this program. The coal analyses are shown in *Table 7*. The ultimate analyses were on a composite sample of the coal fed during the run, but the other analyses were on a previous sample. The coal was ground to -70 mesh and dried under nitrogen to moisture contents of 6 to 9 W%.

START-UP OIL

The run was started using L-742, a distillate obtained from blends of Wilsonville-derived products. The analyses are shown in *Table 8*. This oil was also used as make-up oil in the early part of the run to supplement the process-derived oil for the recycle oil requirements. In the later part of the run, the make-up oil, if required, was made up from the accumulated excess process-derived oil.

CATALYST

The ebullated bed reactors contained partially deactivated Shell S-317 NiMo catalyst. Fresh catalyst was not used because its high activity would have masked the effect of dispersed catalyst. The charged catalyst was made up of the recovered catalyst from the earlier Runs 227-55(CC-1) and 227-57(CC-2). The average (calculated) catalyst analyses are shown in *Table 9*. Note that the catalyst age for the first stage was different from that of the second stage.

ADDITIVES

Two iron-based additives were used in the program. The additives analyses are shown in *Table 10*. Wright Industries (Brooklyn, New York) supplied an iron oxide which was labelled as magnetic pigment. This was received in two shipments, HRI 5670 and HRI 5689. The other additive was pyrrhotite concentrate supplied by INCO (Canada) from its nickel refining operations.

RECOVERED CATALYST

Table 11 shows analyses of the recovered catalyst. Compared with the charged catalysts in *Table 9*, the recovered catalyst in both stages picked up some additional carbon, and the H/C ratio decreased significantly. The pore volume decreased only from 0.42 to 0.39 cc/g for the first stage catalyst and from 0.32 to 0.30 cc/g for the second stage catalyst. Because of the relatively small decrease in catalyst contamination during this run, the changes in yields and product properties would only have been slightly affected by catalyst deactivation.

TABLE 1

Run Plan for Run 227-61 (CC-4)

Condition	<u>1</u>	<u>2</u>	<u>3</u>
Periods	1A-6A*	6B-10A*	10B-14A*
<u>Nominal Conditions</u>			
Lbs Coal/Hr/Ft ³ Catalyst	67	67	67
<u>Recycle Rate</u>			
PFL/Fresh Feed	1.1	1.1	1.1
<u>Temperature, °F</u>			
Reactor 1	750	750	750
Reactor 2	825	825	825
Back Pressure, PSIG	2,500	2,500	2,500
Additive Type	None	HRI 5689/5670	HRI 5646
Additive Rate, W% Dry Coal	0.0	5.2	6.2
H ₂ S Rate, W% Dry Coal	3.8	3.8	3.0

* Each period is divided into three sub-periods and labelled as A, B and C.

TABLE 2

Run Conditions for Run 227-61 (CC-4)

Condition	<u>1</u>	<u>2*</u>	<u>2</u>	<u>3</u>
Periods	1A-6A	6B-8A	9A-14A	14B-18A
<u>Nominal Conditions</u>				
Lbs Coal/Hr/Ft ³ Catalyst	67	67	67	67
<u>Recycle Rate</u>				
PFL/Fresh Feed	1.1	1.1	1.1	1.1
<u>Temperature, °F</u>				
Reactor 1	750	750	750	750
Reactor 2	825	825	825	825
<u>Back Pressure, PSIG</u>				
	2,500	2,500	2,500	2,500
Additive Type	None	HRI 5670	HRI 5689	HRI 5645
Additive Rate, W% Dry Coal	0.0	5.2	5.2	5.2
H ₂ S Rate, W% Dry Coal	3.8	3.8	3.8	3.8

* Aborted Condition

TABLE 3

**Run CC-4 Operating Summary
Dispersed Catalyst run**

Coal: Black Thunder Mine (HRI 5630)
 Catalyst: 1st & 2nd Stage - Recovered NiMo Catalyst
 H₂S Plus Dispersed Additives: No additive (Periods 1-5);
 HRI-5670 (6-9); HRI-5689 (9A-14A); HRI-5646 (14A-18A)

Period Number	1	2	3	4	5
Date (Start-of Period)	10/14/89	10/15/89	10/16/89	10/17/89	10/18/89
Hours of Run (End of Period)	24.	48.	72.	96.	120.
Cat. Age, Lb Dry Coal/Lb Cat - 1st Stage	313.	350.	388.	426.	463
Cat. Age, Lb Dry Coal/Lb Cat - 2nd Stage	660.	700.	739.	780.	819.
1st Stage Temperature, °F	747.	751.	751.	749.	751.
2nd Stage Temperature, °F	811.	825.	825.	826.	827.
Unit Back Pressure, (PSIG)	2,496.	2,498.	2,495.	2,500.	2,501.
Space Velocity per Stage, Lb/Hr/Ft ³ Cat.	67.3	67.3	67.3	68.0	67.3
W% of Dry Coal					
PFL Recycle	109.2	116.0	81.1	107.7	104.4
PFL to Buffer - Stage 1	2.3	4.3	4.6	3.9	3.6
PFL to Buffer - Stage 2	2.1	3.6	3.6	4.7	4.8
Make-Up Oil					3.2
H ₂ S	3.6	3.6	2.2	1.6	1.9
Additive	0.0	0.0	0.0	0.0	0.0
Total Material Recovery (Gross)	97.31	97.57	97.15	100.90	99.43

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	7.46	7.26
C ₄ -C ₇ in Gases	6.24	5.88
IBP-390°F in Liquids	13.34	11.22
390-500°F in Liquids	11.09	9.52
500-650°F in Liquids	18.92	18.10
650-850°F in Liquids	9.00	11.55
850-975°F in Liquids	0.36	1.20
Toluene Soluble 975°F Oil	0.45	1.19
Toluene Insoluble 975°F Oil	0.01	0.05
Unconverted Coal	12.93	12.46
Ash (SO ₂ -free)	5.92	5.92
Water	18.89	19.80
CO	0.46	0.42
CO ₂	1.57	1.75
NH ₃	0.84	0.83
H ₂ S	0.19	0.17
Total (100 + H ₂ Reacted)	107.66	107.32

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal		62.7	61.1
975°F Conversion, W% MAF		85.8	85.4
Coal Conversion, W% MAF	86.3	86.7	86.8
HDS, W%		52.8	47.7
HDN, W%		75.5	73.9

TABLE 3 (continued)

**Run CC-4 Operating Summary
Dispersed Catalyst run**

Coal: Black Thunder Mine (HRI 5630)
 Catalyst: 1st & 2nd Stage - Recovered NiMo Catalyst
 H₂S Plus Dispersed Additives: No additive (Periods 1-5);
 HRI-5670 (6-9); HRI-5689 (9A-14A); HRI-5646 (14A-18A)

Period Number	9	10	11	12	13
Date (Start of Period)	10/30/89	10/31/89	11/01/89	11/02/89	11/03/89
Hours of Run (End of Period)	208.	232.	256.	280.	304.
Cat. Age, Lb Dry Coal/Lb Cat - 1st Stage	585.	622.	659.	697.	736.
Cat. Age, Lb Dry Coal/Lb Cat - 2nd Stage	949.	988.	1,027.	1,067.	1,109.
1st Stage Temperature, °F	738.	751.	749.	751.	751.
2nd Stage Temperature, °F	793.	825.	825.	825.	825.
Unit Back Pressure, (PSIG)	2,734.	2,495.	2,460.	2,519.	2,519.
Space Velocity per Stage, Lb/Hr/Ft ³ Cat.	65.1	65.6	67.6	67.6	69.8
<u>W% of Dry Coal</u>					
PFL Recycle	112.3	103.1	107.5	103.8	97.9
PFL to Buffer - Stage 1	6.3	5.0	7.1	5.6	5.3
PFL to Buffer - Stage 2	6.3	5.7	5.6	6.7	4.9
Make-Up Oil				4.5	10.3
H ₂ S	1.4	1.7	1.7	1.4	2.1
Additive	4.1	4.8	4.6	5.2	5.2
Total Material Recovery (Gross)	102.57	103.51	101.09	99.12	102.50

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	8.61	7.96
C ₄ -C ₇ in Gases	6.42	4.06
IBP-390°F in Liquids	13.40	14.84
390-500°F in Liquids	10.55	11.48
500-650°F in Liquids	19.35	21.18
650-850°F in Liquids	8.97	9.89
850-975°F in Liquids	0.61	0.73
Toluene Soluble 975°F Oil	0.49	0.69
Toluene Insoluble 975°F Oil	0.00	-0.02
Unconverted Coal	11.29	11.23
Ash (SO ₃ -free)	6.71	6.71
Water	20.46	18.45
CO	0.87	0.72
CO ₂	1.35	1.09
NH ₃	0.86	0.85
H ₂ S	-1.85	-1.87
Total (100 + H ₂ Reacted)	108.09	108.08

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal		63.0	66.1
975°F Conversion, W% MAF		87.5	87.4
Coal Conversion, W% MAF	86.4	87.9	88.0
HDS, W%		-	-
HDN, W%		77.3	76.5

TABLE 3 (continued)

**Run CC-4 Operating Summary
Dispersed Catalyst run**

Coal: Black Thunder Mine (HRI 5630)

Catalyst: 1st & 2nd Stage - Recovered NiMo Catalyst

H₂S Plus Dispersed Additives: No additive (Periods 1-5);
HRI-5670 (6-9); HRI-5689 (9A-14A); HRI-5646 (14A-18A)

Period Number	14	15	16	17
Date (Start of Period)	11/04/89	11/05/89	11/06/89	11/07/89
Hours of Run (End of Period)	328.	352.	376.	400.
Cat. Age, Lb Dry Coal/Lb Cat - 1st Stage	774.	812.	848.	886.
Cat. Age, Lb Dry Coal/Lb Cat - 2nd Stage	1,149.	1,189.	1,228.	1,267.
1st Stage Temperature, °F	750.	751.	750.	751.
2nd Stage Temperature, °F	827.	827.	826.	826.
Unit Back Pressure, (PSIG)	2,521.	2,520.	2,518.	2,518.
Space Velocity per Stage, Lb/Hr/Ft ³ Cat.	68.0	67.6	66.0	67.1
W% of Dry Coal				
PFL Recycle	113.2	97.5	104.8	101.2
PFL to Buffer - Stage 1	5.8	6.3	6.7	5.2
PFL to Buffer - Stage 2	4.6	3.8	4.4	5.0
Make-Up Oil			6.3	9.0
H ₂ S	1.4	1.2	1.3	1.2
Additive	5.7	5.9	6.0	6.0
Total Material Recovery (Gross)	102.06	100.35	102.62	103.25

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	11.35	10.75
C ₄ -C ₇ in Gases	5.65	5.10
IBP-390°F in Liquids	11.77	11.64
390-500°F in Liquids	10.50	10.36
500-650°F in Liquids	17.24	17.57
650-850°F in Liquids	9.94	10.60
850-975°F in Liquids	0.96	1.53
Toluene Soluble 975°F Oil	1.77	2.24
Toluene Insoluble 975°F Oil	0.04	0.23
Unconverted Coal	11.12	10.39
Ash (SO ₃ -free)	6.06	6.03
Water	18.15	18.50
CO	0.93	0.84
CO ₂	2.03	1.65
NH ₃	0.77	0.76
H ₂ S	-0.30	-0.36
Total (100 + H ₂ Reacted)	107.99	107.82

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal	59.6	60.4
975°F Conversion, W% MAF	86.2	86.3
Coal Conversion, W% MAF	83.0	88.9
HDS, W%	-	-
HDN, W%	68.9	67.9

TABLE 4

**Summary of Results
Run 227-61 (CC-4)**

Condition	1	2	3
1st Stage Temperature (°F)	750	751	751
2nd Stage Temperature (°F)	826	825	826
<u>Space Velocity</u>			
Lb/Hr/Ft ³ of Catalyst	67.8	68.9	66.6
<u>Catalyst Age (Lb Coal/Lb Cat)</u>			
First Stage	444	717	867
Second Stage	799	1,088	1,248
Additive Type	None	Oxide	Pyrrhotite
Additive Rate, W% Dry Coal	0.00	5.2	6.0
H ₂ S W% Rate, W% Dry coal	1.9	1.8	1.3
<u>Recycle Rate</u>			
PFL (% of Dry Coal)	109.8	112.1	113.7
<u>Yields (% of Dry Feed)</u>			
C ₁ -C ₃	7.36	8.29	11.05
C ₄ -390°F	18.34	19.36	17.08
390-500°F	10.31	11.02	10.43
500-650°F	18.57	20.27	17.41
650-850°F	10.28	9.43	10.27
850-975°F	0.78	0.67	1.25
975°F* Liquid	0.85	0.58	2.14
Unconverted Coal + Mineral Ash	18.62	17.97	16.8
Water	19.35	19.46	18.33
CO + CO ₂	2.10	2.02	2.73
NH ₃	0.83	0.85	0.76
H ₂ S*	0.18	-1.82	-0.33
Total (100 + H ₂ Consumption)	107.49	108.09	107.91
Coal Conversion (W% MAF)	86.6	88.1	88.5
975°F* Conversion (W% MAF)	85.6	87.5	86.3
C ₄ -975°F Yield (W% MAF)	61.9	64.6	60.0
HDS	50.3	-	-
HDN	74.7	76.9	68.4

* Negative amount reflects H₂S consumed by additives.

TABLE 5
Analysis of Products
Run 227-61 (CC-4)

Condition	1	2	3
Period	5	13	17
<u>Catalyst Age (Lb Coal/Lb Catalyst)</u>			
First Stage	463	736	886
Second	819	1,109	1,267
<u>Separator Overhead</u>			
Volume Average BP, °F	478	465	471
°API Gravity	29.1	29.8	29.1
Watson Characterization Factor	10.96	10.92	10.93
Carbon, W%	87.65	87.79	88.25
Hydrogen, W%	12.12	12.73	12.31
Nitrogen, W%	0.14	0.13	0.19
Sulfur, W%	0.02	0.01	0.01
<u>Atmospheric Overhead</u>			
Volume Average BP, °F	457	459	462
°API Gravity	28.3	27.7	27.1
Watson Characterization Factor	10.87	10.88	10.89
Carbon, W%	87.37	87.81	88.01
Hydrogen, W%	12.17	12.67	12.67
Nitrogen, W%	0.13	0.17	0.01
Sulfur, W%	0.03	0.00	0.22
<u>Calculated CAS Bottoms</u>			
IBP-975°F, W%	75.15	71.13	67.93
975°F+ Toluene Soluble Oil	12.08	14.12	17.30
975°F+ Toluene Insoluble Oil	0.36	0.22	1.22
IOM	8.41	7.55	7.54
Ash*	4.00	6.98	6.00

* On an SO₃-Free basis (includes additive, if any).

TABLE 6
Analyses of First and Second Stage Slurry Products
Run 227-61 (CC-4)

Condition	1st Stage*			2nd Stage**		
	1	2	3	1	2	3
Period	6A	14A	18A	5	13	17
THF-Insols, W%	28.88	28.64	31.59			
Liquid						
°API	8.1	8.2	5.8	9.0	7.4	5.7
Carbon, W%	88.51	89.52	89.32	89.50	90.18	90.04
Hydrogen, W%	9.94	10.15	9.81	9.91	10.30	9.48
Nitrogen, W%	0.40	0.34	0.41	0.33	0.32	0.39
Sulfur, W%	0.26	0.01	0.01	0.00	0.01	0.01
IBP-650°F, W%	16.76	19.05	13.96	23.73	22.18	21.14
650-850°F, W%	42.31	43.04	43.65	50.45	49.36	44.71
850-975°F, W%	14.60	12.74	15.13	11.62	11.58	12.71
975°F+, W%	26.33	25.17	27.26	14.20	16.78	21.44
<u>IBP-650°F, W%</u>						
°API	19.7	20.6	18.1	17.5	17.4	16.7
Carbon, W%	88.16	88.64	88.44	88.94	89.10	89.02
Hydrogen, W%	11.42	12.00	11.44	11.09	11.60	11.18
Nitrogen, W%	0.22	0.20	0.19	0.20	0.18	0.27
Sulfur, W%	0.03	0.02	0.01	0.01	0.00	0.00
<u>650-850°F, W%</u>						
°API	12.9	12.3	11.5	11.6	11.4	10.7
Carbon, W%	88.61	89.36	89.43	89.41	89.76	89.52
Hydrogen, W%	10.58	10.77	10.71	10.25	10.71	10.27
Nitrogen, W%	0.29	0.27	0.28	0.27	0.26	0.31
Sulfur, W%	0.04	0.00	0.00	0.01	0.00	0.01
<u>850-975°F Cut</u>						
°API	2.7	0.3	2.4	-0.8	0.3	-1.7
Carbon, W%	89.16	90.07	89.71	90.43	90.58	90.60
Hydrogen, W%	9.63	9.58	9.15	8.84	9.25	8.74
Nitrogen, W%	0.40	0.41	0.23	0.41	0.44	0.48
Sulfur, W%	0.16	0.02	0.01	0.01	0.00	0.01
<u>975°F+ Cut</u>						
°API	-6.0	-7.1	-6.1	-10.0	-8.4	-11.0
Carbon, W%	88.74	90.07	89.63	91.05	91.04	91.15
Hydrogen, W%	8.55	8.39	8.00	7.25	7.86	6.99
Nitrogen, W%	0.67	0.68	0.68	0.61	0.75	0.74
Sulfur, W%	0.17	0.07	0.04	0.02	0.02	0.02
<u>Solids (THF Washed)</u>						
Carbon, W%	61.37	56.14	50.94	50.57	36.70	40.28
Hydrogen, W%	3.80	3.44	2.92	3.30	2.11	2.45
Nitrogen, W%	1.27	1.07	1.02	0.74	0.62	0.66
Sulfur, W%	0.93	3.86	7.45	0.96	8.82	6.51
Ash, W%	19.51	26.80	35.65	35.00	58.91	55.44
Iron, W%	0.56	6.28	11.68	0.87	14.93	10.86

* First-Stage Slurry Sample

** PFL and PFS

TABLE 7**Feed Coal Analyses for Run 227-61 (CC-4)**

HRI No.	5630
Type	Black Thunder Sub-Bituminous
Moisture Content, W%	6-9
<u>Proximate Analysis (W%)</u>	
Volatile Matter	47.61
Fixed Carbon	52.39
<u>Ultimate Analysis (W%, Dry)</u>	
Carbon	67.64
Hydrogen	4.62
Nitrogen	0.98
Sulfur	0.36
Ash	6.69
SO ₃ Free	5.92
<u>Sulfur Types (W% Dry)</u>	
Sulfate	0.04
Pyrittic	0.11
Organic	0.36
<u>Ash Analysis, W% (Ignited Basis)</u>	
Silica	34.61
Alumina	16.98
Titanium Oxide	1.30
Ferric Oxide	6.94
Calcium Oxide	21.74
Magnesium Oxide	4.40
Potassium Oxide	0.35
Sodium Oxide	0.97
Sulfur Trioxide	10.74
Phosphorous Pentoxide	1.01
Strontium Oxide	0.29
Barium Oxide	0.37
Manganese Oxide	0.00
Undetermined	0.30
<u>Maceral Analysis (V%)</u>	
Vitrinite	73.4
Exinite	3.6
Semifusinite	12.5
Micrinite	8.5
Fusinite	2.0

TABLE 8**Analyses of Start-Up Oil
Run 227-61 (CC-4)**

HRI Number	L-742
°API Gravity	6.2
<u>Elemental Analysis (W%)</u>	
Carbon	88.49
Hydrogen	9.22
Nitrogen	0.76
Sulfur	0.05
<u>ASTM D-1160 Distillation</u>	
IBP	485°F
5 V%	547°F
10 V%	586°F
20 V%	630°F
30 V%	695°F
40 V%	717°F
50 V%	753°F
60 V%	780°F
70 V%	816°F
80 V%	854°F
90 V%	887°F
95 V%	930°F
98 V%	975°F

TABLE 9**Analyses of Charged Catalyst
Run 227-61 (CC-4)**

	<u>First Stage</u>	<u>Second Stage</u>
Carbon, W%	10.05	16.47
Hydrogen, W%	1.04	0.99
Nitrogen, W%	0.24	0.16
Sulfur, W%	5.77	5.74
Molybdenum, W%	9.43	8.66
Nickel, W%	1.80	1.60
Iron, W%	0.39	0.07
Titanium, W%	0.02	0.02
Calcium, W%	0.04	0.17
Sodium, W%	0.42	1.18
Pore Volume, cc/g	0.422	0.319
Average Age, Lb Coal/Lb Catalyst	275	620

TABLE 10**Analyses of Additives
Run 227-61 (CC-4)**

HRI No. Type	5689/5670 Magnetic Pigment (Oxide)	5645 Pyrrhotite
<u>Element of Analysis (Dry Basis)</u>		
Carbon, W%	0.14	0.37
Hydrogen, W%	0.00	0.06
Nitrogen, W%	0.00	0.00
Sulfur, W%	0.003	26.90
Iron, W%	61.22	57.38
Water, W%	0.02	1.26
Ash, W%	102.75	84.26
<u>Mineral Analysis (W% Dry)</u>		
Silicon Dioxide	0.93	4.10
Aluminum Oxide	0.07	1.30
Titanium Oxide	0.20	0.50
Iron Oxide	98.36	75.83
Calcium Oxide	0.05	0.59
Magnesium Oxide	0.22	0.55
Potassium Oxide	0.02	0.10
Sodium Oxide	0.07	0.20
Sulfur Trioxide	0.07	16.54
Phosphorous Pentoxide	0.03	0.05
Undetermined	0.02	0.24
<u>Forms of Iron (W% Additive)</u>		
Fe	0.05	
FeO	25.14	
Fe ₂ O ₃	70.42	

TABLE 11**Recovered Catalyst Analyses
Run 227-61 (CC-4)**

	First Stage	Second Stage
Carbon, W%	13.78	19.42
Hydrogen, W%	0.76	0.73
Nitrogen, W%	0.17	0.13
Sulfur, W%	5.10	5.09
Nickel, W%	1.96	1.63
Molybdenum, W%	8.68	7.64
Iron, W%	0.91	0.16
Titanium, W%	0.03	0.02
Calcium, W%	0.19	1.56
Sodium, W%	0.66	1.15
Compacted Bulk Density (g/cc)	0.89	0.97
Particle Density (g/cc)	1.42	1.59
Pore Volume (cc/g)	0.39	0.30
Loss on Ignition (W%)	20.2	23.75
Particle Density (g/cc) (Ignited Catalyst)	1.14	1.20
Pore volume (cc/g) (Ignited Catalyst)	0.64	0.58

DISPERSED CATALYST RUN (CC-4) PROCESS PERFORMANCE

FIGURE 1

DISPERSED CATALYST RUN (CC-4) PROCESS PERFORMANCE

FIGURE 2

DISPERSED CATALYST RUN (CC-4) DISTILLATE YIELD

FIGURE 3

DISPERSED CATALYST RUN (CC-4) DISTILLATE SELECTIVITY

FIGURE 4

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SECTION V

RUN 227-62(CC-5) - CTSL™ EVALUATION OF BLACK THUNDER MINE COAL AFTER THERMAL PRETREATMENT

INTRODUCTION

Run 227-62(CC-5) was a CTSL™ bench unit evaluation of Black Thunder Mine, Wyodak Anderson Seam (Wyoming), sub-bituminous coal obtained from the Thunder Basin Coal Co. This run examined the atmospheric pressure slurry pretreatment of the coal at 500-600°F, drying of the coal when mixed with slurry oil, and addition of H₂S during liquefaction operations to find the effect upon catalytic performance. The catalyst for this run was presulfided using TNPS as the presulfiding agent, in place of the DMDS that had been used in previous runs.

SUMMARY

The Black Thunder Mine Coal was tested in a 21-day run in the CTSL™ Bench Unit. This operation studied four conditions involving two coal pretreatment temperatures, feeding undried coal to the pretreater rather than conventionally partially pre-dried coal, and finally adding 2.7 W% (of dry coal) H₂S to the feed gas.

The pretreatment did not have a detrimental impact upon coal convertibility or liquid product distribution. While some carbon oxides were generated in the pretreatment operations, any consequent reductions in overall process water and light gas yields as well as hydrogen consumption were not apparent. Initiation of H₂S addition during the run reversed declines in hydrogenation and denitrogenation performance, as well as stabilizing a trend of increasing residual oil yield, that had occurred earlier in the run.

The pretreatment was done on a batch basis using eight-hour accumulations of coal feed and recycled solvents. The pretreatment was for one hour at the target temperature, although the entire cycle of heating-treatment-cooling took about six hours. The pretreatment produced some carbon oxides, 2-3% of coal, a very small amount of C₁-C₃ hydrocarbons, less than 0.1%, and water in excess of the nominal water content of the coal fed (D-2961 method), by 2-4%. There was very little difference in these results for the 500°F and 600°F pretreatment temperatures, excepting that the higher amounts of water were obtained at the higher pretreatment temperature.

The experimental coal conversions for the Run 227-62(CC-5) operations using pre-dried coal averaged 0.1% higher than the conversions for similar operations with coal that had not been thermally pretreated. For the operations with undried

coal to the pretreater, and finally with H₂S addition to the feed gas, the experimental conversions averaged 0.3% lower than the projected values. These results indicate that there was essentially no impact upon the coal reactivity of the 500 to 600°F pretreatment, or of slurry drying the coal, or of H₂S addition to the process gas.

The combined pretreatment/CTSL™ operation produced 3-4 W% carbon oxides compared to yields of 0.3-1.4 W% obtained in the reference operation of Run 227-55(CC-1). However, the concurrent impacts of the pretreatment upon product structure that might be expected were not apparent from the run data. That is, water yields that might be expected to be lower by 1-2 W%, because of greater elimination of oxygen in the carbon oxides, actually averaged 0.7 W% higher in these operations with coal pretreatment than in the reference operations. Also, light gas yields which might have been expected to be lowered by about 1 W%, because of reduced opportunity for hydrocarbon synthesis reactions of the carbon oxides, actually averaged 1 W% higher in the operations with coal pretreatment. The sum of the carbon, hydrogen, nitrogen and sulfur contents for the various products indicate the products from the operation with pretreated coal had a lower oxygen by about 0.7 W% than those where the coal had not been pretreated. Calculated water yields, using an oxygen balanced normalization procedure, indicate that the pretreatment lowered water yields by about 2 W%.

In this run, before the use of H₂S addition, hydrogen contents of the liquids were lower, while nitrogen contents were higher, than during the reference operations in earlier runs. Rather than reflecting the use of coal pretreatment or of TNPS presulfiding, the probable cause of these differences was the substantial quantities of a relatively low hydrogen content, high nitrogen content, distillate obtained from the Wilsonville Coal Liquefaction Facility which was used as make-up oil to compensate for the oils vaporized at the pretreatment temperatures.

SCOPE OF WORK

The coal used in Run 227-62(CC-5) was characteristic of commercial shipments from the Black Thunder Mine. The catalyst for both stages was Shell S-317 1/32" nickel molybdate on alumina extrudates, a commercially available catalyst. This catalyst shipment was the same as that used in Runs 227-55(CC-1) through 227-61(CC-4).

The operating conditions for the four conditions used during the run are summarized in *Table 1*. The first Condition was with a pretreatment temperature of 500°F, using a coal feed rate and stage temperatures that were the same as had been used in Run 227-5(CC-1). In Condition 2 of Run 227-62(CC-5) the pretreatment temperature was increased to 600°F. An operation was then attempted with steam addition during the pretreatment, but the resulting increase

in oil vaporization made the feed slurry difficult to pump, and this operation was abandoned. However, as a consequence increased solvent recycle, from 1.2 to 1.8 lbs/lb coal, was employed to improve the pumping of the feed slurry. For Condition 3 the coal feed was undried, with about 26 W% water, rather than the pre-dried material with 5 W% water content that was used in the other operations of the run. For Condition 4, H₂S addition at a rate of 2.7 W% of the coal rate was started.

Samples of the slurry circulating in the first stage were taken for each of the Conditions for use in evaluating the performance of the individual stages.

PROGRAM RESULTS AND ANALYSES - RUN 227-62(CC-5)

This section discusses the conversions, product yields, process performance and product quality for Run 227-62(CC-5). *Table 2* is the operating summary for the run, giving the principal operating conditions for each Period (day) and normalized product distributions for periods which were considered to represent equilibrated results (note in this table the ash values are on an SO₃-free basis, for reasons which are discussed below in the section concerning coal analyses).

Figures 1 to 12 graphically summarize the conversion parameters and the yields of the major product fractions against operating period, identifying the principal operating conditions for each of the points. These figures also show the yields for comparable operations of Run 227-55(CC-1), the earlier run with the Black Thunder Mine coal in which there was no pretreatment of the coal. The comparison of the results of the two runs is summarized in the section, below, Comparison With Results With Unpretreated Coal.

PRETREATER PERFORMANCE

The pretreatment was done on a batch basis using eight-hour accumulations of coal feed and recycled solvents along with makeup oil as needed. The slurry constituents were put into the pretreatment vessel at about 200°F, which was then increased in temperature to the target pretreatment temperature, at which temperature it was held for one-hour. The treated slurry was then cooled to normal feed temperature, about 300°F, and transferred to the normal feed slurry holder of the CTSL™ unit. The heating, pretreatment and cooling cycle took about six hours.

Table 3 summarizes the yields of carbon oxides, water, and light hydrocarbons from the Pretreater. With the Pretreater at 500°F, the carbon oxides yields from the Pretreater, ranged from 0.7 to 3.1 W% of dry coal, averaging 1.6 W%. With the Pretreater at 600°F, this yield range from 2.1 to 2.5 W%, averaging 2.3 W%. These yields are 0.5-1.0 W% higher than were obtained in microautoclave pretreatment tests at the same temperatures.

The light hydrocarbon generation in the pretreater was less than 0.1 W% of dry coal in all of the pretreater tests.

The water recovery from the pretreater was slightly higher than the nominal moisture content (ASTM D-3173 mod) of the dried coal, by 1.8-3.4 W% of dry coal for the 500°F pretreatment, and 3.7-4.0 W% for the 600°F pretreatment. In the test in which undried coal was fed to the pretreater the water recovery was slightly less than the nominal water content of the coal fed, by 0.1-0.6 W%, which is not considered a significant difference.

COAL CONVERSION

Figure 1 summarizes the coal conversions during Run 227-62(CC-5) and compares them with those during Run 227-55(CC-1) at a comparable reactor severity. For the Condition 1 (500°F Pretreater) and Condition 2 (600°F Pretreater) coal conversion ranged from 91.6 to 92.5%, averaging 91.9%, which is not significantly different from the average for the Run 227-55(CC-1) operations compared, 91.6%. However, for the Condition 3 (Undried Coal to the Pretreater) and Condition 4 (2.7% H₂S addition, coal conversions ranged from 87.3 to 89.1%, averaging 88.2%. The probable cause for this change was the increase in solvent recycle to 1.6 lbs/lb coal, from 1.1 lbs/lb coal. Calculations based on kinetic parameters developed from Run 227-55(CC-1) results projected that the increase in solvent recycle would cause conversion to decrease from 92.0 to 88.1%, which is in good agreement with the experimental impact. These results indicate that none of the four parameters changed in Run 227-62(CC-5), 500°F pretreatment, 600°F pretreatment, undried coal to pretreatment, and H₂S addition to the process gas, had a substantial impact upon coal conversion.

975°F+ CONVERSION

Figure 2 is a summary of the 975°F+ Conversions (100 minus unconverted coal minus residual oil yield) through Run 227-62(CC-5), plotted against operating period (Days) with identification of the principal changes in operating conditions. This figure includes values for operations of Run 227-55(CC-1) at the same severity as used in the later run.

975°F+ conversion ranged from 85.3% to 93.1% of maf coal. The highest level of 975°F+ conversion was during the Condition 1 and Condition 2 operations of Run 227-62(CC-5), an average of 90.6%, slightly above that of the Run 227-55(CC-1) operation, 88.5%. This difference is probably due to the higher catalyst age of the Run 227-55(CC-1) operation used for comparison, since the two runs appear to have a common downward trend of this parameter with increasing catalyst age. The lowest level of 975°F+ conversion was during the Condition 3 and Condition 4 operations of Run 227-62(CC-5), an average of 86.1%. The greater part of the difference from the earlier 975°F+ conversion was the decrease in coal conversion associated with the increased solvent/coal ratio for the later operations, although there was some impact of lowered catalyst activity in those operations. Actually, the 975°F+ conversion during the Condition 4 operations (with 2.7 W% H₂S addition) were possibly slightly higher than the value during the Condition 3 operation. This factor indicates some stabilization of catalytic performance because of the H₂S addition, which is discussed more fully, below, with regard to residual oil yield and hydrogen and nitrogen contents of the products.

PRODUCT DISTRIBUTION

C₁-C₃ Gas Yields

Figure 3 summarizes the normalized yield of C₁-C₃ hydrocarbon gases through Run 227-62(CC-5). The gas yields ranged from 9.6 to 11.7 W% of dry coal, averaging 10.4%, which is higher than the average, 8.6%, of the Run 227-55(CC-1) yields also summarized in Figure 3. Such a difference is nominally highly significant, over 99% statistical confidence level, although unexpected. Actually, it was expected that with pretreatment, the carbon eliminated as CO₂ and CO would result in reduced hydrocarbon synthesis conversion to methane (later bench unit experiments with CO₂ addition clearly showed that CO₂ can be converted to methane in the liquefaction environment), by about 1 W% of dry coal.

The distribution of the light gas products also was different for the two runs, as summarized below giving the collected yields of the individual gaseous hydrocarbon fractions:

Run	227-62(CC-5)				227-55(CC-1)
Condition	1	2	3	4	2 & 3
Pretreatment, °F	500	600	500	500	NO
Coal Drying	Yes	Yes	No	Yes	Yes
H ₂ S, W%	0.0	0.0	0.0	2.7	0.0
Yields, W% Dry Coal					
C ₁	3.7	3.0	3.2	3.0	3.2
C ₂	3.0	2.6	2.5	2.2	2.4
C ₃	3.9	3.8	3.8	4.8	2.7
C ₄	2.1	1.8	1.8	1.7	1.5

The yields of C₁ and C₂ hydrocarbons for the two runs were essentially the same within the precision of the data. However, the yields of C₃ hydrocarbons were appreciably higher for Run 227-62(CC-5), as well as the C₄ hydrocarbons yields.

A possible factor contributing to the difference in light gas yields between the two runs was the use of a considerable amount of make-up oil (from Wilsonville coal liquefaction operations) during Run 227-62(CC-5), while none was used in Run 227-55(CC-1). Also, because of vaporization of oils in the pretreater there was a higher proportion of 650-975°F (HGO) components and lower proportion of 400-650°F (LGO) components in the reactor slurry (see below, in the discussion of the 650-975°F (HGO) yields. Microautoclave tests on these gas oil fractions indicate higher gas yields for the HGO components than for the LGO

components, by a factor of about 1.4. However, the 10% change in gas oil composition would have been expected to cause an increase in C_1 - C_3 gas yield of only a 0.2-0.4 W% of dry coal for Run 227-62(CC-5).

C_4 -390°F Naphtha Yields

Figure 4 summarizes the normalized yield of C_4 -390°F Naphtha through the run, which ranged from 19.8 to 29.3 W% of dry coal. This range is generally higher than that of Run 227-55(CC-1), 18.9-20.7 W%. The greater part of this discrepancy is in Condition 1 naphtha yields of Run 227-62(CC-5). The naphtha yields during Run 227-62(CC-5) during operations with 500°F pretreater were generally higher than with 600°F pretreater, averaging 23.2 W% compared to 19.8 W%, but because of the scatter of the data this difference is marginally significant, 90-95% confidence level.

The use of a considerable amount of make-up oil during Run 227-62(CC-5) possibly had some impact upon the naphtha yield during the run.

390-650°F Light Distillate Yield

Figure 5 summarizes the yield of 390-650°F light distillate through Run 227-62(CC-5), with a comparison with the results of Run 227-55(CC-1). The 390-650°F light distillate yield in Run 227-62(CC-5) ranged from 27.0 to 42.5 W% of dry coal. The lower level of this yield was maintained during the Condition 2, 3, and 4 operations, averaging 28.3 W%, which was the level of this yield in Run 227-55(CC-1). The higher level of this yield in Run 227-62(CC-5) was in the Condition 1 operation, an average of 39.8 W%.

This anomalous pattern of 390-650°F distillate yield during Run 227-62(CC-5), which is also reflected in C_1 - C_3 and C_4 -390 Naphtha yields, does not appear to be associated with any of the parameters that were varied during the run which had common values during Condition 1 and in some part of the later Conditions, viz. pretreater temperature, oil/coal ratio, drying, make-up oil type (which was changed from HRI L-742 to HRI 5648 after Condition 2), no H_2S in feed, atmospheric still temperature.

650-975°F Heavy Distillate Yield

Figure 6 summarizes the yield of 650-975°F heavy distillate through Run 227-62(CC-5), with a comparison with the results of Run 227-55(CC-1). The 650-975°F heavy distillate yield in Run 227-62(CC-5) ranged from -13.8 to +2.1 W% of dry coal, although only the first normalized result, for Period 4 operations, was out of the range of -3.8 to +2.1 W%, where the average was -0.9 W%. These yields considerably lower than those of Run 227-55(CC-1), where the average yield was +13.8 W%.

The lower yields of this fraction in Run 227-62(CC-5) can be ascribed to higher proportion in this run of this fraction in the recycle oils going to the reactor and in reactor environment resulting from the higher atmospheric still temperature and the vaporization of light oils in the pretreater, as indicated in the following tabulation comparing these compositions for the two runs:

Run	227-55(CC-1)	227-62(CC-5)
<hr/>		
Recycle Oil, W%		
IBP-650, °F	31.0	9.2
650-975, °F	53.6	76.9
975°F+ Residuum	15.4	13.9
Reac. Product Slurry, W%		
IBP-650, °F	27.7	18.1
650-975, °F	47.3	56.7
975°F+ Residuum	12.7	12.5
Solids	12.1	12.5

These results indicate the feasibility of complete elimination of this product fraction by appropriate recycle oil composition and reaction severity.

This interpretation assumes that the conversion activity of the Wilsonville oils used as makeup oil in Run 227-62(CC-5) is similar to that of CTSL™ oils of the same boiling range.

Because of these considerations, there is no indication that coal pretreatment, etc. in Run 226-62(CC-5) had any substantial impact upon the formation of this product fraction.

975°F+ Residual Oil Yield

Figure 7 summarizes the yield of 975°F+ Residual Oil through Run 227-62(CC-5), with a comparison with the results of Run 227-55(CC-1). The 975°F+ Residual Oil yield in Run 227-62(CC-5) ranged from -0.5 to +2.7 W% of dry coal, averaging 1.5 W%. The changes in operating conditions and the problems with solvent balance necessitating the use of makeup oil obscure a clear definition of the trend in yields during the run; although it is notable that this yield in the final operations of the run, where H₂S addition was used, at the highest catalyst age, were no higher than the level of yield that had been reached earlier in the run. This yield in Run 227-55(CC-1) averaged 2.9 W%, nominally higher than in Run 227-62(CC-5) (95% statistical confidence level) although the difference is probably due to the complete elimination of filtered liquid (containing residual oil)

from the recycle solvent pool in the later run.

To provide a further insight into the difference of residual oil kinetics for the two runs, *Figure 8* is a plot of residual oil concentration in the reactor product slurry against time on stream (or catalyst age) for the runs. Through 390 hours of the runs (Condition 3 of Run 227-62(CC-5)) the trends for the two runs correspond closely, indicating that various pretreatment temperatures and the use of undried coal had virtually no impact on the convertibility of the residual oil deriving from the primary liquefaction of the coals.

However, in the final operation of Run 227-62(CC-5), where H₂S addition was used, the upward trend with time, evident in the other operations, did not continue, and the residual oil concentration remained at a constant level. Apparently, sulfiding of the catalyst caused by the H₂S balanced the further deactivation caused by carbon and metals accumulation. This pattern of improved catalyst performance with H₂S addition corresponds to the results of Run 227-61(CC-4) in which H₂S addition resulted in improved performance relative to that of Run 227-55(CC-1). Also, in Run 227-62(CC-5) there was a favorable impact of H₂S addition upon hydrogenation and denitrogenation performance (see below).

Carbon Oxides and Water Yields

Figure 9 summarizes the CO plus CO₂ yields for Run 227-62(CC-5), and *Figure 10* summarizes the net water yields for the run (the total from the pretreater and the hydrogenation reactors in each case), with a comparison with Run 227-55(CC-1) yields.

The carbon oxides yields for Run 227-62(CC-5) ranged from 2.8 to 4.9 W% of dry coal, averaging 3.6 W%. This compares with an average of 0.5 W% for the Run 227-55(CC-1). The carbon oxides yields for Run 227-62(CC-5) Condition 2 operation with 600°F pretreatment was slightly higher than this average, at 4.1%, not itself a significant difference, but consistent with a similar pattern in microautoclave pretreatment tests.

The net total water yield for Run 227-62(CC-5) ranged from 18.2 to 20.7 W% of dry coal, averaging 19.5 W%. This compares with an average of 18.4 W% for Run 227-55(CC-1). While this difference is only marginally significant (89% statistical confidence level), directionally it is unexpected in that the increased carbon oxides yield of Run 226-62(CC-5) should have resulted in a decrease in water yield corresponding to the oxygen content of the incremental carbon oxides production, by about 2.4 W% of dry coal.

Figure 11, which compares for the two runs the oxygen elimination in the water and carbon oxides formation, demonstrates this inconsistency, where such oxygen elimination averaged 19.7 W% of dry coal for Run 227-62(CC-5)

operation, and only 16.7 W% for Run 227-55(CC-1) operations. This difference of 3.0 W% indicates that the liquid and solids products from Run 227-62(CC-5) should have lower oxygen contents by this amount. No direct oxygen analyses are available for any of the products. However, the relative "oxygen-by-difference" values using the total of the carbon, hydrogen, sulfur, and nitrogen analyses do not indicate such a large difference. The following tabulation compares the average values of this parameter for the two runs:

Product	Run 227-55(CC-1)	Run 227-62(CC-5)
Separator Overhead	99.79	100.78
Atmospheric Overhead	99.76	100.47
Filtered Liquid	99.45	100.09
SO ₃ -Free-Ash Free Solids	83.79	84.50

Evidently there is an anomaly in the analyses of the Run 227-62(CC-5) products, possibly associated with putting a new analytical instrument into service. Even so, if these differences are taken at face value, with the usual product distribution there was 0.8 W% (of dry coal) lower oxygen content in the liquid and solids products of Run 226-62(CC-5). Another consideration is that the apparent oxygen in the unreacted coal of Run 227-62(CC-5) corresponded to 1.1 W% of dry coal (the yield of unreacted coal, 7.2%, times the nominal oxygen content, 100 - 84.5 W%). This value along with the nominal oxygen content of coal feed, 20.2 W% (see *Table 10*), indicates that the oxygen elimination to carbon oxides and water should have been less than 19.1 W% of dry coal, slightly lower than the average value of 19.7 W% noted above.

The difference in calculated net water yields for the two runs is probably due to two possible experimental anomalies: 1) possible unaccounted loss of water in feed slurry preparation, especially in Run 227-55(CC-1) where the slurry preparation system was open to the atmosphere, and 2) errors in the amount of water injection into the high pressure system downstream of the reactors to prevent solid ammonium sulfide deposition. This factor should be considered in comparing the other yields for the two runs.

C₄-975°F Distillate Yields

Figure 12 summarizes the yield of C₄-975°F Distillate Oil through Run 227-62(CC-5), with a comparison with the results of Run 227-55(CC-1). The C₄-975°F Distillate Oil yield in Run 227-62(CC-5) ranged from 54.3 to 58.0 W% of dry coal, averaging 56.7 W%. The lowest C₄-975°F distillate yields were in the Condition 3 and 4 operations of the run, associated with 3% lower coal conversions caused by the higher solvent to coal ratio of those operations. These yields are 5-7 W% lower than the average for the operations of Run 227-55(CC-1). This difference reflects the higher yields for

Run 227-62(CC-5) of C₁-C₃ gases, by 1.8 W%, of carbon oxides, by 3.1 W%, of water, by 1.1 W%, and of unconverted coal (for the Condition 3 and 4 operations), by 3 W%.

The anomalies concerning the carbon oxides and water yields have been discussed above, with some uncertainty in the indicated increase by coal pretreatment of the total oxygen elimination as these products. Adjusting water yields to equalized oxygen eliminations would still leave a deficiency in distillate yield of about 3 W% since the carbon eliminated as carbon oxides did not have a corresponding decrease in carbon eliminated as light gases, rather there was an actual increase in carbon eliminated as light gases.

Hydrogen Consumption

Figure 13 summarizes the hydrogen consumptions through Run 227-62(CC-5), with a comparison with the results of Run 227-55(CC-1). The hydrogen consumptions during Run 227-62(CC-5) ranged from 7.2 to 8.7 W% of dry coal, with a persistent downward trend through the run. These hydrogen consumptions are very nearly the same as those of Run 227-55(CC-10) at the same stage of operations.

PRODUCT QUALITY

The elemental analyses of the net product fractions were made only on the heavy gas oil and residual oil constituents of the filtered liquid produced in excess of solvent recycle requirements. These analyses for Run 227-62(CC-5) product fractions are summarized in Table 4. In addition, Table 5 summarizes the analyses that were obtained for the lower boiling product streams, namely the Separator Overhead Product of about 130°F to 700°F boiling range, and the Atmospheric Still Overhead product of about 250°F to 675°F boiling range.

Hydrogen Contents

The hydrogen contents of the lower boiling products from Run 226-62(CC-5) were slightly higher than those of the corresponding products from Run 227-55(CC-1), which are compared in the following tabulation:

Run	Product	VABP, °F	H ₂ , W%
227-55(CC-1)	Sep. Ovhd.	422	12.42
227-62(CC-5)	Sep. Ovhd.	431	12.76
227-55(CC-1)	Atm. Ovhd.	363	13.00
227-62(CC-5)	Atm. Ovhd.	527	11.80
227-55(CC-1)	PFL IBP-650	572	11.20
227-62(CC-5)	PFL IBP-650	613	10.94

When the differences in Volume Average Boiling Points (VABP) are considered, the Run 227-62(CC-5) hydrogen contents are 0.3 W% higher than those of Run 227-55(CC-1), 99.9% statistical confidence level. In Run 227-62(CC-5) the hydrogen contents of the low boiling products did not change appreciably in the course of the run, nor did the initiation of H₂S addition in Condition 4 of the run change these hydrogen contents. These patterns are different from those apparent for the heavier boiling fractions, which are discussed below.

The hydrogen contents of gas oil and residual oil cuts in the recycle (product) PFL for Run 227-62(CC-5) are plotted in *Figure 14* against time on stream, and compared to those for Run 227-55(CC-1). Three factors are evident here:

A) For early operations of the two runs, the hydrogen contents are lower in Run 227-62(CC-5) than in Run 227-55(CC-1), by 0.6-1.5 W%.

B) In Run 227-62(CC-5), the hydrogen contents remained at the same general level throughout the run, while in Run 227-55(CC-1) hydrogen contents declined persistently through the run, by 0.8-1.9 W% in the course of the run, to levels that were slightly below those of the later run.

C) The addition of H₂S for the final operation of Run 227-62(CC-5) resulted in the hydrogen contents that were higher than the contents earlier in that run and higher than those at a comparable stage of Run 227-55(CC-1). The following tabulation compares the hydrogen contents for the two phases of Run 227-62(CC-5):

	120-360 Hours Average	490 Hours
H ₂ S Addition, W%	0.0	2.9
Hydrogen, W%		
IBP-650°F Fraction	10.94	11.27
850-850°F Fraction	10.02	10.07
850-975°F Fraction	8.54	8.84
975°F+ Fraction	6.81	6.96

There was a 97.9% statistical confidence level in the apparent average impact, +0.21 W%, of the addition of H₂S.

Nitrogen Contents

In Run 227-62(CC-5), the nitrogen contents of the light product streams increased by a factor of two between the fifth and fifteenth days of operations, but were then lower, by a factor of 0.7-0.8, in the 20th day of operations when H₂S addition had been started.

The nitrogen contents of gas oil and residual oil cuts in the recycle (product) PFL for Run 227-62(CC-5) are plotted in *Figure 15* against time on stream, and compared to those for Run 227-55(CC-1). Three factors are evident here:

A) For early operations of the two runs, the nitrogen contents were higher in Run 227-62(CC-5) than in Run 227-55(CC-1), by 0.1-0.2 W%.

B) For operations without H₂S addition, as the runs continued nitrogen contents increased at about the same rate in the two runs.

C) The addition of H₂S for the final operation of Run 227-62(CC-5) resulted in nitrogen contents that were lower than the contents that had been reached earlier in the run, and lower than those at a comparable stage of Run 227-55(CC-1). This improvement in nitrogen content, 0.07-0.15 W%, was about as great as the deterioration between 120 and 360 hours earlier in the run.

Discussion

The principal cause of the relatively low hydrogen contents and high nitrogen contents in the Run 227-62(CC-5) gas oil fractions is probably the use, in place of some of the recycled solvent, of L-742 distillate makeup oil of lower hydrogen content and higher nitrogen content than contained in CTSLTM derived recycle oils. This difference is discussed more fully below in the section Start-up and Make-up Oils. In summary, the hydrogen content of the L-742 oil was about 0.5 W% lower than that of the equivalent boiling range materials recycled in Run 227-55(CC-1), while its nitrogen content was 2-4 times that of the recycled oils in the earlier run. This difference required substantially greater hydrogenation of these gas oil fractions during Run 227-62(CC-5), particularly in the first stage, where the net hydrogen input to these fractions was increased by a factor of two, see below in the discussion of the first stage samples.

Other factors that might have contributed to the relatively poor hydrogenation and denitrogenation performance during Run 227-62(CC-5) the change in presulfiding agent to TNPS in place of DMDS and the use of pretreated coal. However, Microautoclave evaluations for CTSLTM residual oil conversion activity showed at least equal, and possibly superior performance of the TNPS presulfided catalyst, but no data concerning hydrogenation/denitrogenation performance were obtained. There is no strictly comparable bench unit operation with untreated

coal and TNPS presulfided catalyst. However, in subsequent runs the TNPS was used as a presulfiding agent, but with the difference that H₂S was fed continuously throughout the runs. These later runs showed hydrogenation/denitrogenation performance superior to that of Run 227-62(CC-5), even for the earliest operations of those runs where the nominal stabilizing impact upon catalyst performance of the H₂S addition would be the lowest, as follows (For operations with Black Thunder Mine Coal):

Run 227-69(CC-11) - (The principal difference from 227-62(CC-5) was a 50% higher space velocity). The PFL cuts for Period 5 of that run averaged less than one-half the nitrogen content, and 0.7 W% higher hydrogen content than at the comparable stage of Run 227-62(CC-5).

Run 227-70(CC-12) - (The principal difference from 227-62(CC-5) was the use of Rejuvenated Catalyst). The PFL cuts for Period 5 of that run averaged about one-half the nitrogen content, and 0.3 W% higher hydrogen content than at the comparable stage of Run 227-62(CC-5).

These results indicate TNPS presulfided catalysts can give performance equivalent to DMDS presulfided catalyst and that the poor hydrogenation/denitrogenation performance during Run 227-62(CC-5) was probably the result of other differences associated with the coal pretreatment run.

The impact of coal pretreatment upon hydrogenation/denitrogenation is unclear in view of the other parameters that were changed. However, since there appeared to be little impact upon convertibility and product selectivity, it is probable that there is also little impact of coal pretreatment upon these factors.

COMPARISON WITH RESULTS WITH UNPRETREATED COAL

The operating results for Run 227-62(CC-5), with pretreated coal, and Run 227-55(CC-1), where there was no pretreatment, have been compared in the figures detailing the yields of the specified product fractions. *Table 6* is a tabular comparison of the results for the two runs. The following is a summary of the conclusions drawn above about the impact of coal pretreatment and the other changes for Run 227-62(CC-5).

Carbon Oxides and Water Yields - The 500°F pretreatment generated about 1.5 W% (of dry coal) carbon oxides, and the 600°F pretreatment generated about 2.5 W%. Water evolution in the pretreater with partially dried coal was 2.5-4.0 W% more than the nominal ASTM water analysis of the coal. The overall process carbon oxides yield with coal pretreatment was about 3 W% higher than without pretreatment. Overall net process water yield with coal pretreatment averaged 1.0 W% higher with pretreatment than without pretreatment. The apparent oxygen elimination as carbon oxides and water was 3.0 W% of dry coal higher with pretreatment than without pretreatment, although the available

elemental analyses of the other products do not correspond to such a change in oxygen retention in those products.

Coal Conversions - Process coal conversions for operations with either 500°F or 600°F pretreatment were essentially the same as those without coal pretreatment.

C₁-C₃ Light Gas Yields - There was virtually no light hydrocarbon generation in the pretreatment step. However, process light gas yields in Run 227-62(CC-5) averaged almost 2 W% higher than in operations without coal pretreatment.

975°F⁺ Residual Oil Yield - There was no apparent difference in residual oil kinetics for the two types of coal pretreatment, in that the same concentration of residual oil was required in the two runs to obtain a minimal yield of this component. When H₂S was added to the process gases in Run 227-62(CC-5) the progressive increase in this concentration with time, characteristic of usual CTSL™ operations, did not continue indicating stabilization of catalyst performance because of the H₂S addition.

C₄-975°F Distillate Yield - The total distillate yields for Run 227-62(CC-5) averaged about 5 W% lower than in Run 227-55(CC-1), because of increased light gas, water, and carbon oxides yields. Even if the relative yields were adjusted to a common oxygen elimination, the deficiency in total distillate yield would be about 3 W%, because of increased carbon elimination as carbon oxides and light hydrocarbon gases.

Product Quality - In the operations with coal pretreatment the hydrogen content of the low boiling products, to about 650°F boiling point, were about 0.3 W% higher than in the operations with no coal pretreatment. However, the higher boiling liquids were initially of 1-1.5 W% lower hydrogen content than the products from the operation without coal pretreatment, although as the runs progressed these contents in the Run 227-55(CC-1), without coal pretreatment, declined to the levels obtained in the later run.

When H₂S addition was initiated in Run 227-62(CC-5) hydrogen contents of the liquids increased by about 0.2 W%. The pattern of nitrogen contents was similar to that of the hydrogen contents.

FIRST STAGE SLURRY ANALYSES AND INTERPRETATION

Samples of the first stage slurry were obtained during each of the Conditions in Run 227-62(CC-5). The analyses of the samples that were obtained were used in conjunction with the second stage net product and recycle solvent analyses to characterize the performance of the individual stages. The analyses were conventional D-1160 distillation characterization of the filterable portion, and solvent fractionation of the 975°F⁺ residuum as 975°F⁺ Oil (cyclohexane soluble),

975°F+ Asphaltenes (toluene soluble, cyclohexane insoluble), and 975°F+ Pre-asphaltenes (toluene insoluble). The THF insoluble solids were characterized as ASTM ash and unconverted coal (the balance of the quinoline insoluble portion). Elemental analyses were obtained on the THF washed solids, the total filtered portion, and product fractions obtained by D-1160 distillation.

Table 7 summarizes the distillation characterization of the first and second stage slurry phase liquid and the elemental analyses that were obtained on these liquids, some product fractions, and on the oil-free solids obtained.

Table 8 interprets the distillations and solids-content analyses in terms of first and second stage product fraction flows relative to the amount of coal feed to the operating system.

Table 9 interprets the flows of *Table 8* individual stage performances in terms of apparent formation or reaction of the product fractions as a percentage of the coal fed to the operation. It should be noted that the quantities given in *Tables 8 and 9* are only for the slurry phase, and that any vapor phase content, particularly significant for the lighter distillate fractions, is not included.

An estimated vapor phase flow for the first stage is included in *Table 8*, the value used is based on the experimental vapor flow from the second stage, by assuming that the vapor generation in each stage was proportional to the amount of coal reacted in that stage. This current procedure attempts to deal with the considerable variations in the first stage severity in Run 227-55(CC-1). The alternative of basing the first stage slurry phase flow (and apparent vapor flow) on the apparent ash content of the first stage sample and an ash balance, gave very erratic results.

Coal Conversion

The coal conversion after the first stage for Condition 1 operations was 79.0 W% of maf coal, which is considerably higher than obtained in Run 227-55(CC-1) where the first stage coal conversion was 66-69 W% at comparable conditions. Presumably, this difference indicates some coal dissolution or solvent/coal interaction in the 500°F pretreatment step. However, in Condition 2, with the pretreater at 600°F, first stage conversion was lower at 71.5%. In the Condition 3 and 4 operations, first stage coal conversions were 66.8 and 63.7 W%, reflecting the dilution of solids caused by the higher ratio of recycle solvent to coal for these operations and little impact of the feed of undried coal to the pretreater in Condition 3 or of the inclusion of H₂S in the feed gas in Condition 4.

Residual Oil Formation

Net residual oil formation in the first stage amounted to 5.3 to 10.1 W% of dry coal for the operations of Run 227-62(CC-5). This range is slightly below that experienced in Run 227-55(CC-1), 11-12 W% of dry coal. This difference reflects generally lower first stage residual oil concentrations in Run 227-62(CC-5) than in Run 227-55(CC-1), as follows, comparing the residual oil concentrations in the liquid phase for operations over a common range of catalyst ages:

Run	First Stage		Second Stage	
	Range	Average	Range	Average
227-55(CC-1)	21.2-28.1	24.4	14.5-19.6	16.9
227-62(CC-5)	16.7-17.3	17.0	15.3-16.8	16.0

These analyses indicate that the 500-600°F pretreatment, or TNPS presulfiding, increases the degree of secondary conversion of residuum to light products in the first stage.

Analytical and interpretative uncertainties qualify any conclusions with respect to the impact upon residual oil formation of the various operating parameters changed during Run 227-62(CC-5). However, the change in the stage-to-stage residual oil concentration pattern between Condition 3 and Condition 4, an increase in first stage concentration and a level second stage concentration, suggests that the addition of H₂S in Condition 4 improved second stage performance in this regard to a greater degree than first stage performance.

Hydrogenation and Heteroatom Removal

Hydrogen contents of the gas oil components were generally slightly higher in the first stage components than in the second stage components throughout Run 227-62(CC-5), by an average of 0.3 W%. This average change is virtually the same as obtained during Run 227-55(CC-1) with the same first stage/second stage temperature configuration. Actually, this pattern may signify slightly more gas oil hydrogenation in the first stage during Run 227-62(CC-5), since the hydrogen content of the actual gas oil introduction to that stage was slightly lower than that of the gas oils being recycled from the second stage because of the relatively low hydrogen content of the L-721 being used as makeup oil feed to that stage. The following tabulation summarizes this pattern of hydrogen contents:

Period	Fraction	Recycle	Make-up	First Feed	First Product	Second Product
5	INP-650°F	11.03	10.40	10.59	11.65	11.03
	650-850°F	10.20	9.55	9.74	10.47	10.20
	850-975°F	8.51	8.35	8.40	9.37	8.51
9	IBP-650°F	10.97	10.40	10.56	10.86	11.03
	650-850°F	10.09	9.55	9.74	10.05	10.09
	850-975°F	8.34	8.35	8.35	8.95	8.34

The average of the above increases in hydrogen contents in the first stage was 0.66 W%, compared to an average decrease of 0.36 W% in the second stage.

After Period 10 of Run 227-62(CC-5) the makeup oil was changed to HRI 5648 which had a hydrogen content more nearly that of the recycled components.

Nitrogen Contents

For the Condition 1, 2, and 3 operations of Run 227-62(CC-5) the nitrogen content of the second stage product fractions averaged 0.05 W% less than the nitrogen contents in first stage product fractions. For Condition 4, with H₂S added to feed streams, nitrogen contents in both stages was generally lower than had been obtained in Condition 3, but the change was greater in the first stage products, an average decrease of 0.18 W% compared to 0.08 W% for the second stage liquids, so that nitrogen contents after the second stage were then higher by an average of 0.07 W%.

This pattern of relative nitrogen contents of the first and second stage liquids is similar to that noted for Run 227-55(CC-1) where the early results showed lower nitrogen contents in the second stage liquids, and the later results showed higher nitrogen contents in the second stage liquids. This was interpreted as indicating a greater degree of deactivation of the second stage catalyst for denitrogenation. While H₂S addition clearly improved the denitrogenation performance in Run 227-62(CC-5), apparently it did not reverse the pattern of more rapid deactivation of the second stage catalyst.

Sulfur contents of the product fractions were generally low in the range of 0.003 to 0.036 W%, for the most part lower in the second stage liquids. Because of the scatter of the data any difference in sulfur contents of the various product fraction is uncertain. However, there appears to be a significant difference in the first and second stage sulfur contents, with the first stage liquids averaging 0.017 W% sulfur, and the second stage liquids averaging 0.007 W% sulfur.

DETAILS OF OPERATIONS

This report summarizes the operations of Run 227-62(CC-5) in the CTSL™ bench unit using Black Thunder Mine Wyoming Coal. This run examined the atmospheric pressure slurry pretreatment of the coal at 500-600°F, drying of the coal when mixed with slurry oil. Also, H₂S was added during final liquefaction operations to study the effect upon catalytic performance. The catalyst used in this run was Shell S-317 1/32" extrudate nickel molybdate. Shell S-317 catalyst had also been used in the earlier runs with the Black Thunder Mine coal.

Run 227-62(CC-5) completed 512 hours of operation with Black Thunder Mine (Wyoming) coal.

The only operating problem during the run was after stripping steam was added to the coal pretreater during Period 10, which caused increased stripping of light oils, increased viscosity of the feed slurry that was circulating, and erratic feed slurry delivery to the high pressure system. This difficulty was ameliorated by increasing the ratio of oil/coal to 1.6 lbs/lb (from 1.1 lbs/lb) after Period 11. However, no problems were apparent in the high pressure system throughout the run. The final day of the run, Period 21, was with no recycle of solvent to the feed slurry system, the inventory of which was allowed to run down to maintain normal flows to the higher pressure system. During this period, the accumulation of net product slurry was saved for other experimental studies.

COAL PRETREATMENT SYSTEM

The pretreatment was done on a batch basis using eight-hour accumulations of coal feed and recycled solvents. The slurry constituents were put into the pretreatment vessel at about 200°F, which was then increased in temperature to the target pretreatment temperature, at which temperature it was held for one-hour. The treated slurry was then cooled to normal feed temperature, about 300°F, and transferred to the normal feed slurry holder of the CTSL™ unit. The heating, pretreatment and cooling cycle took about six hours. *Figure 16* is a schematic flow diagram for the pretreatment apparatus.

OPERATIONS

Pre-Operational Procedures - Operations were started using HRI L-742 catalytic distillate prepared from material obtained from the Wilsonville coal liquefaction facility. This feed was used with TNPS (di-tertiary nonyl polysulfide) added in the catalyst presulfiding operation summarized below in the section concerning the fresh catalyst. At the time of coal introduction the slurrying oil was recycle material recovered during the heatup/presulfiding operations.

Operating Summary - A summary of the four sets of conditions used during the run is given in *Table 1*. The final eight hours at each condition (an "A" period)

was used to obtain a sample of slurry from the internal recycle line of the first stage as characteristic of material circulating through the first stage reactor. A considerable amount of makeup oils (distillates obtained from the Wilsonville Coal Liquefaction facility) were used throughout the run. This was required because the atmospheric still removing the light ends from the recycle solvent was set at a relatively high temperature, 600°F, to minimize vaporization in the coal pre-treater. Consequently, atmospheric overhead withdrawals were relatively high, at 13-22 W% dry coal (about 10-15% more than in usual operations). Also, there was some hydrocarbon vaporization in the pretreater (up to 18 W% of dry coal at the higher pretreater temperature). The possible way to deal with the solvent balance in this type of operation would be to operate the pretreater at a moderate pressure.

Condition 1 (Periods 1A-6A) - The operating conditions were similar to those used in Condition 2 and 5 of Run 227-55(CC-1), excepting for the pretreatment of the coal for a one-hour hold at 500°F. The first and second stage temperatures were 750 and 825°F, respectively. The coal feed rate was 44 lbs/hr/ft³ catalyst (per stage). The solvent recycle was 1.1 lbs/lb coal consisting of pressure filter liquid (PFL) obtained by filtration of reactor product slurry which had been topped of light distillate in the atmospheric still which was held at 500°F. This recycle pattern differed slightly from that of Run 227-55(CC-1), where the recycles were 0.7 lbs/lb of PFL and 0.4 lbs/lb of TSB (unfiltered reactor product slurry, which consequently recycled some unreacted solids). The unit and pretreatment ran very well through this interval of the run.

Condition 2 (Periods 6B-10B) - The pretreatment temperature was increased to 600°F, with no other changes in conditions. The unit and pretreatment continued to run very well.

After the completion of the Condition 2 operations a modification of the pretreatment was attempted, in which steam, an amount equivalent to 38 W% of the coal being treated, was introduced during the hold at the pretreatment temperature, to subject the coal to the steam atmospheric. Circulation of the feed slurry to the high pressure system became very erratic, when the stripping of oils in the pretreater increased two to three fold. Steam flow was stopped after about 12 hours.

Condition 3 (Periods 11B-16A) - The feed coal was changed to undried material containing 26 W% moisture (compared to 5 W% for the dried coal). The pretreater temperature was returned to 500°F. The difficulties with feed slurry circulation persisted, so the oil/coal ratio of the feed slurry was increased to 1.6 lbs/lb. The high pressure system operated smoothly throughout this operation.

Condition 4 (Periods 16B-21) - Hydrogen sulfide addition was started at a rate corresponding to 2.7 W% of dry coal fed. Also, the dried feed coal was used again. The unit ran smoothly until the end of scheduled operations at the end of Period 21.

During inspection after the run, the catalyst from both stages flowed freely from the reactors. The catalysts were found in the normal settled positions in the reactors, at levels corresponding to 91% and 93% of original catalyst volumes, in the first and second stages, respectively. Down-stream lines and vessels were free of deposits. However, there were substantial accumulations of carbonaceous deposits at the inlet of both reactors, although neither stage had excess pressure drop through all of the coal operations of the run.

COAL FEED

The coal feed for Run 227-62(CC-5) was obtained from the Black Thunder Mine (Wright, Wyoming) of the Thunder Basin Coal Company. The material used in the run, designated HRI 5630, was part of a three ton shipment received in drums about 11 months before the start of the run.

The HRI 5630 shipment was crushed to -1/2 inch, and ground to pass a 70 mesh screen in a micropulverizer. Before the start of Run 227-62(CC-5) the ground coal was dried in a nitrogen swept tray oven at 200°F to an average moisture content of 6.8 W% (from about 27 W%), requiring 8-10 hours. The dried coal was stored in drums under nitrogen blanket until fed to the bench unit. The range of moisture contents for the dried coal actually fed to the CTSL™ pretreatment operation was 4.0 to 8.3 W%. For Condition 3 operations undried coal was fed directly to the pretreater.

Table 10 summarizes the analyses obtained on the dried, ground HRI 5630 coal feed to Run 227-62(CC-2) as well as the feed to Run 227-55(CC-1), and a smaller sample of the Black Thunder Mine coal, HRI 5613, which had been evaluated in the microautoclave. A factor to be noted in this table is the expression of the ash content on an SO₃-free basis. The feed coal ash and the ash obtained from the CTSL™ product solids differ markedly in sulfur contents (6.35 W% sulfur and 2.1-2.9 W%, respectively) so that they are not truly equivalent materials in considering the ash (mineral matter) balance of the CTSL™ operations. The apparent reason for the anomaly is that in the combustion during ash analysis the sulfur oxides formed from organic sulfur and pyritic/pyrrhotite sulfur react with alkali metal oxides and are retained in the ash, apparently over 90% of the available sulfur in both types of samples. Since there is less sulfur available in the product solids because of desulfurization/conversion reactions, less sulfur is retained in those products. It is considered that a reasonable estimate of "true" mineral matter is on this SO₃-free ash basis, and this is the best for comparing equivalent materials when calculating yields from the ash (mineral water) balance.

START-UP AND MAKE-UP OILS

The start-up oil for Run 227-62(CC-5) was a heavy distillate, HRI L-742, produced at the Wilsonville Coal Liquefaction facility. It was used to provide the initial inventory of the system, and as the carrier oil during the presulfiding operations prior to the start of the coal feed. The L-742 oil was also used as a makeup oil through Period 10 of the run, to replace the distillate material withdrawn as hydrocarbons vaporized in the pretreater and as the atmospheric overhead product obtained by atmospheric pressure distillation of the recycle solvent to the operation. After Period 10, another Wilsonville derived oil having a considerably high boiling range, HRI 5648, was used for this make-up service. Although it did not completely eliminate the need for makeup, this change did reduce the amount of makeup oil required. *Table 11* summarizes the analyses of these two oils used as makeup during the run.

The solvent quality evaluations of these oils were very similar, and somewhat higher, by 5-10% coal conversion units, than the start-up oil used for Run 227-55(CC-1). However, the hydrogen content of the L-721, the start-up oil and makeup until Period 10, was somewhat lower than equivalent boiling range materials generated as recycle oils in Run 227-55(CC-1), 9.45 W% against about 9.9 W%. Also the characterization factor of the L-721 oil was lower than that of the Run 227-55(CC-1) products, 10.35 compared to about 10.8, indicating lower hydroaromaticity for the L-721 oil. These differences probably contributed to the relatively low hydrogen contents of the gas oil fractions of Run 227-62(CC-5), since there was a considerable amount of L-721 oil used as makeup in Run 227-62(CC-5) in place of the recycled oils.

The nitrogen content of the L-721 makeup oil was relative high, 0.74%, which compares to a range of 0.17-0.31 W% for equivalent oils in the PFL recycle during Run 227-55(CC-1). This difference probably was a factor in the relatively high nitrogen contents of the products from Run 226-62(CC-5).

The HRI 5648 oil used as makeup oil after Period 10 of Run 227-62(CC-5) was of higher hydrogen content, 10.01 W%, than the L-721 oil despite its higher boiling range. This hydrogen content is higher even than that of the equivalent recycled material in Run 227-55(CC-1), about 9.2 W%, although its characterization factor, 10.7, was slightly lower. This change in makeup oil characteristics accounts for the pattern of the hydrogen contents of the products from the two runs approaching more closely as the runs continued. The nitrogen content of HRI 5648 oil, 0.46 W%, was lower than that of the L-721 oil, although not as low as the equivalent recycled materials in Run 227-55(CC-1).

FRESH CATALYST

The catalyst used in both stages for Run 227-62(CC-5) was Shell S-317, 1/32" extrudate, nickel-molybdate on alumina. The designation was HRI No. 5394, the same lot that had been used for Illinois Coal and Ohio Coals in previous CTSL™ operations, as well as the previous runs with the Black Thunder Mine coal. The inspections on the fresh catalyst are presented in *Table 12*.

The catalyst charged to the reactors was presulfided during the run start-up by treating with start-up oil spiked with 3.5 W% TNPS (di-tertiary nonyl polysulfide). This run was the first in which TNPS was used as the sulfiding agent, in place of DMDS (Dimethyl Disulfide) after microautoclave and fixed bed tests showed that the TNPS was an effective sulfiding agent, and possibly superior to DMDS. As product oil at the time of the presulfiding became available, it was spiked and recycled as the presulfiding solvent. The presulfiding operation consisted of two 6-hour holding periods with the reactors at 450°F, and at 550°F, and a 4-hour holding period at 650°F while feeding the spiked oil at about 1.0 V/Hr/V (total catalyst). The first and second stage reactor temperatures were then increased to 700 and 750°F, respectively, before coal feed was started. The first and second stage temperatures were then increased to the specified initial condition temperatures over a 48 hour period.

RECOVERED CATALYST

Analyses of the catalysts recovered from the two stages after Runs 227-62(CC-5) are given in *Table 13*.

The catalyst recovery from the first stage reactor was 92% based on the relative volumes of charged and recovered +20 mesh oil-free catalysts, and 95% based on the reported molybdenum contents for the charged and recovered catalyst. There was also some catalyst in the 20/100 mesh material recovered, with the molybdenum content corresponding to 1.2% of the amount of molybdenum in the catalyst charged.

The carbon accumulation on the catalyst in the first stage reactor, 13.6 W%, was virtually the same as on the first stage catalyst after Run 227-55(CC-1). The principal metals accumulation was iron, 0.66 W%, and sodium, 0.50 W%. The total analyzed metals contamination was 1.31 W%. The total of the analyzed contaminants on the Run 227-62(CC-5) catalyst was 22.0 W%, compared to a value of 23 W% based on the reported molybdenum contents of the charged and recovered catalysts. The pore volume of the recovered catalyst (on a contaminant-free basis) was about 71% of that of fresh catalyst than when compared on a common catalyst content basis, which is higher the range of the pore volume retention experienced in other runs. Ignition of the recovered first stage catalyst increased the pore volume to over 90% of that of fresh catalyst.

The catalyst recovery from the second stage was 90% based on the relative volumes of charged and recovered +20 mesh oil-free catalysts, and 97% based on the reported molybdenum contents of the charged and recovered catalysts. The molybdenum content of the 20/100 mesh recovered material corresponded to 1.4% of the amount in the catalyst charged.

The carbon accumulation on the second stage catalyst was 18.2 W%, again virtually the same as on the second stage catalyst after Run 227-55(CC-1), 18.9 W%. The iron accumulation, 0.12 W%, was lower than on the first stage catalyst, while the sodium accumulation, 1.18 W%, was higher. The total metallic contamination was 1.5 W%. The total of the analyzed contaminants of the second stage catalyst was 26.4 W%, while the total contaminants estimated on the basis of the molybdenum contents was 26 W%. The pore volume (contaminant-free basis) of the recovered second stage catalyst was 63% of that of fresh catalyst. Ignition of the recovered second stage catalyst increased the pore volume to about 98% of that of fresh catalyst.

The sulfur contents of the catalysts recovered after Run 226-62(CC-5) were slightly higher than the catalysts recovered after Run 227-55(CC-1), as follows:

	CC-1		CC-5	
Stage	First	Second	First	Second
Sulfur, W%	5.59	5.42	5.81	5.84
Mo, W%	8.47	8.26	8.82	8.45
Ni, W%	1.66	1.57	1.85	1.71
S/Mo + Ni	0.55	0.55	0.54	0.58

This summary indicates that the difference in sulfur contents does not necessarily indicate a greater degree of catalyst sulfiding as a consequence of the addition H₂S to the process gas in the last 5 days of Run 227-62(CC-5).

TABLE 1**Run 227-62(CC-5) Operating Conditions**

Catalyst - Shell S-317 (HRI 5394) in both stages
 Coal Feed - Black Thunder Mine (Wyoming), Thunder Basin Coal Co.

Condition	1	2	3	4
Period, (Days)	1A-6A	6B-10B⁽¹⁾	11B-16A	16B-21C
Nominal Conditions				
Unit Pressure, psig	2500	2500	2500	2500
Coal, Lb(dry)/hr/ft ³ (catalyst)				
First Stage	44	44	44	44
Second Stage	44	44	44	44
Solvent recycle, Lb/Lb coal				
Filtered Liquid	0.45	0.40	1.1	1.1
Make-up Oil (L-742, HRI 5648)	0.40	0.43	0.38	0.38
Topped Separator Bottoms	0.38	0.39	0.38	0.38
Oil/Solids in Feed	1.1	1.1	1.6	1.6
Pretreater Temperature, °F	500	600	500	500
Hold time, hours	1	1	1	1
Coal Feed, W% H ₂ O	5	5	26	5
Atmospheric Still, Tem. °F	500	500	500	500
H ₂ S, W% of dry coal	0	0	0	0
Reactor Temperatures, °F				
First Stage	750	750	750	750
Second Stage	825	825	825	825

- (1) After Period 10C, attempted operation with steam addition to pretreater to maintain steam atmosphere during pretreatment was abandoned when feed slurry became too viscous to pump because of increased stripping of light oil components.

TABLE 2
RUN 227-62 OPERATING SUMMARY

COAL: BLACK THUNDER MINE (HRI 5630)
CATALYST: BOTH STAGES: SHELL S-317 NIMO 1/32" (HRI 5394)

Period Number	1	2	3	4	5	6	7
Hours of Run (End of Period)	32.	56.	80.	104.	128.	152.	176.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	34.	63.	92.	114.	140.	171.	196.
Moisture in Coal to Pretreater, W%	8.25	8.25	8.25	8.25	5.44	4.04	4.04
TEMPERATURES, °F							
First Stage Reaction	743.	749.	749.	751.	750.	749.	750.
Second Stage Reaction	805.	827.	826.	828.	829.	828.	825.
Slurry Mix Tank	140.	170.	199.	223.	246.	266.	343.
Pretreater Max Temp		500.	500.	500.	500.	600.	600.
PRESSURES, PSIG							
Unit Back Pressure	2509.	2507.	2507.	2508.	2533.	2535.	2536.
Overall DP	15.1	13.9	15.3	15.0	14.9	15.4	18.4
SPACE VELOCITY							
Dry Coal Sp. Vel. - Stg. 1, Lb/Hr/Ft ³ (Catalyst)	44.4	48.9	48.4	38.9	43.8	51.5	43.1
RECYCLES, W% OF DRY COAL							
Pressure Filter Liquid	77.9	23.8	71.0	35.7	29.3	52.7	47.7
PFL to Buffer - Stage 1	4.1	4.0	3.8	4.1	3.8	4.2	4.3
PFL to Buffer - Stage 2	4.7	4.6	4.8	5.2	4.7	3.8	4.5
Separator Bottoms	38.9	11.9	38.6	39.2	37.8	37.2	37.2
Make-up Oil (L-742)	0.0	81.3	6.7	41.6	46.3	21.8	26.9
Pretreater Oil Vaporization	0.0	3.0	3.7	5.5	3.9	13.0	17.1
Hydrogen Sulfide Feed	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TOTAL MATERIAL RECOVERY (GROSS)	95.07	99.08	91.37	91.86	99.01	100.38	97.94
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED							
C ₁ -C ₃ in Gases				11.22	11.68		
C ₄ -C ₇ in Gases				6.21	5.39		
IBP-390 °F in Liquids				23.11	18.46		
390-500 °F in Liquids				16.20	13.64		
500-650 °F in Liquids				26.29	23.37		
650-850 °F in Liquids				-9.25	-0.28		
850-975 °F in Liquids				-4.57	-2.70		
Toluene Soluble 975°F+ Oil				-0.54	1.66		
Toluene Insoluble 975°F+ Oil				0.02	0.05		
Unconverted Coal				7.07	7.29		
Ash (SO ₃ -free)				5.89	5.89		
Water				20.53	19.81		
CO				1.31	0.71		
CO ₂				3.58	2.26		
NH ₃				1.28	1.28		
H ₂ S				0.15	0.22		
Total (100 + H ₂ Reacted)				108.49	108.71		
PROCESS PERFORMANCE							
C ₄ -975 °F Distillates, W% of MAF Coal				61.6	61.5		
975°F+ Conversion, W% MAF				93.1	90.4		
Coal Conversion, W% MAF		91.8	91.2	92.5	92.3		92.1
HDS, W%				32.7	47.3		
HDN, W%				109.1	108.4		

TABLE 2
RUN 227-62 OPERATING SUMMARY

COAL: BLACK THUNDER MINE (HRI 5630)
CATALYST: BOTH STAGES: SHELL S-317 NIMO 1/32" (HRI 5394)

Period Number	8	9	10	11	12	13	14
Hours of Run (End of Period)	200.	224.	248.	272.	296.	320.	344.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	223.	249.	274.	293.	316.	342.	370.
Moisture in Coal to Pretreater, W%	5.03	5.55	5.55	26.41	26.41	25.94	25.70
TEMPERATURES, °F							
First Stage Reaction	750.	750.	750.	750.	748.	748.	751.
Second Stage Reaction	825.	825.	826.	828.	826.	826.	826.
Slurry Mix Tank	352.	382.	392.	388.	389.	388.	382.
Pretreater Max Temp	600.	600.	500.	500.	500.	500.	500.
PRESSURES, PSIG							
Unit Back Pressure	2535.	2531.	2526.	2526.	2527.	2526.	2526.
Overall DP	18.7	19.2	18.1	18.7	20.7	23.4	21.5
SPACE VELOCITY							
Dry Coal Sp. Vel. - Stg. 1, Lb/Hr/Ft ³ (Catalyst)	44.4	44.0	42.2	33.3	38.0	44.7	46.9
RECYCLES, W% OF DRY COAL							
Pressure Filter Liquid	32.4	31.4	33.0	70.6	34.0	74.5	116.4
PFL to Buffer - Stage 1	4.2	4.9	4.7	5.5	4.8	4.4	4.1
PFL to Buffer - Stage 2	4.6	4.8	5.0	5.2	5.1	4.4	4.2
Separator Bottoms	37.8	37.3	37.8	51.1	57.7	38.3	38.5
Make-up Oil (L-742, HRI 5648 After Period 10)	42.8	42.0	42.6	92.2	35.2	56.2	13.5
Pretreater Oil Vaporization	-18.8	-13.9	-25.9	-43.3	-4.1	-2.8	-2.0
Hydrogen Sulfide Feed	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TOTAL MATERIAL RECOVERY (GROSS)	96.82	98.52	100.44	94.43	101.24	102.42	100.72
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED							
C ₁ -C ₃ in Gases	9.56	9.79					
C ₄ -C ₇ in Gases	4.77	5.31					
18P-390 °F in Liquids	14.98	14.65					
390-500 °F in Liquids	11.46	11.22					
500-650 °F in Liquids	26.18	23.99					
650-850 °F in Liquids	2.51	4.15					
850-975 °F in Liquids	-2.91	-2.06					
Toluene Soluble 975°F+ Oil	1.66	2.52					
Toluene Insoluble 975°F+ Oil	0.07	0.21					
Unconverted Coal	7.45	7.92					
Ash (SO ₃ -free)	5.89	5.89					
Water	20.73	19.06					
CO	1.13	1.19					
CO ₂	3.14	2.72					
NH ₃	1.19	1.16					
H ₂ S	0.22	0.21					
Total (100 + H ₂ Reacted)	108.02	107.95					
PROCESS PERFORMANCE							
C ₄ -975 °F Distillates, W% of MAF Coal	60.6	60.9					
975°F+ Conversion, W% MAF	90.2	88.7					
Coal Conversion, W% MAF	92.1	91.6	91.2	91.6	89.1	88.8	
HDS, W%	47.6	45.8					
HDN, W%	100.9	98.7					

TABLE 2
RUN 227-62 OPERATING SUMMARY

COAL: BLACK THUNDER MINE (HRI 5630)
CATALYST: BOTH STAGES: SHELL S-317 NIMO 1/32" (HRI 5394)

Period Number	15	16	17	18	19	20	21
Hours of Run (End of Period)	368.	392.	416.	440.	464.	488.	512.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	397.	424.	452.	480.	507.	535.	560.
Moisture in Coal to Pretreater, W%	25.42	14.80	6.84	6.84	4.61	4.61	4.61
TEMPERATURES, °F							
First Stage Reaction	749.	750.	751.	751.	748.	750.	750.
Second Stage Reaction	825.	827.	827.	826.	824.	827.	827.
Slurry Mix Tank	345.	333.	333.	327.	324.	323.	323.
Pretreater Max Temp	500.	500.	500.	500.	500.	500.	500.
PRESSURES, PSIG							
Unit Back Pressure	2524.	2532.	2531.	2530.	2531.	2533.	2531.
Overall DP	20.8	19.3	19.5	19.3	19.8	20.1	20.2
SPACE VELOCITY							
Dry Coal Sp. Vel. - Stg. 1, Lb/Hr/Ft ³ (Catalyst)	45.5	45.5	47.7	46.2	46.9	47.1	42.2
RECYCLES, W% OF DRY COAL							
Pressure Filter Liquid	102.6	103.1	108.1	117.5	109.0	103.9	97.1
PFL to Buffer - Stage 1	4.2	4.4	4.1	4.4	4.0	4.5	4.4
PFL to Buffer - Stage 2	5.7	5.1	4.5	4.5	5.0	4.4	5.0
Separator Bottoms	38.2	38.5	38.7	38.3	37.7	40.2	37.6
Make-up Oil (HRI-5648)	27.8	27.4	22.4	12.8	18.3	19.9	8.9
Pretreater Oil Vaporization	-1.7	-4.4	-2.0	-2.4	-2.3	-2.3	-0.3
Hydrogen Sulfide Feed	0.0	0.0	4.6	2.9	2.7	2.9	3.3
TOTAL MATERIAL RECOVERY (GROSS)	95.59	103.73	100.35	100.69	100.16	97.72	107.83
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED							
C ₁ -C ₃ in Gases	10.15				10.42	10.24	
C ₄ -C ₇ in Gases	5.31				4.80	7.51	
IBP-390 °F in Liquids	17.53				16.18	17.78	
390-500 °F in Liquids	11.01				9.33	10.28	
500-650 °F in Liquids	24.20				21.92	23.07	
650-850 °F in Liquids	5.01				6.73	3.88	
850-975 °F in Liquids	-7.86				-4.61	-6.18	
Toluene Soluble 975°F+ Oil	1.86				1.83	0.86	
Toluene Insoluble 975°F+ Oil	0.11				0.10	0.10	
Unconverted Coal	11.24				11.94	11.32	
Ash (SO ₃ -free)	5.92				5.89	5.89	
Water	19.21				18.19	18.82	
CO	1.33				1.84	1.80	
CO ₂	1.50				1.52	1.14	
NH ₃	0.85				0.95	0.97	
H ₂ S	0.23				0.23	0.24	
Total (100 + H ₂ Reacted)	107.60				107.25	107.74	
PROCESS PERFORMANCE							
C ₄ -975 °F Distillates, W% of MAF Coal	58.7				57.7	59.9	
975°F+ Conversion, W% MAF	86.0				85.3	87.0	
Coal Conversion, W% MAF	88.1		87.4	88.8	87.3	88.0	
HDS, W%	50.3				51.1	53.2	
HDN, W%	71.9				80.5	82.6	

TABLE 3

Coal Pretreater Performance - Run 227-62(CC-5)

Period	Treater	Feed H ₂ O	Treater Product, W% of Dry Coal				
			Temp. °F	W% Dry Coal	CO	CO ₂	C ₁ -C ₇ HC
4	500	9.0	0.08	3.04	0.03	12.4	3.4
5	500	5.8	0.05	1.99	0.01	8.7	3.0
8	600	5.3	0.10	2.44	0.06	9.0	3.7
9	600	5.9	0.05	2.09	0.06	9.9	4.0
14	500	34.6	0.03	1.67	0.02	34.0	-0.6
15	500	34.1	0.03	1.09	0.01	34.0	-0.1
19	500	4.8	0.08	1.03	0.01	6.6	1.8
29	500	4.8	0.04	0.63	0.00	6.7	1.8

TABLE 4

PRODUCT FRACTION ANALYSES - RUN 227-62(CC-5)

Condition	1	2	3	4
Period Number	5	9	15	20
Catalyst Age, Lbs Coal/Lb Catalyst	140	249	396	534
TOTAL LIQUID				
Gravity, deg-API	7.1	4.9	4.3	4.7
Elemental Analyses, W%				
Carbon, W%	90.23	90.17	90.04	90.18
Hydrogen, W%	9.89	9.44	9.27	9.45
Sulfur, W%	0.007	0.002	0.006	0.002
Nitrogen, W%	0.34	0.37	0.58	0.34
Total:	100.47	99.98	99.90	99.97
IBP, °F	510	549	563	531
650°F-, W%	15.9	11.4	9.5	10.5
650-850 °F, W%	62.8	60.4	56.0	56.2
850-975 °F, W%	10.2	12.1	16.7	15.9
975 °F+, W%	10.7	15.3	16.8	16.7
Loss, W%	0.4	0.8	1.0	0.7
LGO (IBP-650°F)				
Gravity, deg-API	15.7	14.2	13.9	16.1
Carbon, W%	89.93	89.55	89.36	89.48
Hydrogen, W%	11.03	10.97	10.81	11.27
Sulfur, W%	0.001	0.002	0.002	0.003
Nitrogen, W%	0.20	0.27	0.27	0.27
VGO (650-850°F)				
Gravity, deg-API	10.5	9.6	8.8	10.7
Carbon, W%	90.06	89.94	89.83	89.81
Hydrogen, W%	10.02	10.09	9.96	10.07
Sulfur, W%	0.003	0.009	0.007	0.015
Nitrogen, W%	0.25	0.28	0.37	0.28
HVGO (850-975°F)				
Gravity, deg-API	-2.3	-2.3	-1.3	-0.5
Carbon, W%	90.17	90.61	90.44	90.86
Hydrogen, W%	8.51	8.34	8.76	8.84
Sulfur, W%	0.004	0.014	0.018	0.007
Nitrogen, W%	0.44	0.52	0.49	0.42
RESIDUUM (975°F+)				
Gravity, deg-API	-11.5	-13.3	-11.6	-10.8
Carbon, W%	91.77	91.11	91.41	91.46
Hydrogen, W%	6.93	6.66	6.83	6.96
Sulfur, W%	0.004	0.003	0.007	0.014
Nitrogen, W%	0.58	0.67	0.76	0.61
Cyclohexane Insolubles, W%	20.44	24.38	26.10	22.00
Toluene Insolubles, W%	1.60	4.68	3.18	4.57
Ash, W%	0.18	0.01	0.26	0.01
SOLIDS (THF INSOLUBLE)				
Ash, W%	48.96	46.61	35.07	36.20
Elemental Analyses, Ash-free Basis				
Carbon, W%	74.84	75.61	78.93	77.85
Hydrogen, W%	4.02	4.01	4.85	4.69
Sulfur, W%	2.51	2.40	1.39	1.76
Nitrogen, W%	1.39	1.25	1.25	1.25
Total	82.76	83.27	86.42	85.55
Sulfur/Ash	0.028	0.028	0.026	0.031
Sulfur In Ash, W%	2.73	2.83	2.55	3.14

TABLE 5

PRODUCT STREAM ANALYSES - RUN 227-62(CC-5)

Operations With Black Thunder Mine Coal - Shell S-317 Catalyst

Period Number	5	9	15	20
Catalyst Age, Lbs Coal/Lb Catalyst	140	249	397	535
SEPARATOR OVERHEAD				
Volume Average Boiling Point, °F	423	444	434	426
Gravity, deg-API	34.00	31.20	33.00	33.10
Watson Characterization Factor	11.02	10.93	10.98	10.97
Carbon, W%	87.87	88.09	87.94	87.55
Hydrogen, W%	12.75	12.69	12.85	12.74
Sulfur, W%	0.01	0.00	0.01	0.02
Nitrogen, W% (Kjeldahl)	0.10	0.13	0.20	0.16
Total	100.73	100.91	101.00	100.47
H/C Ratio	1.73	1.72	1.75	1.73
ATMOSPHERIC OVERHEAD				
Volume Average Boiling Point, °F	520	536	524	527
Gravity, deg-API	23.30	21.50	22.80	23.10
Watson Characterization Factor	10.82	10.75	10.78	10.81
Carbon, W%	88.49	88.34	88.51	88.53
Hydrogen, W%	11.89	11.61	11.84	11.84
Sulfur, W%	0.00	0.01	0.01	0.01
Nitrogen, W% (Kjeldahl)	0.12	0.25	0.26	0.17
Total	100.50	100.21	100.62	100.55
H/C Ratio	1.60	1.57	1.59	1.59
PRESSURE FILTER LIQUID PRODUCT (SOLVENT)				
Gravity, deg-API	7.10	4.90	4.30	4.70
Composition				
IBP-650°F, W%	15.86	11.38	9.50	10.49
650-850°F, W%	62.84	60.37	56.05	56.21
850-975°F, W%	10.21	12.15	16.70	15.88
975°F+ Residuum, W%	10.70	15.33	16.79	16.75
Loss, W%	0.39	0.77	0.96	0.67
Carbon, W%	90.23	90.17	90.04	90.18
Hydrogen, W%	9.89	9.44	9.27	9.45
Sulfur, W%	0.01	0.05	0.01	0.00
Nitrogen, W% (Perkin-Elmer)	0.34	0.37	0.58	0.34
Total:	100.47	100.03	99.90	99.97
H/C Ratio	1.31	1.25	1.23	1.25
SOLIDS (THF INSOLUBLE)				
Ash, W%	48.96	46.61	35.07	36.20
Elemental Analyses, Ash-free Basis				
Carbon, W%	74.84	75.61	78.93	77.85
Hydrogen, W%	4.02	4.01	4.85	4.69
Sulfur, W%	2.51	2.40	1.39	1.76
Nitrogen, W%	1.39	1.25	1.25	1.25
Total:	82.76	83.27	86.42	85.55
Sulfur/Ash	0.0284	0.028	0.026	0.031
Sulfur In Ash, W%	2.73	2.83	2.55	3.14
Nitrogen, W% (Perkin-Elmer) - Analysis with Perkin-Elmer 240B Elemental Analyzer				
Nitrogen, W% (Kjeldahl) - Wet Chemical determination				

TABLE 6
BENCH-SCALE TWO STAGE COAL LIQUEFACTION

OPERATIONS WITHOUT AND WITH THERMAL COAL PRETREATMENT
RUN 227-55 AND 227-62 OPERATING SUMMARY
COAL: BLACK THUNDER MINE (HRI 5630)
CATALYST: BOTH STAGES: SHELL S-317 NIMO 1/32" (HRI 5394)

Run	-----227-55-----				-----227-62-----			
Period Number	9	10	18	19	4	5	8	9
Pretreater Maximum Temperature, °F	-----No Pretreatment-----				500.	500.	600.	600.
Hydrogen Sulfide Feed, W% of Dry Coal	--	--	--	--	0.0	0.0	0.0	0.0
Hours of Run (End of Period)	216.	240.	432.	456.	104.	128.	200.	224.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	256.	284.	513.	541.	114.	140.	223.	249.
Moisture in Coal, W%	6.37	6.37	6.37	6.37	8.25	5.44	5.03	5.55
TEMPERATURES, °F								
First Stage Reaction	750.	750.	750.	750.	751.	750.	750.	750.
Second Stage Reaction	825.	824.	824.	824.	828.	829.	825.	825.
Slurry Mix Tank	189.	234.	200.	208.	223.	246.	352.	382.
PRESSURE, PSIG								
Unit Back Pressure	2497.	2499.	2497.	2503.	2508.	2533.	2535.	2531.
SPACE VELOCITY								
Dry Coal Sp. Vel. - Lb/Hr/Ft ³ Cat.	45.6	44.7	46.0	44.9	38.9	43.8	44.0	44.1
REACTOR FEED OIL:SOLIDS RATIO	1.06	1.06	1.06	1.06	1.00	0.99	0.82	0.89
RECYCLES, W% OF DRY COAL								
Pressure Filter Liquid	76.3	76.3	75.7	76.3	35.7	29.3	32.4	31.4
PFL to Buffer - Stage	2.9	4.8	2.7	4.3	4.1	3.8	4.2	4.9
PFL to Buffer - Stage	4.3	3.8	3.0	3.3	5.2	4.7	4.6	4.8
Separator Bottoms	38.1	38.1	38.1	38.1	39.2	37.8	37.8	37.3
Make-up Oil (L-742)	--	--	--	--	41.6	46.3	42.8	42.0
Hot Slurry Tank Condensate Oil (Off Recycle)	--	--	--	--	5.5	3.9	18.8	13.9
TOTAL MATERIAL RECOVERY (GROSS)	96.04	96.04	96.06	96.05	91.86	99.01	96.82	98.52
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED								
C ₁ -C ₃ in Gases	8.64	7.74	12.46	8.88	11.22	11.68	9.56	9.79
C ₄ -C ₇ in Gases	5.06	4.06	8.00	5.30	6.21	5.39	4.77	5.3
180-390 °F in Liquids	15.21	15.96	14.51	14.60	23.11	18.46	14.98	14.65
390-500 °F in Liquids	10.21	10.62	10.03	10.16	16.20	13.64	11.46	11.22
500-650 °F in Liquids	18.40	19.12	15.31	17.14	26.29	23.37	26.18	23.99
650-850 °F in Liquids	12.15	12.03	7.21	10.57	-9.25	-0.28	2.51	4.15
850-975 °F in Liquids	2.11	2.00	1.27	1.97	-4.57	-2.70	-2.91	-2.06
Toluene Soluble 975°F+ Oil	2.40	2.67	2.22	3.88	-0.54	1.66	1.66	2.52
Toluene Insoluble 975°F+ Oil	0.02	0.02	0.04	0.27	0.02	0.05	0.07	0.21
Unconverted Coal	8.35	8.04	7.47	7.71	7.07	7.29	7.45	7.92
Ash (SO ₃ -free)	6.01	6.01	6.01	6.01	5.89	5.89	5.89	5.89
Water	17.55	17.79	20.97	18.90	20.53	19.81	20.73	19.0
CO	0.25	0.20	0.27	0.19	1.31	0.71	1.13	1.1
CO ₂	0.14	0.08	1.10	0.63	3.58	2.26	3.14	2.7
NH ₃	0.97	0.96	1.01	0.97	1.28	1.28	1.19	1.1
H ₂ S	0.37	0.36	0.37	0.36	0.15	0.22	0.22	0.2
Total (100 + H ₂ Reacted)	107.83	107.66	108.27	107.56	108.49	108.71	108.02	107.9
PROCESS PERFORMANCE								
C ₄ -975°F Distillates, W% of MAF Coal	67.2	67.9	59.9	63.6	61.6	61.5	60.6	60.
975°F+ Conversion, W% MAF	88.5	88.6	89.6	87.4	93.1	90.4	90.2	88.
Coal Conversion, W% MAF	91.1	91.4	92.0	91.8	92.5	92.3	92.1	91.
HDS, W%	72.1	71.0	72.9	71.3	32.7	47.3	47.6	45.
HDN, W%	76.0	75.4	79.1	75.7	109.1	108.4	100.9	98.

TABLE 6 (continued)

RUN 227-55 AND 227-62 OPERATING SUMMARY
 COAL: BLACK THUNDER MINE (HRI 5630)
 CATALYST: BOTH STAGES: SHELL S-317 NIMO 1/32" (HRI 5394)

Run	-----227-55-----				-----227-62-----		
Period Number	9	10	18	19	15	19	20
Pretreater Maximum Temperature, °F	-----No Pretreatment-----				500.	500.	500.
Hydrogen Sulfide Feed, W% of Dry Coal	--	--	--	--	0.0	2.7	2.9
Hours of Run (End of Period)	216.	240.	432.	456.	368.	464.	488.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	256.	284.	513.	541.	397.	507.	535.
Moisture in Coal, W%	6.37	6.37	6.37	6.37	25.42	4.61	4.61
TEMPERATURES, °F							
First Stage Reaction	750.	750.	750.	750.	749.	748.	750.
Second Stage Reaction	825.	824.	824.	824.	825.	824.	827.
Slurry Mix Tank	189.	234.	200.	208.	345.	324.	323.
PRESSURE, PSIG							
Unit Back Pressure	2497.	2499.	2497.	2503.	2524.	2531.	2533.
SPACE VELOCITY							
Dry Coal Sp. Vel. - Stg. 1, Lb/Hr/Ft ³	20.5	20.1	20.7	20.2	20.5	21.1	21.2
REACTOR FEED OIL:SOLIDS RATIO	1.06	1.06	1.06	1.06	1.54	1.54	1.52
RECYCLES, W% OF DRY COAL							
Pressure Filter Liquid	76.3	76.3	75.7	76.3	102.6	109.0	103.9
PFL to Buffer - Stage 1	2.9	4.8	2.7	4.3	4.2	4.0	4.5
PFL to Buffer - Stage 2	4.3	3.8	3.0	3.3	5.7	5.0	4.4
Separator Bottoms	38.1	38.1	38.1	38.1	38.2	37.7	40.2
Make-up Oil (HRI 5648)	--	--	--	--	27.8	18.3	19.9
Hot Slurry Tank Condensate Oil (Off Recycle)	--	--	--	--	1.7	2.3	2.3
TOTAL MATERIAL RECOVERY (GROSS)	96.04	96.04	96.06	96.05	95.59	100.16	97.72
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED							
C ₁ -C ₃ in Gases	8.64	7.74	12.46	8.88	10.15	10.42	10.24
C ₄ -C ₇ in Gases	5.06	4.06	8.00	5.30	5.31	4.80	7.51
IBP-390 °F in Liquids	15.21	15.96	14.51	14.60	17.53	16.18	17.78
390-500 °F in Liquids	10.21	10.62	10.03	10.16	11.01	9.33	10.28
500-650 °F in Liquids	18.40	19.12	15.31	17.14	24.20	21.92	23.07
650-850 °F in Liquids	12.15	12.03	7.21	10.57	5.01	6.73	3.88
850-975 °F in Liquids	2.11	2.00	1.27	1.97	-7.86	-4.61	-6.18
Toluene Soluble 975°F+ Oil	2.40	2.67	2.22	3.88	1.86	1.83	0.86
Toluene Insoluble 975°F+ Oil	0.02	0.02	0.04	0.27	0.11	0.10	0.10
Unconverted Coal	8.35	8.04	7.47	7.71	11.24	11.94	11.32
Ash (SO ₃ -free)	6.01	6.01	6.01	6.01	5.92	5.89	5.89
Water	17.55	17.79	20.97	18.90	19.21	18.19	18.82
CO	0.25	0.20	0.27	0.19	1.33	1.84	1.80
CO ₂	0.14	0.08	1.10	0.63	1.50	1.52	1.14
NH ₃	0.97	0.96	1.01	0.97	0.85	0.95	0.97
H ₂ S	0.37	0.36	0.37	0.36	0.23	0.23	0.24
Total (100 + H ₂ Reacted)	107.83	107.66	108.27	107.56	107.60	107.25	107.74
PROCESS PERFORMANCE							
C ₄ -975°F Distillates, W% of MAF Coal	67.2	67.9	59.9	63.6	58.7	57.7	59.9
975°F+ Conversion, W% MF	88.5	88.6	89.6	87.4	86.0	85.3	87.0
Coal Conversion, W% MAF	91.1	91.4	92.0	91.8	88.1	87.3	88.0
HDS, W%	72.1	71.0	72.9	71.3	50.3	51.1	53.2
HDN, W%	76.0	75.4	79.1	75.7	71.9	80.5	82.6

TABLE 7
COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES
RUN 227-62

Condition	--First Stage--		--Second Stage--	
	1	2	1	2
Period Number	5	9	5	9
Catalyst Age, Lbs Coal/Lb Catalyst	140	249	140	249
TOTAL LIQUID				
Gravity, deg-API	9.3	5.9	7.1	4.9
Elemental Analyses, W%				
Carbon, W%	89.39	89.25	90.23	90.17
Hydrogen, W%	10.24	9.55	9.89	9.44
Sulfur, W%	0.003	0.020	0.007	0.002
Nitrogen, W%	0.23	0.47	0.34	0.37
Total	99.86	99.29	100.47	99.98
650°F-, W%	20.6	14.4	15.9	11.4
650-850 °F, W%	51.1	53.4	62.8	60.4
850-975 °F, W%	11.4	14.5	10.2	12.1
975°F+, W%	16.1	16.7	10.7	15.3
Loss, W%	0.8	1.0	0.4	0.8
LGO (IBP-650°F)				
Gravity, deg-API	18.5	15.3	15.7	14.2
Carbon, W%	88.71	88.63	89.33	89.55
Hydrogen, W%	11.65	10.86	11.03	10.97
Sulfur, W%	0.018	0.021	0.001	0.002
Nitrogen, W%	0.19	0.32	0.20	0.27
VGO (650-850°F)				
Gravity, deg-API	11.1	8.9	10.5	9.6
Carbon, W%	89.02	89.08	90.06	89.94
Hydrogen, W%	10.47	10.05	10.02	10.09
Sulfur, W%	0.011	0.002	0.003	0.009
Nitrogen, W%	0.31	0.42	0.25	0.28
HVGO (850-975°F)				
Gravity, deg-API	0.7	-0.6	-2.3	-2.3
Carbon, W%	90.14	89.48	90.17	90.61
Hydrogen, W%	9.37	8.95	8.51	8.34
Sulfur, W%	0.011	0.019	0.004	0.014
Nitrogen, W%	0.47	0.53	0.44	0.52
RESIDUUM (975°F+)				
Gravity, deg-API	-5.1	-7.1	-11.5	-13.3
Carbon, W%	89.50	89.56	91.77	91.11
Hydrogen, W%	8.40	7.75	6.93	6.66
Sulfur, W%	0.036	0.020	0.004	0.003
Nitrogen, W%	0.72	0.75	0.58	0.67
Cyclohexane Insolubles, W%			20.44	24.38
Toluene Insolubles, W%			1.60	4.68
Ash, W%			0.18	0.01
SOLIDS (THF INSOLUBLE)				
Ash, W%	24.16	21.66	48.96	46.61
Elemental Analyses, Ash-free Basis				
Carbon, W%	78.46	77.16	74.84	75.61
Hydrogen, W%	5.22	5.12	4.02	4.01
Sulfur, W%	1.79	1.02	2.51	2.40
Nitrogen, W%	1.71	1.57	1.39	1.25
Total:	87.18	84.87	82.76	83.27
Sulfur/Ash	0.056	0.037	0.028	0.028
Sulfur In Ash, W%	5.73	3.75	2.73	2.83
SAMPLE FILTRATION				
Filter Cake, Percent of Sample	44.98	41.41	22.65	26.52
THF Insolubles, W% of Filter Cake	58.58	52.44	59.61	59.88

TABLE 7
COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES-RUN 227-62

Condition	--First Stage--		--Second Stage--	
	3	4	3	4
Period Number	15	20	15	20
Catalyst Age, Lbs Coal/Lb Catalyst	396	534	396	534
TOTAL LIQUID				
Gravity, deg-API	5.3	6.7	4.3	4.7
Elemental Analyses, W%				
Carbon, W%	89.66	89.47	90.04	90.18
Hydrogen, W%	9.52	9.82	9.27	9.45
Sulfur, W%	0.010	0.009	0.006	0.002
Nitrogen, W%	0.50	0.31	0.58	0.34
Total	99.69	99.61	99.90	99.97
650°F-, W%	9.3	9.3	9.5	10.5
650-850 °F, W%	52.9	52.1	56.0	56.2
850-975°F, W%	19.8	18.0	16.7	15.9
975 °F+, W%	17.3	19.6	16.8	16.7
Loss, W%	0.7	1.0	1.0	0.7
LGO (IBP-650°F)				
Gravity, deg-API	15.7	16.5	13.9	16.1
Carbon, W%	88.10	88.59	89.36	89.48
Hydrogen, W%	11.22	11.42	10.81	11.27
Sulfur, W%	0.035	0.003	0.002	0.003
Nitrogen, W%	0.21	0.19	0.27	0.27
VGO (650-850°F)				
Gravity, deg-API	9.8	10.0	8.8	10.7
Carbon, W%	89.25	89.27	89.83	89.81
Hydrogen, W%	10.25	10.34	9.96	10.07
Sulfur, W%	0.011	0.004	0.007	0.015
Nitrogen, W%	0.36	0.18	0.37	0.28
HVGO (850-975°F)				
Gravity, deg-API	1.0	1.3	-1.3	-0.5
Carbon, W%	89.99	89.77	90.44	90.86
Hydrogen, W%	9.35	9.35	8.76	8.84
Sulfur, W%	0.017	0.018	0.018	0.007
Nitrogen, W%	0.55	0.33	0.49	0.42
RESIDUUM (975°F+)				
Gravity, deg-API	-7.6	-7.0	-11.6	-10.8
Carbon, W%	89.66	90.44	91.41	91.46
Hydrogen, W%	7.79	7.96	6.83	6.96
Sulfur, W%	0.029	0.017	0.007	0.014
Nitrogen, W%	0.89	0.61	0.76	0.61
Cyclohexane Insolubles, W%			26.10	22.00
Toluene Insolubles, W%			3.18	4.57
Ash, W%			0.26	0.01
SOLIDS (THF INSOLUBLE)				
Ash, W%	17.91	18.16	35.07	36.20
Elemental Analyses, Ash-free Basis				
Carbon, W%	74.94	77.11	78.93	77.85
Hydrogen, W%	4.95	5.17	4.85	4.69
Sulfur, W%	0.63	0.99	1.39	1.76
Nitrogen, W%	1.57	1.59	1.25	1.25
Total:	82.09	84.86	86.42	85.55
Sulfur/Ash	0.029	0.045	0.026	0.031
Sulfur In Ash, W%	3.51	3.85	2.55	3.14
SAMPLE FILTRATION				
Filter Cake, % of Sample (or TSB)	39.26	42.22	20.24	16.95
THF Insolubles, W% of Filter Cake	44.02	57.77	59.47	59.99

TABLE 8

FIRST AND SECOND STAGE FLOWS - RUN 227-62 (CC-5)
Flows - Percent of Dry Coal Feed

Period	5	9	15	20
Coal Rate, Lbs/Hr/Ft ³	43.8	44.0	45.5	47.1
Recycle PFL, W% of Dry Coal Feed	29.3	31.4	102.6	103.9
Recycle TSB, W% of Dry Coal Feed	37.8	37.3	38.2	40.2
Makeup Oil, W% of Dry Coal Feed	46.3	42.0	27.8	19.9
Catalyst Age, Lb/Lb	140	249	397	488
First Stage Temperature, °F	750	750	749	750
Second Stage Temperature, °F	829	825	825	827
Pretreater Temperature, °F	500	600	500	500
H ₂ S Feed, W% of Dry Coal	0	0	0	2.9
Coal Feed, W% H ₂ O	5.4	5.6	25.4	4.6
FIRST STAGE FEED				
650°F-	18.85	9.73	13.49	14.13
650-850°F	67.41	59.66	92.93	90.05
850-975°F	12.82	13.76	34.92	30.82
975°F+	8.89	12.04	25.22	23.93
Quinoline IOM	96.99	97.57	96.98	96.81
Ash	8.22	8.46	7.45	7.29
Total	213.18	201.23	271.00	264.14
SECOND STAGE BUFFER				
650°F-	0.76	0.58	0.60	0.49
650-850°F	2.95	2.90	3.19	2.47
850-975°F	0.48	0.58	0.95	0.70
975°F+	0.51	0.74	0.96	0.70
Quinoline IOM	0.00	0.00	0.00	0.00
Ash	0.00	0.00	0.00	0.00
Total	4.70	4.80	5.70	4.40
FIRST STAGE PRODUCT				
650°F-	25.25	16.43	17.57	17.29
650-850°F	60.27	57.19	93.31	87.44
850-975°F	13.51	15.59	34.98	30.21
975°F+	19.02	17.88	30.54	32.89
Quinoline IOM	22.64	30.24	34.14	36.88
Ash	8.22	8.46	7.45	7.29
Vapor (estimated)	64.27	55.44	53.03	52.13
Total	213.18	201.23	271.00	264.14
SECOND STAGE PRODUCT				
650°F-	36.98	26.73	34.05	32.58
650-850°F	65.74	60.92	94.97	90.54
850-975°F	10.60	12.19	28.02	25.35
975°F+	11.11	15.38	28.17	25.51
Quinoline IOM	10.17	11.38	14.14	14.02
Ash	8.22	8.46	7.45	7.29
Vapor	75.05	70.96	69.91	72.02
Total	217.88	206.03	276.70	268.54

TABLE 9
FIRST AND SECOND STAGE YIELDS
RUN 227-62 (CC-5)

Period	5	9	15	20
Coal Rate, Lbs/Hr/Ft ³	43.8	44.0	45.5	47.1
Recycle PFL, W% of Dry Coal Feed	29.3	31.4	102.6	103.9
Recycle TSB, W% of Dry Coal Feed	37.8	37.3	38.2	40.2
Makeup Oil, W% of Dry Coal Feed	46.3	42.0	27.8	19.9
Catalyst Age, Lb/Lb	140	249	397	488
First Stage Temperature, °F	750	750	749	750
Second Stage Temperature, °F	829	825	825	827
Pretreater Temperature, °F	500	600	500	500
H ₂ S Feed, W% of Dry Coal	0	0	0	2.9
Coal Feed, W% H ₂ O	5.4	5.6	25.4	4.6
FIRST STAGE FORMATION				
W% of Dry Coal Feed				
Vapors	64.27	55.44	53.03	52.13
650°F-	6.40	6.70	4.07	3.15
650-850°F	-7.15	-2.47	0.38	-2.61
850-975°F	0.68	1.83	0.06	-0.61
975°F+	10.14	5.84	5.30	8.96
Quinoline IOM	-74.35	-67.34	-62.85	-59.93
Ash	0.00	0.00	0.00	0.00
Total 975°F-	64.20	61.49	57.54	50.97
Total 975°F+ Residuum	10.14	5.84	5.30	8.96
Coal Converted (W% of maf Coal)	79.00	71.55	66.80	63.68
SECOND STAGE FORMATION				
W% of Dry Coal Feed				
Vapors	10.78	15.52	16.88	19.89
650°F-	10.97	9.72	15.88	14.80
650-850°F	2.52	0.83	-1.53	0.62
850-975°F	-3.38	-3.98	-7.91	-5.56
975°F+	-8.42	-3.24	-3.32	-8.08
Quinoline IOM	-12.48	-18.85	-20.00	-22.87
Ash	0.00	0.00	0.00	0.00
Total 975°F-	20.89	22.09	23.32	30.95
Total 975°F+ Residuum	-8.42	-3.24	-3.32	-8.09
Coal Converted (W% of maf Coal)	13.26	20.03	21.26	24.30
TWO STAGE FORMATION				
W% of Dry Coal Feed				
650°F-	17.37	16.42	19.96	17.95
650-850°F	-4.62	-1.64	-1.16	-1.98
850-975°F	-2.70	-2.15	-7.85	-6.17
975°F+	1.72	2.60	1.99	0.87
Quinoline IOM	-86.82	-86.19	-82.84	-82.79
Ash	0.00	0.00	0.00	0.00
Total 975°F-	60.15	45.88	40.86	36.19
Total 975°F+ Residuum	1.72	2.60	1.99	0.87
Coal Converted (W% of maf Coal)	92.26	91.58	88.06	87.97

TABLE 10
FEED COAL ANALYSES FOR RUN 227-62(CC-5)
Run 227-62 Feed: Black Thunder Mine (Wyoming) Coal

FEED DESIGNATION, HRI NO. TESTS	5630 ⁽¹⁾ 227-62	5630 227-55	5613 Micro
PROXIMATE ANALYSIS, W%			
Moisture, W%	6.51a	6.37	
Volatile Matter (MAF Basis)	44.2	47.73	
Fixed Carbon (MAF Basis)	55.8	52.27	
ULTIMATE ANALYSIS (W%, Dry Basis)			
Carbon	68.55	67.70	70.50
Hydrogen	4.61	4.54	4.47
Sulfur	0.43	0.48	0.46
Nitrogen	0.97	1.05	0.98
Chlorine	--	0.04	0.03
Ash	(6.93)	(7.15)	(6.55)
Sulfur in Ash	(6.00)	(6.35)	(7.56)
Ash (SO ₃ -free)	5.89	6.01	5.31
Oxygen (By Difference)	19.55	20.18	18.15
SULFUR FORMS (W%, Dry Basis)			
Sulfate		0.04	0.01
Pyrite		0.11	0.06
Organic		0.36	0.46
HEATING VALUE, Btu/lb(Dry)			
Btu/Lb MAF		11797 12551	12048 12724
MINERAL ANALYSIS OF ASH (W%, Ignited)			
Silica, SiO ₂		34.61	27.96
Alumina, Al ₂ O ₃		16.98	15.81
Titania, TiO ₂		1.30	1.20
Ferric Oxide, Fe ₂ O ₃		6.94	5.77
Lime, CaO		21.74	26.77
Magnesia, MgO		4.40	5.27
Potassium Oxide, K ₂ O		0.35	0.37
Sodium Oxide, NaO		0.97	1.34
Sulfur Trioxide, SO ₃		10.74	13.45
Phosphorous Pentoxide, P ₂ O ₅		1.01	0.63
Strontium Oxide, SrO		0.29	0.29
Barium Oxide, BaO		0.37	0.26
Manganese Oxide, Mn ₃ O ₄		0.00	0.00
Undetermined		0.30	1.34
MICROAUTOCLAVE RESULTS			
Thermal Coal Conversion		76.6	84.6
Thermal 975°F+ Conversion		44.3	52.0
Catalytic Coal Conversion		87.9	94.6
Catalytic 975°F+ Conversion		72.9	75.2
MACERAL ANALYSIS, V% Reactives			
Vitrinites		73.4	
Exinite		3.6	
Resinite		---	
1/3 Semifusinite		4.1	
Total		81.1	
Inerts			
2/3 Semifusinite		8.4	
Micrinite		8.5	
Fusinite		2.0	
Total		18.9	
Ash		----	

(1) Dried Black Thunder coal feed to Run 227-62. Wet coal feed for 227-62 Periods 11-15 contained 26.05% H₂O.

TABLE 11

INSPECTION OF STARTUP AND MAKEUP OILS
FOR RUN 227-62 (CC-5)

Designation	L-742	HRI 5648
Gravity, API	6.9	6.4
Distillation, °F		
IBP	475	696
5 V%	561	769
10 V%	600	789
20 V%	637	807
30 V%	678	820
40 V%	710	831
50 V%	736	841
60 V%	760	875
70 V%	797	892
80 V%	832	909
90 V%	930	950
E.P.	975	975
V% @ 650°F	24	
V% @ 850°F	83	53
V% @ 975°F	95	94
Watson Character. Factor	10.35	10.69
IBP-650°F, W%	22.6	0.0
650-850°F, W%	58.0	52.5
850-975°F W%	13.2	41.1
975°F+, W	4.0	5.9
Loss, W%	2.2	0.5
Carbon, W%	88.59	89.27
Hydrogen, W%	9.45	10.01
Sulfur, W%	0.04	0.01
Nitrogen, W%	0.74	0.46
Total:	98.82	99.75
Solvent Quality Test ⁽¹⁾		
Illinois Coal	60.8	70.1
Black Thunder Coal	63.7	61.5

(1) Coal conversion, 750°F, 30 Minutes, 2000 psig N₂ 2/1 solvent/coal

TABLE 12

FRESH CATALYST PROPERTIES - RUN 227-62(CC-5)

HRI No.	5394
Designation	Shell S-317
Nominal Size	1/32" Extrudates
Charge to Reactors	
Volume (compacted), cc/reactor	900
Weight, grams (First Stage)	555
(Second Stage)	576
CHEMICAL ANALYSIS (W%, DRY BASIS)	
Molybdenum, HRI Analyses	10.76, 11.02, 11.58, 12.26
Vendor Specification	12.0
Nickel, HRI Analyses	2.00, 2.00, 2.25, 2.60
Vendor Specification	2.5
PHYSICAL PROPERTIES	
Bulk Density, Compacted, Lb/Ft ³	36.7
Particle Density, gm/cc	0.941
Surface Area (Calc.), M ² /gm	267
M ² /cc particle	251
Pore Volume, cc/gm	0.697
cc/cc particle	0.656
Average Crush Strength, Lb/mm	1.94
PORE SIZE DISTRIBUTION, CC/GM	
Diameter > 30 A	0.70
Diameter > 100 A	0.40
Diameter > 250 A	0.15
Diameter > 500 A	0.14
Diameter > 1500 A	0.11
Diameter > 4000 A	0.03
PENETRATION TEST	
Average Penetration, % of Diameter	34.9

TABLE 13
RECOVERED CATALYSTS ANALYSES
RUN 227-62(CC-5)

STAGE	First	Second
CATALYST AGE, LB COAL/LB		
Catalyst Recovery, VOL %	91.7	90.0
Bulk Density, Gm/cc	0.834	0.905
ANALYSES OF OIL-FREE +20 MESH CATALYST, W%		
Carbon	13.64	18.19
Hydrogen	1.02	0.78
H/C Ratio	0.90	0.51
Nitrogen	0.21	0.12
Sulfur	5.81	5.84
Molybdenum	8.82	8.45
Cobalt	-	-
Nickel	1.85	1.71
Titanium	0.04	0.004
Iron	0.66	0.12
Calcium	0.11	0.16
Sodium	0.50	1.18
Total Metal Contaminants:	1.31	1.46
Loss on Ignition, W%	19.83	23.34
Particle Density, Gm/cc particle ⁽¹⁾		1.542
Pore Volume (D>30 A), cc/gm	0.380	0.323
cc/cc particle		.498
Surface Area (calc.), M ² /gm	163	131
M ² /cc particle		
Modal Pore Diameter, Angstrom		
Macro-pores	1463	1980
Mini-pores	68	63
ANALYSES OF IGNITED CATALYST		
Particle Density, gm/cc particle ⁽¹⁾		1.040
Pore Volume (D>30 A), cc/gm	0.632	0.618
cc/cc particle		0.642
Surface Area (calc.), M ² /gm	221	212
M ² /cc particle		220
Modal Pore Diameter, Angstrom		
Macro-pores	1993	2095
Mini-pores	88	87
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS		
Weight, Grams	10.81	14.0
Molydenum, W%	6.98	6.25

(1) In mercury at 10 psia.

FIGURE 1

COAL CONVERSION

Run 227-62 and 227-55

FIGURE 2

975 F+ CONVERSION

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 3

C1-C3 GAS YIELDS

Run 227-62 and 227-55

FIGURE 4

C4-390 F NAPHTHA YIELD

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 5

390-650 F GAS OIL YIELD

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 6

650-975 GAS OIL YIELD

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 7

975 F+ RESIDUAL OIL YIELD

Run 227-62 (CC-5) and 227-55 (CC-1)

4 of 7

FIGURE 8

RESIDUAL OIL CONCENTRATION IN PRODUCT SLURRY

Runs 227-55(CC-1) and 227-62(CC-5)

FIGURE 9

CARBON OXIDES YIELDS

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 10

TOTAL WATER YIELDS

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 11

OXYGEN ELIMINATION IN WATER AND CARBON OXIDE:

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 12

C4-975 DISTILLATE YIELD

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 13

HYDROGEN CONSUMPTION

Run 227-62 (CC-5) and 227-55 (CC-1)

FIGURE 14

HYDROGEN CONTENT OF PRODUCT FRACTIONS

Runs 227-55(CC-1) and 227-62(CC-5)

FIGURE 15

NITROGEN CONTENT OF PRODUCT FRACTIONS

Runs 227-55(CC-1) and 227-62(CC-5)

227 UNIT SLURRY PRETREATMENT SYSTEM

FEED TANK

GAS/LIQUID
SEPARATOR

DRYING TANK

FIGURE 16

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SECTION VI

RUN 227-64 (CC-7) - REACTOR CONFIGURATION STUDY: CATALYTIC/THERMAL VS. THERMAL/CATALYTIC WITH DISPERSED IRON OXIDE ADDITIVE

SUMMARY

The objective of this run was to study the effect of two different reactor configurations, catalytic/thermal and thermal/catalytic, in a two-stage liquefaction system with sub-bituminous coal. The catalytic stage is the normal ebullated-bed reactor holding supported catalyst while the thermal stage does not contain any supported catalyst. The run was conducted using an iron oxide additive (dispersed catalyst). This additive had been tested before in Run 227-61(CC-4) and was found to improve process performance. This additive would provide the only catalytic activity in the thermal stage and would provide an incremental activity in the catalytic stage.

The run was conducted using Black Thunder mine sub-bituminous coal. The catalytic stage contained partially deactivated NiMo catalyst (Shell S-317 catalyst recovered from earlier bench runs). Its temperature was maintained at 750°F. The temperature of the thermal stage was varied from 825 to 840°F, and the space velocity was varied from 44 to 67 lb/hr/ft³ (supported catalyst). Iron oxide additive was added at about 5.5 W% of dry coal. Hydrogen sulfide was injected continuously at about 5 W%.

In catalytic/thermal mode of operation, increasing the thermal stage temperature from 825°F to 840°F increased the C₄-975°F distillate by 2.0 W% (maf) as the 3.5 W% (maf) higher 975°F⁺ conversion outpaced the 1.9 W% (dry coal) higher gas yield. With the thermal stage at 840°F, the catalytic/thermal configuration gave higher coal and 975°F⁺ conversions relative to the thermal/catalytic configuration. The coal and 975°F⁺ conversions were 93.3 W% and 89.0 W% for the catalytic/ thermal configuration and 91.2 W% and 87.8 W% for the thermal/catalytic configuration.

The 975°F⁺ conversion, distillate yield, and product quality in Run 227-64(CC-7), with only one catalytic stage, were inferior to these measures of performance in Run 227-61 (CC-4), with supported catalyst in both stages. Compared with the catalytic/thermal configuration in Run 227-64(CC-7) Condition 1, the 975°F⁺ conversion was 2.0 W% (maf) higher, the C₄-975°F distillate yield was 6.1 W% higher, and the denitrogenation was 19.5 W% higher for the catalytic/catalytic operations.

SCOPE OF WORK

In the discussion of this run, the term "catalytic" means that the reactor contains supported catalyst and is operated as an ebullated bed reactor while "thermal" means that there is no supported catalyst. Dispersed (additive) catalyst provides the catalytic activity in the thermal stage. Both reactors were the same volume.

Run 227-64(CC-7), with Black Thunder mine sub-bituminous coal feed, was conducted in two parts. In the first part, supported catalyst was charged to the first stage, and the second stage was empty. The run was then halted; catalyst from the first stage was withdrawn and transferred to the second stage, and the run was resumed.

The additive was an iron oxide. It had been tested previously in Run 227-61(CC-4), during which it had improved the liquefaction performance in the catalytic/catalytic mode of operation. A continuous stream of hydrogen sulfide was used to activate this additive. Partially deactivated Shell S-317 NiMo catalyst (recovered from the earlier run 227-62(CC-5)) along with a small amount of fresh S-317 catalyst was used in the catalytic reactor. All fresh catalyst was not used as its rapid deactivation in the early part of the run would have obscured the response of other operating variables.

The run conditions are shown in *Table 1*. The plan called for five operating conditions over 20 (+1/3) days. The reactors were configured for catalytic/thermal operation in the first two conditions and for thermal/catalytic operation for later conditions. Iron oxide and H₂S were added at 5.2 W% and 3.8 W% of coal, respectively. The catalytic stage was maintained at 750°F throughout the run. In Condition 1, the thermal stage was at 825°F. It was raised to 840°F in Condition 2. The order of the catalytic and thermal reactors was reversed in Condition 3. In Condition 4, the space velocity was reduced from 67 to 44 lb/hr/ft³ (catalyst). The thermal stage temperature was reduced to 825°F in Condition 5, keeping the lower space velocity.

PROGRAM RESULTS AND ANALYSES RUN 227-64 (CC-7)

Table 2 is the Operating Summary for the run, giving the principal operating conditions for each Period (day), and normalized product distributions for periods that were considered to represent equilibrated results. *Table 3* shows the yields and process performance for the five conditions, using averages of the results when yields were calculated for more than one period in a condition.

Coal And 975°F Conversion

Coal conversions were calculated by making the same ash adjustments for the iron additive that were discussed in the Run 227-61(CC-4) section.

Coal and resid (975°F) conversions are shown in *Figure 1*. In Condition 1 (catalytic/thermal; 750/825°F), the coal conversion was 90.4 W% (maf), and the resid conversion was 85.5 W% (maf). When the thermal stage temperature was increased to 840°F in Condition 2, the coal conversion increased by about 3 W%, and resid conversion increased by about 4.5 W%. In Condition 3, the reactor configuration was switched from catalytic/thermal to thermal/catalytic. This change resulted in a 2.1 W% decrease in coal conversion and a 1.2 W% decrease in resid conversion. When the space velocity was decreased in Condition 4, there was only a minor increase in coal conversion and no change in resid conversion. The resid conversion also remained essentially unchanged in Condition 5 when the thermal stage temperature was decreased to 825°F, but the coal conversion decreased from 92.4 to 90.8 W%.

Normalized Product Distribution

Figures 2 and 3 show distillate yields and *Figure 4* shows distillate selectivity. In catalytic/thermal configuration, higher C₄-975°F distillate yield was obtained with the thermal stage at 840°F than at 825°F, 60.5 W% (maf) vs. 58.5 W%, despite the 1.9 W% (dry coal) increase in C₁-C₃ gas yield. The distillate yield was lower for the thermal/catalytic configuration (Condition 3) than for the catalytic/thermal configuration (Condition 2), decreasing from 60.5 W% (maf) to 58.1 W% as the C₁-C₃ gas yield increased from 11.3 to 13.5 W% (dry coal) and the 975°F conversion decreased by 1.2 W% (maf). Increasing the thermal stage temperature from 825°F to 840°F was counterproductive (Condition 4) as the 2.75 W% (dry coal) higher gas yield resulted in 2.2 W% (maf) lower distillate yield. Although the thermal/catalytic configuration tended to give the lower distillate yield, the distillate slate was lighter with more naphtha content. In Condition 5 (thermal/catalytic, 825°F/750°F, lower space velocity), the distillate yield, 59.0 W% (maf), was comparable to the distillate yield in catalytic/catalytic operations, and at the same time, the products were lighter. However, the lower space velocity was required.

Heteroatom Removal

The H₂S and NH₃ yields and the hydrodenitrogenation (HDN) are included in *Table 3*, and the denitrogenation is plotted in *Figure 2*. The yield of H₂S was negative because the added dispersed catalyst caused its net consumption through additive sulfidation. The HDN was, in general, much higher for the thermal/catalytic configuration, averaging 70.1 W% for Conditions 3 and 4 compared to 56.3 W% for Conditions 1 and 2. The relatively low 53.9 W% HDN for Condition 5 (thermal/catalytic operation at 825°F and lower space velocity) is

not easily explainable, except for the small decrease due to additional catalyst deactivation.

Product Quality

Table 4 shows analyses of the product streams removed from the unit. The quality of the Separator Overhead (SOH) and Atmospheric Still Overhead (ASOH) was generally better for the operations with the thermal/catalytic reactor configuration. Comparing the SOH and ASOH from Condition 3 with these products from Condition 2, the hydrogen contents were higher by about 0.4 W%, the nitrogen contents were lower by about 65 %, and the Watson Characterization Factors increased by 0.16.

Tables 5 and 6 show analyses of the first-stage and second-stage (PFL) liquid products, distillation fractions, and THF-washed solids. The first-stage samples were withdrawn at the end of each condition. The PFL fractions also show the improved product quality obtained with the thermal/catalytic operation in Condition 3. Compared to Condition 2 (catalytic/thermal), the hydrogen contents were 0.11 to 0.58 W% higher, the nitrogen contents were 0.17 to 0.24 W% lower, and the gravities were 0.4 to 4.8 API higher. In each case, the lowest difference is for the 650-850°F fraction, and the highest difference is for the 975°F+ fraction, with intermediate differences for the 850-975°F fraction. It is logical that there should be higher product quality in the thermal/catalytic operations, in which most of the products formed have a chance to be upgraded in the second stage. When most of the products are formed in the thermal second stage, there is no opportunity for upgrading.

The product quality of the three defined liquid fractions (650-850°F, 850-975°F, and 975°F+) declined markedly in the second (thermal) stage during Condition 1 and even more during Condition 2 with the second stage temperature increased to 840°F. These differences between the first and second stage are listed below:

Differences between First and Second Stage Product Quality:

Condition	Hydrogen, W%		Gravity, API		Nitrogen, W%	
	<u>1</u>	<u>2</u>	<u>1</u>	<u>2</u>	<u>1</u>	<u>2</u>
650-850°F	-0.43	-0.68	-1.3	-2.2	+0.17	+0.15
850-975°F	-0.67	-1.16	-3.7	-5.2	+0.15	+0.27
975°F+	-0.82	-1.43	-5.1	-8.4	+0.26	+0.13

These changes in product quality were much greater than had been experienced in previous runs with catalyst in both stages. Thus, even in the higher temperature stage where hydrogenation and HDN are not favored by the shifted

equilibrium, the presence of catalyst helps maintain the quality of the products as they are formed.

First Stage Coal Conversion

The coal conversions calculated from the analyses of the solids portion of the first stage samples are shown along with the two-stage conversions in *Table 7*. The first stage coal conversions for the 750°F catalytic reactor in Conditions 1 and 2 were 65.1 and 71.4 W% of maf coal, very similar to previous first stage coal conversions at the same conditions. In the thermal/catalytic configuration, almost all coal conversion was completed in the first stage.

Hydrogen Consumption

Figure 5 shows the hydrogen consumption for the five conditions. The hydrogen consumption increased from 6.34 W% (dry coal) to 7.01 W% when the second stage temperature was increased from 825°F to 840°F in Condition 2. The hydrogen consumption was also higher for the thermal/catalytic configuration (7.21 % in Condition 3) because of increased hydrogenation and heteroatom removal and higher gas yields. With the lower space velocity in Condition 4, the hydrogen consumption increased to 7.78 W%.

Comparison of Catalytic/Thermal and Catalytic/Catalytic Configurations

The iron oxide additive and the Black Thunder coal used in this run were also used in Run 227-61(CC-4). It is possible to make a direct comparison between catalytic/catalytic and catalytic/thermal configurations from Condition 2 of Run 227-61(CC-4) and Condition 1 of Run 227-64(CC-7). The reactor temperatures and space velocity were identical in these conditions. The comparison is shown in *Table 8* and in *Figures 6 through 8*.

Catalytic/thermal mode of operation gave 2.3 W% (maf) higher coal conversion than did catalytic/catalytic. Typically, conversion of sub-bituminous coals is quite sensitive to residence time, which was less in the catalytic/catalytic mode of operation due to catalyst displacement of reactor volume. However, 975°F+ conversion and distillate yield were higher in the catalytic/catalytic configuration by 2.0 and 6.1 W% (maf), respectively. The process performance in this configuration was superior with less gas yield and a lighter distillate slate. Hydrogen consumption was higher, but it was used efficiently to produce a better quality product.

The above comparison was for the two reactor configurations at identical reactor temperatures. The conclusions remain valid even when the comparison is made between the catalytic/catalytic performance shown in *Table 8* and the catalytic/thermal performance in Condition 2 of Run 227-64(CC-7) at higher thermal stage temperature. The catalytic/catalytic configuration would also give

higher distillate yield than would the thermal/catalytic configuration because the latter gave less yield than the catalytic/thermal configuration.

DETAILS OF OPERATION

The start-up commenced January 4, 1990 after charging catalyst to the first stage. The supported catalyst was sulfided prior to coal cut-in by holding the catalyst at several temperatures in the presence of flowing hydrogen sulfide. Condition 1 and 2 were completed successfully with no major operational problems except for a power failure for two minutes in Condition 1. The run was halted at the end of Condition 2 (Period 9A), and the unit was cooled down.

The catalyst was removed from the first stage, washed, and screened to +20 mesh, and then charged to the second stage after adding a small amount of fresh Shell S-317 catalyst to make up the catalyst charge to the required volume. The run was restarted, with Condition 3 commencing January 18, 1990. The run continued smoothly and was terminated at the conclusion of Condition 5 (Period 21A).

COAL FEED

The bench run was conducted using Black Thunder mine sub-bituminous coal. Two shipments of Black Thunder coal were used, HRI-5630 for the first two conditions and HRI-5713 for the last three conditions. As shown in *Table 9*, the analyses of the two coal shipments were fairly similar. The HRI-5713 coal did have a somewhat higher ash, 6.65 W% compared to 5.74 W% (SO₃-free) for the HRI-5630 coal. Also, the coal conversion for the HRI-5713 coal was higher by 3.7 W% (maf) in thermal microautoclave tests and 1.9 W% higher in catalytic microautoclave tests.

The feed coal was screened to -70 mesh and dried under nitrogen to obtain moisture contents between 5 and 10 W%.

START-UP OIL

The run was started using HRI-648, an Illinois coal-derived heavy distillate obtained from Wilsonville. The analyses are shown in *Table 10*. Most of the recycle oil requirements were met from the filter liquid produced at that time. Only on a few occasions the amount of liquid produced was insufficient. In such cases, filter liquid generated in the run at an earlier time was used as make-up oil.

CATALYST

The supported catalyst in Run 227-64(CC-7) was charged to the first stage for Conditions 1 and 2 and then transferred to the second stage. It was a blend of fresh Shell S-317 1/32-in NiMo catalyst (16.8 V%, 12.5 W%) and recovered Shell S-317 catalyst (83.2 V%, 87.5 W%) from the first stage of Run 227-62(CC-5). The (weight) average catalyst analyses are shown in *Table 11*. The catalyst was

sulfided during the start-up by injecting H_2S continuously and holding the catalyst bed at several temperatures prior to feeding coal.

The additive used in the run was an iron oxide (62.9 W% Fe) supplied by Wright Industries of Brooklyn, New York and labelled as magnetic pigment. The analyses are shown in *Table 12*. This same additive had been used in Run 227-61(CC-4).

RECOVERED CATALYST

Table 13 shows analyses of the recovered catalyst. Compared with the charged catalyst in *Table 11*, the recovered catalyst picked a substantial amount of additional carbon. The catalyst carbon content increased from 11.9 W% to 16.7 W% even though the catalytic stage was never hotter than 750°F. The metal contaminants also increased, and the final pore volume was a relatively low 0.34 cc/g.

TABLE 1
RUN PLAN - (CC-7)

RUN 227-64

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
PERIOD	<u>1A-6A</u>	<u>6B-9B</u>	<u>10A-15A</u>	<u>15B-19A</u>	<u>19B-21A</u>
NOMINAL CONDITIONS					
<u>SPACE VELOCITY</u>					
Lbs Coal/Hr/Ft ³ Catalyst	67	67	67	44	44
<u>RECYCLE RATE</u>					
PFL/Fresh Feed	1.1	1.1	1.1	1.1	1.1
<u>TEMPERATURE, °F</u>					
Reactor 1	750	750	840	840	825
Reactor 2	825	840	750	750	750
BACK PRESSURE, PSIG					
	2500	2500	2500	2500	2500
Additive Rate **, W% Dry Coal	5.2	5.2	5.2	5.2	5.2
H ₂ S Rate, W% Dry Coal	3.8	3.8	3.8	3.8	3.8

Catalyst was charged to first stage; second stage contained no catalyst. After Period 9 unit was cooled and catalyst transferred from first to second stage.

** Magnetic pigment (iron oxide, HRI-5723) was used as additive.

TABLE 2

Part 1 of 4

CTSL™ THERMAL/CATALYTIC/DISPERSED CATALYST RUN

COAL: BLACK THUNDER MINE (HRI-5630/5713)
 CATALYST: PERIODS 1-8: RECOVERED NiMo CATALYST IN ST 1, NONE IN ST2
 PERIODS 10-17: RECOVERED NiMo CATALYST IN ST2, NONE IN ST1
 H₂S PLUS DISPERSED ADDITIVE (HRI-5723)

Period Number	1	2	3	4	5
Date (Start of Period)	1/06/90	1/07/90	1/08/90	1/09/90	1/10/90
Hours of Run (End of Period)	24	48	72	96	120
Catalyst Age, Lb Dry Coal/Lb Cat	510	552	594	636	679
First Stage Temperature °F	732	747	746	748	748
Second Stage Temperature °F	783	819	822	825	824
Unit Back Pressure, PSIG	2519	2519	2517	2516	2505
Space Velocity, Lb/Hr/Ft ³ Supported Cat	62.9	67.1	67.8	66.0	67.8

W% OF DRY COAL

PFL Recycle	128.3	108.6	108.6	108.6	108.6
PFL to Buffer - Stage 1	1.8	2.5	2.6	2.9	2.8
PFL to Buffer - Stage 2	3.1	2.7	2.6	2.8	2.7
Make-up Oil					
H ₂ S	3.7	2.2	4.7	4.6	4.4
Additive	6.0	5.5	5.5	5.5	5.5

TOTAL MATERIAL RECOVERY (GROSS)	94.77	98.37	97.27	99.37	98.20
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ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases				9.29	9.49
C ₄ -C ₇ in Gases				4.89	4.62
IBP-390°F in Liquids				8.65	9.56
390-500°F in Liquids				9.34	9.70
500-650°F in Liquids				15.73	16.27
650-850°F in Liquids				13.40	12.84
850-975°F in Liquids				2.65	2.52
Toluene Soluble 975°F+ Oil				3.95	4.39
Toluene Insoluble 975°F+ Oil				0.62	0.21
Unconverted Coal				8.99	9.27
Ash (SO ₃ -free)				6.60	6.60
Water				18.53	17.17
CO				0.92	1.00
CO ₂				3.20	3.19
NH ₃				0.66	0.67
H ₂ S				-1.09	-1.16
Total (100 + H ₂ Reacted)				106.32	106.35

PROCESS PERFORMANCE

G ₄ -975°F Distillates, W% of MAF Coal				58.0	58.9
975°F+ Conversion, W% MAF				85.6	85.3
Coal Conversion, W% MAF		89.1	89.4	90.5	90.2
HDS, W%					
HDN, W%				56.9	57.9

CTSL™ THERMAL/CATALYTIC/DISPERSED CATALYST RUN

COAL: BLACK THUNDER MINE (HRI-5630/5713)
 CATALYST: PERIODS 1-8: RECOVERED NiMo CATALYST IN ST 1, NONE IN ST2
 PERIODS 10-17: RECOVERED NiMo CATALYST IN ST2, NONE IN ST1
 H₂S PLUS DISPERSED ADDITIVE (HRI-5723)

Period Number	6	7	8	9	10
Date (Start of Period)	1/11/90	1/12/90	1/13/90	1/14/90	1/18/90
Hours of Run (End of Period)	144	168	192	198	211
Catalyst Age, Lb Dry Coal/Lb Cat	719	760	801	813	830
First Stage Temperature °F	747	749	750	747	765
Second Stage Temperature °F	831	838	838	820	720
Unit Back Pressure, PSIG	2500	2497	2498	2499	2501
Space Velocity, Lb/Hr/Ft ³ Supported Cat	64.2	65.1	65.6	77.6	48.7

W% OF DRY COAL

PFL Recycle	93.9	105.8	110.0	110.0	202.4
PFL to Buffer - Stage 1	2.7	2.9	2.7	1.8	3.7
PFL to Buffer - Stage 2	2.7	2.6	2.3	1.7	3.4
Make-up Oil					
H ₂ S	4.7	4.9	4.7	4.7	7.9
Additive	5.5	5.6	5.3	5.6	7.9
TOTAL MATERIAL RECOVERY (GROSS)	99.03	99.08	97.58	91.13	99.48

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	11.33
C ₄ -C ₇ in Gases	5.64
IBP-390°F in Liquids	10.82
390-500°F in Liquids	10.23
500-650°F in Liquids	15.66
650-850°F in Liquids	12.69
850-975°F in Liquids	2.02
Toluene Soluble 975°F Oil	2.93
Toluene Insoluble 975°F Oil	1.14
Unconverted Coal	6.32
Ash (SO ₃ -free)	6.57
Water	17.43
CO	1.23
CO ₂	3.71
NH ₃	0.64
H ₂ S	-1.37
Total (100 + H ₂ Reacted)	107.01

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal	60.5
975°F Conversion, W% MAF	89.0
Coal Conversion, W% MAF	93.2
HDS, W%	93.3
HDN, W%	55.1

CTSL™ THERMAL/CATALYTIC/DISPERSED CATALYST RUN

COAL: BLACK THUNDER MINE (HRI-5630/5713)
 CATALYST: PERIODS 1-8: RECOVERED NiMo CATALYST IN ST 1, NONE IN ST2
 PERIODS 10-17: RECOVERED NiMo CATALYST IN ST2, NONE IN ST1
 H₂S PLUS DISPERSED ADDITIVE (HRI-5723)

Period Number	11	12	13	14	15
Date (Start of Period)	1/19/90	1/20/90	1/21/90	1/22/90	1/23/90
Hours of Run (End of Period)	235	259	283	307	331
Catalyst Age, Lb Dry Coal/Lb Cat	869	910	953	996	1029
First Stage Temperature °F	821	838	838	838	838
Second Stage Temperature °F	745	751	751	750	748
Unit Back Pressure, PSIG	2504	2490	2474	2500	2498
Space Velocity, Lb/Hr/Ft ³ Supported Cat	66.4	65.8	68.0	68.7	52.9

W% OF DRY COAL

PFL Recycle	109.7	106.9	93.8	103.1	108.5
PFL to Buffer - Stage 1	2.8	2.7	2.8	2.7	3.6
PFL to Buffer - Stage 2	2.4	2.5	2.7	2.7	3.1
Make-Up Oil			13.5	9.5	
H ₂ S	4.4	4.5	4.1	4.5	3.7
Additive	5.6	5.5	5.5	5.5	5.3

TOTAL MATERIAL RECOVERY (GROSS)	99.69	97.86	99.50	99.03	99.99
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ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	12.91	14.11
C ₄ -C ₇ in Gases	6.27	6.75
IBP-390°F in Liquids	12.89	14.18
390-500°F in Liquids	10.91	12.17
500-650°F in Liquids	15.02	14.79
650-850°F in Liquids	7.74	7.01
850-975°F in Liquids	0.10	0.58
Toluene Soluble 975°F Oil	3.76	1.55
Toluene Insoluble 975°F Oil	0.56	0.45
Unconverted Coal	8.36	8.15
Ash (SO ₃ -free)	7.51	7.51
Water	17.51	16.63
CO	1.50	1.38
CO ₂	2.82	2.86
NH ₃	0.76	0.79
H ₂ S	-1.58	-1.56
Total (100 + H ₂ Reacted)	107.05	107.36

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal		56.7	59.4
975°F Conversion, W% MAF		86.4	89.1
Coal Conversion, W% MAF	86.7	90.3	91.0
HDS, W%		91.0	91.3
HDN, W%		68.9	71.2

CTSL™ THERMAL/CATALYTIC/DISPERSED CATALYST RUN

COAL: BLACK THUNDER MINE (HRI-5630/5713)
 CATALYST: PERIODS 1-8: RECOVERED NiMo CATALYST IN ST 1, NONE IN ST2
 PERIODS 10-17: RECOVERED NiMo CATALYST IN ST2, NONE IN ST1
 H₂S PLUS DISPERSED ADDITIVE (HRI-5723)

Period Number	16	17	18	19	20
Date (Start of Period)	1/24/90	1/25/90	1/26/90	1/27/90	1/28/90
Hours of Run (End of Period)	355	379	403	427	451
Catalyst Age, Lb Dry Coal/Lb Cat	1058	1087	1115	1143	1170
First Stage Temperature °F	839	839	838	828	825
Second Stage Temperature °F	749	751	750	750	750
Unit Back Pressure, PSIG	2497	2496	2496	2496	2496
Space Velocity, Lb/Hr/Ft ³ Supported Cat	45.3	45.6	45.8	43.3	43.8

W% OF DRY COAL

PFL Recycle	89.0	94.1	88.7	95.9	105.1
PFL to Buffer - Stage 1	3.7	3.7	3.5	3.9	3.9
PFL to Buffer - Stage 2	4.3	4.1	4.1	4.2	4.1
Make-Up Oil		13.1	18.9		6.9
H ₂ S	4.4	3.6	6.3	5.0	5.4
Additive	5.4	5.4	5.4	5.7	5.7

TOTAL MATERIAL RECOVERY (GROSS)	98.52	100.28	98.36	98.70	100.86
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ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	16.53	15.98	13.17
C ₄ -C ₇ in Gases	7.47	6.31	6.72
IBP-390°F in Liquids	15.44	16.13	15.19
390-500°F in Liquids	12.39	12.54	11.71
500-650°F in Liquids	16.78	18.73	15.65
650-850°F in Liquids	3.09	3.05	6.74
850-975°F in Liquids	-3.17	-4.51	-0.89
Toluene Soluble 975°F Oil	3.06	4.54	2.81
Toluene Insoluble 975°F Oil	0.50	0.81	0.44
Unconverted Coal	8.08	6.03	8.55
Ash (SO ₃ -free)	7.50	7.50	7.54
Water	17.06	17.39	17.33
CO	1.21	1.36	1.27
CO ₂	2.21	2.17	2.15
NH ₃	0.77	0.76	0.60
H ₂ S	-0.99	-1.15	-1.25
Total (100 + H ₂ Reacted)	107.94	107.62	107.73

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal		55.7	56.0	59.0
975°F Conversion, W% MAF		87.5	87.8	87.4
Coal Conversion, W% MAF	92.5	91.3	93.5	90.8
HDS, W%				
HDN, W%		69.3	68.6	53.9

TABLE 3

SUMMARY OF RESULTS - CC-7

RUN 227-64 (CC-7)

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
PERIOD	<u>4/5</u>	<u>8</u>	<u>13/14</u>	<u>17/18</u>	<u>20</u>
TEMPERATURE, °F					
First Stage	748	750	838	839	825
Second Stage	825	838	757	751	750
SPACE VELOCITY					
Lbs Coal/Hr/Ft ³ Catalyst	66.9	65.6	68.4	45.8	43.8
CATALYST AGE (LB COAL/LB CATALYST)	658	807	975	1101	1170
ADDITIVE, W% DRY COAL	5.5	5.3	5.5	5.4	5.7
H ₂ S, W% COAL	4.5	4.7	4.3	5.0	5.4
YIELDS (% OF DRY COAL)					
C ₁ -C ₃	9.39	11.33	13.51	16.26	13.17
C ₄ -390°F	13.86	16.46	20.05	22.68	21.91
390-500°F	9.52	10.23	11.54	12.47	11.71
500-650°F	16.00	15.66	14.91	17.76	15.65
650-850°F	13.12	12.69	7.38	3.07	6.74
850-975°F	2.59	2.02	0.34	-3.84	-0.89
985°F+ Liquid	4.59	4.07	3.16	4.46	3.25
Unconverted Coal + Ash	15.73	12.79	15.77	14.56	16.09
Water	17.85	17.43	17.07	17.23	17.33
CO + CO ₂	4.16	4.94	4.28	3.48	3.42
NH ₃	0.67	0.64	0.78	0.77	0.60
H ₂ S	-1.13	-1.37	-1.57	-1.07	-1.25
TOTAL (100+H ₂ Consumption)	106.34	107.01	107.21	107.78	107.73
PROCESS PERFORMANCE					
Coal Conversion, W% MAF	90.4	93.3	91.2	92.4	90.8
975°F Conversion, W% MAF	85.5	89.0	87.8	87.7	87.4
C ₄ -975°F Yield, W% MAF	58.5	60.5	58.1	55.9	59.0
Hydrodenitrogenation	57.4	55.1	71.1	60.5	53.9

Negative yield represents net consumption of that particular cut when make-up oil was used.

Negative yield of H₂S indicates net H₂S consumption by the additive.

TABLE 4
ANALYSES OF PRODUCTS - CC-7
RUN 227-64 (CC-7)

CONDITION NUMBER	1	2	3	4	5
PERIOD	<u>5</u>	<u>8</u>	<u>14</u>	<u>18</u>	<u>20</u>
CATALYST AGE (LB COAL/LB CATALYST)	679	807	996	1115	1170
<u>SEPARATOR OVERHEAD</u>					
Volume Average BP, °F	488	486	451	430	436
°API Gravity	24.7	24.6	28.7	30.3	30.1
Watson Characterization Factor	10.67	10.66	10.82	10.82	10.83
Carbon, W%	85.83	86.28	87.13	87.02	87.11
Hydrogen, W%	11.54	11.61	12.04	12.27	12.35
Nitrogen, W%	0.40	0.43	0.29	0.33	0.47
Sulfur, W%	0.05	0.04	0.07	0.04	0.04
<u>ATMOSPHERIC OVERHEAD</u>					
Volume Average BP, °F	470	469	466	481	475
°API Gravity	21.7	20.8	23.4	22.2	22.9
Watson Characterization Factor	10.51	10.47	10.63	10.60	10.64
Carbon, W%	85.44	84.96	86.40	87.38	86.66
Hydrogen, W%	11.81	11.17	11.54	11.42	11.63
Nitrogen, W%	0.46	0.53	0.34	0.43	0.46
Sulfur, W%	0.03	0.03	0.03	0.03	0.06
<u>CALCULATED CAS BOTTOMS</u>					
IBP-975°F, W%	60.27	60.04	63.63	62.04	63.35
975°F* Toluene Soluble Oil	25.29	20.51	20.49	21.61	21.49
975°F* Toluene Insoluble	1.211	7.98	3.24	3.30	3.08
IOM	6.27	3.84	5.38	4.74	5.25
ASH	6.96	5.94	7.25	8.32	6.84

On an SO₃-Free basis, including additives

TABLE 5
ANALYSES OF FIRST-STAGE LIQUIDS SOLIDS - CC-7
RUN 227-64 (CC-7)

CONDITION NUMBER	1	2	3	4	5
PERIOD	6A	9A	15A	19A	21A
CATALYST AGE (LB COAL/LB CATALYST)	679	801	996	1115	1170
LIQUID					
°API	-0.8	-0.5	-8.2		-8.1
Carbon, W%	89.17	89.02	90.10	90.21	90.05
Hydrogen, W%	8.78	8.77	7.66	7.32	7.11
Nitrogen, W%	0.80	0.80	0.98	0.90	0.90
Sulfur, W%	0.023	0.016	0.065	0.044	0.040
IBP-650°F, W%	10.16	9.44	14.28		10.47
650-850°F, W%	35.73	38.52	32.06		35.55
850-975°F, W%	16.90	19.63	15.42		15.81
975°F, W%	37.21	32.41	38.24	36.69	38.17
IBP-650°F					
°API	16.0	15.3	18.5		11.17
Carbon, W%	87.69	88.18	87.45		87.80
Hydrogen, W%	11.03	10.93	10.88		10.17
Nitrogen, W%	0.56	0.54	0.46		0.61
Sulfur, W%	0.030	0.005	0.048		0.040
650-850°F					
°API	8.2	7.7	3.0		2.3
Carbon, W%	88.61	88.63	89.57		90.03
Hydrogen, W%	9.89	9.90	8.70		8.67
Nitrogen, W%	0.54	0.53	0.66		0.61
Sulfur, W%	0.026	0.009	0.035		0.032
850-975°F					
°API	-1.7	-1.1	-8.0		-8.3
Carbon, W%	89.42	89.87	90.53		90.78
Hydrogen, W%	8.68	8.86	7.44		7.26
Nitrogen, W%	0.79	0.68	0.90		0.90
Sulfur, W%	0.032	0.027	0.048		0.029
975°F					
°API	-9.5	-9.9	-16.3		-16.9
Carbon, W%	88.88	88.96	90.63		91.17
Hydrogen, W%	7.21	7.07	8.82		5.67
Nitrogen, W%	1.13	1.20	1.44		1.26
Sulfur, W%	0.054	0.068	0.066		0.062
SOLIDS (THF Washed)					
Carbon, W%	58.04	53.35	31.52	31.33	34.92
Hydrogen, W%	3.92	3.40	1.61	1.66	1.85
Nitrogen, W%	1.11	1.01	0.46	0.41	0.53
Sulfur, W%	4.18	5.33	9.53	11.00	8.33
Ash, W%	27.45	34.37	62.28	65.29	58.68

Complete analyses could not be done because of sample.

TABLE 6

**ANALYSES OF PRESSURE FILTER LIQUIDS/SOLIDS - CC-7
RUN 227-64 (CC-7)**

CONDITION NUMBER	1	2	3	4	5
PERIOD	5	8	14	18	20
CATALYST AGE (LB COAL/LB CATALYST)	679	801	996	1115	1170
LIQUID					
°API	-2.8	-6.6	-1.6	-3.9	-2.3
Carbon, W%	89.39	88.38	90.42	90.32	90.25
Hydrogen, W%	8.41	7.86	8.38	8.04	8.24
Nitrogen, W%	0.96	0.93	0.68	0.72	0.87
Sulfur, W%	0.027	0.021	0.019	0.011	0.005
IBP-650°F, W%	11.99	9.80	15.89	17.21	14.42
650-850°F, W%	40.73	41.13	42.88	41.44	43.93
850-975°F, W%	16.73	15.62	14.05	12.70	13.70
975°F, W%	30.55	33.45	27.18	28.65	27.95
IBP-650°F					
°API	13.3	12.2	13.7	12.4	13.1
Carbon, W%	88.16	88.22	88.91	88.93	88.78
Hydrogen, W%	10.39	10.34	10.49	10.70	10.46
Nitrogen, W%	0.72	0.86	0.30	0.48	0.26
Sulfur, W%	0.029	0.020	0.002	0.024	0.006
650-850°F					
°API	6.9	5.5	5.9	4.0	5.5
Carbon, W%	89.17	89.46	89.83	90.07	89.91
Hydrogen, W%	9.46	9.22	9.33	9.42	9.31
Nitrogen, W%	0.71	0.68	0.51	0.69	0.62
Sulfur, W%	0.023	0.030	0.021	0.010	0.007
850-975°F					
°API	-5.4	-6.3	-5.0	-6.8	-5.7
Carbon, W%	90.10	90.30	90.47	90.90	91.58
Hydrogen, W%	8.01	7.70	7.89	7.89	7.84
Nitrogen, W%	0.94	0.95	0.73	0.75	0.87
Sulfur, W%	0.045	0.035	0.021	0.006	0.013
975°F					
°API	-14.6	-18.3	-13.5	-13.8	-15.6
Carbon, W%	89.88	89.24	91.42	91.32	91.77
Hydrogen, W%	6.39	5.64	6.22	5.87	6.06
Nitrogen, W%	1.39	1.33	1.09	1.14	1.13
Sulfur, W%	0.049	0.069	0.023	0.014	0.024
SOLIDS (THF Washed)					
Carbon, W%	32.64	27.11	28.61	25.04	30.17
Hydrogen, W%	1.89	1.47	1.34	1.07	1.38
Nitrogen, W%	0.54	0.41	0.44	0.38	0.45
Sulfur, W%	10.80	12.10	9.27	11.00	9.27
Ash, W%	61.09	58.43	68.55	73.78	66.58

TABLE 7
COAL CONVERSION
RUN 227-64 (CC-7)

<u>CONDITION</u>	<u>Coal Conversion, W% of MAF Coal</u>	
	<u>First-Stage</u>	<u>Two-Stage</u>
1	65.1	90.4
2	71.4	93.3
3	90.4	91.2
4	90.8	92.4
5	88.6	90.8

TABLE 8

COMPARISON BETWEEN REACTOR CONFIGURATION

CONFIGURATION RUN CONDITION PERIOD	CATALYTIC/CATALYTIC CC-4 2	CATALYTIC/THERMAL CC-7 1
<u>CATALYST AGE (LB COAL/LB CAT)</u>		
First Stage	717	658
Second Stage	1088	---
<u>REACTOR TEMPERATURE, °F</u>		
First Stage	751	748
Second Stage	825	825
SPACE VELOCITY (LB COAL/HR/FT ³ CAT)	68.9	66.9
ADDITIVE RATE (W% COAL)	5.2	5.5
H ₂ S RATE (W% COAL)	1.8	4.5
<u>YIELDS (W% COAL, MAF)</u>		
C ₁ -C ₃	8.75	9.96
C ₄ -390°F	20.58	14.70
390-500°F	11.71	10.10
500-650°F	21.54	16.97
650-850°F	10.02	13.92
850-975°F	0.71	2.75
975°F+ Liquid	0.62	4.87
Unconverted Coal	11.9	9.69
Water	20.68	18.94
CO+CO ₂	2.15	4.41
NH ₃	0.90	0.71
H ₂ S	-1.93	-1.20
Hydrogen Consumption (W% MFD)	8.60	6.73
Coal Conversion (W% MAF)	88.1	90.4
975°F+ Conversion (W% MAF)	87.5	85.5
HDN, (W%)	76.9	57.4
C ₄ -975°F Yield (W% MAF)	64.6	58.5

TABLE 9

FEED COAL ANALYSES

RUN 227-64 (CC-7)

HRI NUMBER

5630

5713

TYPE

<----- Black Thunder Sub-Bituminous ----->

PROXIMATE ANALYSIS, (W%, MAF)

Volatile Matter	44.2
Fixed Carbon	55.8

ULTIMATE ANALYSIS, W% DRY BASIS

Carbon	68.01	67.57
Hydrogen	4.71	4.75
Nitrogen	0.96	0.91
Sulfur	0.41	0.46
Ash	6.60	7.66
SO ₃ - Free	5.74	6.65

SULFUR TYPES (W%)

Sulfate	0.04
Pyritic	0.11
Organic	0.36

MINERAL ANALYSIS, (W%, IGNITED BASIS)

Silica	34.61	36.16
Alumina	16.98	17.54
Titanium Oxide	1.30	1.27
Iron Oxide	6.94	5.01
Calcium Oxide	21.74	19.69
Magnesium Oxide	4.40	3.99
Potassium Oxide	0.35	0.43
Sodium Oxide	0.97	0.39
Sulfur Trioxide	10.74	12.93
Phosphorous Pentoxide	1.01	0.89
Strontium Oxide	0.29	0.95
Barium Oxide	0.37	0.64
Manganese Oxide	0.00	0.11
Undetermined	0.30	0.00

MACERAL ANALYSIS, V%

Vitrinite	73.4
Exinite	3.6
Semifusinite	12.5
Micrinite	8.5
Fusinite	2.0

TABLE 10

ANALYSES OF START-UP OIL

RUN 227-64 (CC-7)

HRI NUMBER	<u>5648</u>
<u>ELEMENTAL ANALYSIS, W%</u>	
Carbon	90.14
Hydrogen	9.85
Nitrogen	0.37
Sulfur	0.13
<u>ASTM D-1160 DISTILLATION</u>	
IBP	735°F
5 V%	776°F
10 V%	798°F
20 V%	810°F
30 V%	830°F
40 V%	842°F
50 V%	858°F
60 V%	876°F
70 V%	888°F
80 V%	902°F
90 V%	930°F
95 V%	952°F
FBP	1008°F

TABLE 11
ANALYSES OF CHARGED CATALYST
RUN 227-64 (CC-7)

ELEMENTAL ANALYSIS, W%

Carbon	11.93
Hydrogen	0.89
Nitrogen	0.18
Sulfur	5.08

Molybdenum, W%	9.10
Nickel, W%	1.93
Iron, W%	0.58
Titanium, W%	0.03
Calcium, W%	0.09
Sodium, W%	0.43

Average Age, Lb Coal/Lb Catalyst	468
----------------------------------	-----

TABLE 12
ANALYSES OF ADDITIVES
RUN 227-64 (CC-7)

HRI NUMBER TYPE	5689/5723 MAGNETIC PIGMENT (Oxide)
<u>ELEMENTAL ANALYSIS, W%</u>	
Carbon	0.14
Hydrogen	0.00
Nitrogen	0.00
Sulfur	0.003
Water, W%	0.02
Ash, W%	102.75
<u>MINERAL ANALYSIS (W%)</u>	
Silicon Dioxide	0.93
Aluminum Oxide	0.07
Titanium Oxide	0.20
Iron Oxide	98.36
Calcium Oxide	0.05
Magnesium Oxide	0.22
Potassium Oxide	0.02
Sodium Oxide	0.07
Sulfur Trioxide	0.07
Phosphorous Pentoxide	0.03
Undetermined	0.02
<u>FORMS OF IRON (W% ADDITIVE)</u>	
Fe	0.05
FeO	25.14
Fe ₂ O ₃	70.42

HRI-5723 was used in the test. The reported analyses are of HRI-5689, an earlier shipment of the same material.

TABLE 13
RECOVERED CATALYST ANALYSES
RUN 227-64 (CC-7)

Carbon, W%	16.69
Hydrogen, W%	0.90
Nitrogen, W%	0.19
Sulfur, W%	6.20
Nickel, W%	1.83
Molybdenum, W%	8.36
Iron, W%	0.82
Titanium, W%	0.068
Calcium, W%	0.39
Sodium, W%	1.02
	0.07
Pore Volume, cc/g	0.34
Compacted Density, cc/g	0.89
Particle Density, g/cc	1.45
Loss on Ignition, W%	21.31
Pore Volume (Ignited catalyst) cc/g	0.66
Particle Density (Ignited Catalyst) g/cc	1.15

FIGURE 1

REACTOR CONFIGURATION RUN (CC-7) CONVERSIONS

REACTOR CONFIGURATION RUN (CC-7) PROCESS PERFORMANCE

FIGURE 2

REACTOR CONFIGURATION RUN (CC-7) YIELDS

FIGURE 3

REACTOR CONFIGURATION RUN (CC-7) DISTILLATE SELECTIVITY

FIGURE 4

FIGURE 5

REACTOR CONFIGURATION RUN (CC-7) HYDROGEN CONSUMPTION

REACTOR CONFIGURATION RUN (CC-7) CONVERSION

FIGURE 6

REACTOR CONFIGURATION RUN (CC-7) DISTILLATE YIELD

FIGURE 7

REACTOR CONFIGURATION RUN (CC-7) DISTILLATE SELECTIVITY

CC-4; CONDITION 2 CC-7; CONDITION 1
750 / 825 F 750 / 825 F

FIGURE 8

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SECTION VII

RUN 227-68 (CC-10) - CTSL™ PROCESSING OF NEW MEXICO COAL WITH ON-LINE HYDROTREATING

SUMMARY

The objectives of this run were to study on-line hydrotreating of CTSL™ liquid products and to evaluate the performance of New Mexico McKinley Mine coal in the CTSL™ process.

The gaseous product stream from liquefaction reactors has high hydrogen partial pressure. The concept of on-line hydrotreating is attractive because one can make use of this stream to hydrotreat liquid products without having to use a separate high pressure section to achieve improved product quality. Vapors from the CTSL™ liquefaction section can be sent directly to a fixed-bed hydrotreating reactor.

The New Mexico coal was liquefied at a space velocity of 67 lb/hr/ft³ catalyst with the first stage temperature maintained at 760°F and the second stage maintained at 815°F. The 16-day operation included 5 conditions with and without the hydrotreater, and with hydrotreater feed of three different cut points. The hydrotreater temperature was 650°F except for the last condition, in which it was 675°F.

The on-line hydrotreating was very effective in reducing the heteroatom contents of the distillate and caused significant saturation of the aromatics, especially in the middle distillate range. The sulfur contents of the hydrotreated Separator Overhead were between 2 and 14 ppm. The nitrogen contents were reduced to 9 ppm with the lightest hydrotreater feed, but were 89 and 72 ppm with the heavier hydrotreater feeds.

The New Mexico coal was not as active as the Wyoming coal in terms of coal or resid conversion, but it yielded more distillate because of slightly less gas production and much less water production.

SCOPE OF WORK

A nominal-1200-cc downflow hydrotreater was added to the 227 Unit for Run 227-68(CC-10). The feed to the hydrotreater was all of the Hot Separator Overhead (SOH), but Atmospheric Still Overhead (ASOH) and Vacuum Still Overheads (VSOH) could also be pumped to the hydrotreater from downstream separations.

The run plan is shown in *Table 1*. The liquefaction conditions were kept constant during the 16 day run. The coal space velocity was 67 lb coal/hr/ft³ of catalyst (per stage), the first stage liquefaction temperature was 760°F, and the second stage temperature was 815°F. In Condition 1 the hydrotreater was on-line at 650°F and the hot separator was 550°F. In Condition 3 the hot separator temperature was increased to 625°F to pass heavier distillate into the hydrotreater. Additionally, ASOH and VSOH were injected into the 675°F hydrotreater during Condition 5. The VSOH had been obtained from the batch distillation of the liquid recovered from toluene extraction of the filter cake from the early part of the run. The hydrotreater was off-line during Conditions 2 and 4, with the hot separator at the same temperature as the respective previous condition, to provide comparisons of the hydrotreated and unhydrotreated SOH. The run plan called for continuous addition of H₂S at 2 W% of feed coal to provide a sulfiding atmosphere, but the H₂S injection system was inoperable for the first five days of the run, and ditertiary nonyl polysulfide (TNPS) was added at an equivalent sulfur rate during this period.

PROGRAM RESULTS AND ANALYSES

RUN 227-68 (CC-10)

Table 2 shows the yields and process performance for the five conditions, using averages for the results when yields were calculated for more than one period in a condition.

COAL AND 975°F⁺ CONVERSION

The coal and resid (975°F⁺) conversions are shown in *Figure 1*. Coal conversion ranged from 83 to 87 W% (maf), and resid conversion ranged from 77 to 83 W% (maf). The low coal and resid conversions that occurred in Periods 11 and 12 are not representative of the general process performance. It is likely that the feed coal around this period was relatively unreactive. The lower resid conversion was a direct consequence of the lower coal conversion. Typically, no effect of catalyst deactivation on coal conversion is observed in CTSLTM operations. Neglecting coal conversion in Periods 11 and 12, the average coal conversion was 85.8 W%. The catalyst deactivation over the 16-day run caused the resid conversion to decrease by about 4 W%.

COMPARISON WITH WYOMING COAL

Although there is no available direct comparison, with identical conditions, of the results from this run with those from a run using Black Thunder coal, approximate comparisons can be made. In Run 227-61(CC-4), the severity in Condition 1 was just a little higher (750/825°F vs. 760/815°F). Using this comparison, the average coal conversion with the New Mexico coal, 85.8 W%, was slightly lower than the 86.6 W% with the Wyoming coal. The difference for the resid conversion was higher: 80.1 W% for the New Mexico coal vs. 85.6 W% for the Wyoming coal. However, the C₄-975°F distillate yield was higher for the New Mexico coal. It averaged 64.1 W% (maf) for the four conditions with reliable data compared to the 61.9 W% (maf) for the Wyoming coal. This advantage for the New Mexico coal was due to the lower gas yield (6.4 W% average vs. 7.4 W%) and the lower water yield (12.6 W% vs. 19.3 W%). Denitrogenation was similar for the two coals, 72.6 % (average) for the New Mexico coal and 74.7 % for the Wyoming coal in Run 227-61 (CC-4) Condition 1.

HEAVY PRODUCT QUALITY

Because the liquefaction conditions were kept constant throughout the run, the change in the properties of the heavy products (filter liquid and filter cake), if any, were a result of the catalyst deactivation. The analyses of the PFL and its fractions are presented in *Table 3*, and those of the THF-washed filter cake are shown in *Table 4*. The quality of the PFL fractions, as indicated by heteroatom content and H/C ratio (*Figure 2*), was quite stable with the exception of the Period 16 data. It appears that the hydrogenation activity of the liquefaction

catalyst was relatively constant during most of the run although the overall activity towards resid conversion was steadily decreasing. The composition of the unconverted coal was not affected by the increasing catalyst age.

A first-stage slurry sample was withdrawn in Period 17A. The analyses of the solid and the liquid portion are given in *Table 5*. The coal conversion in the first stage was 77.1 W% (maf) while the corresponding two-stage conversion was 85.7 W%. The hydrogen content of the first-stage unconverted coal was higher than that of the two-stage product (5.07 W% (ash-free) vs. 4.70 W% (ash-free)), but lower than that of the feed coal (5.20 W% (ash-free)). The sulfur contents of the product solids were substantially higher (on an ash-free basis) than the sulfur content of the feed coal, probably due to the sulfidation of the mineral matter by the H₂S stream.

HYDROTREATER PERFORMANCE

The analyses of the Separator Overhead (SOH) product and the Atmospheric Still Overhead (ASOH) product are shown in *Table 6 and 7*. On-line hydrotreating was very effective in reducing the heteroatom content of the SOH. This large improvement is not readily apparent from the HDN and HDS levels, because most of the unconverted nitrogen and sulfur remain with the heavy products (mainly solids), which are unaffected by the hydrotreating step. The catalyst space velocity at the hydrotreater ranged from 0.46 to 1.04 lb product (SOH) per lb catalyst per hour as shown in *Table 2*. Obviously, it is not possible to control the space velocity at the on-line hydrotreater independent of the quality (boiling point range) of the hydrotreater feed because the hydrotreater is close-coupled with the liquefaction section. Also note that the space velocity mentioned above is expressed in terms of the flow rate of the liquid hydrocarbon product. It does not consider the flow rates of other streams such as light hydrocarbon gases and heterogases. (The hydrotreater feed contains a large amount of water.).

The hydrotreater had a large effect on the quality of the SOH product, as shown in *Table 6*. With the hot separator maintained at 550°F, the nitrogen contents of the untreated and hydrotreated products were 1280 and 9 ppm respectively, and the sulfur contents were 230 and 14 ppm respectively. When the separator temperature was increased to 625°F to pass heavier distillate into the hydrotreater, the nitrogen and the sulfur contents of the products were 89 and 6 ppm, respectively. This lower nitrogen removal indicates that the efficiency of the hydrotreating is dependent upon the feed end point. In Condition 5, VSOH obtained from heavy liquid produced in Periods 2 through 9 and the entire ASOH stream were injected into the hydrotreater (in addition to the SOH stream entering it directly). This condition simulates hydrotreating the entire distillate product. The rate of VSOH injection was 11.0 W% (coal), the same as the rate of net VSOH production in prior periods. The VSOH analyses are shown in *Table 8*. The hydrotreating was done at 675°F in Condition 5 instead of the 650°F used in the other hydrotreating conditions. The nitrogen and the sulfur contents of the

hydrotreated products in Condition 5 were 72 and 2 ppm respectively. Thus, even with the increased amount of heavy distillate, increased space velocity, and increased catalyst age in Condition 5, the hydrotreater products had slightly better product quality in terms of nitrogen and sulfur content than they had in Condition 3. The 25°F higher hydrotreater temperature would have been partly responsible for this difference.

The increase in hydrogen consumption due to hydrotreating was small. Comparing Conditions 1 and 2, hydrogen consumption with the hydrotreater on line was 6.93 W% (coal) compared with 6.48 W% with no hydrotreating. There was no major change in yield distribution for these two conditions. However, when heavier distillate was injected into the hydrotreater (Condition 3), the relative yield of this portion (especially the 650-850°F) decreased, indicating its conversion to lighter distillate in the hydrotreater.

In order to understand the changes in the product properties due to on-line hydrotreating, full-range distillate samples from the hydrotreated Condition-5 SOH and the unhydrotreated Condition 4 SOH, ASOH, and VSOH (blended in the proportion of production) were separated into IBP-180°F, 180-390°F, 390-500°F, 500-650°F, and 650-850°F TBP cuts. The analyses of the cuts are shown in *Table 9*. In addition, the components of the IBP-180°F cuts were identified and are shown in *Tables 10 and 11*. The IBP-180°F cut from the unhydrotreated cut had traces of olefins present. No such olefins were detected in the cut from the hydrotreated product. Cyclohexane was the major component in both cuts, and the benzene content was quite small. The nitrogen content of this light naphtha decreased from 41 ppm to 20 ppm on hydrotreating. The sulfur content of the hydrotreated naphtha was analyzed as 126 ppm, but this high indicated sulfur content was probably due to sample contamination during handling. The GC did not show any sulfur compound at this concentration.

The analyses reported in *Table 9* show that on-line hydrotreating resulted in significant saturation of aromatics, especially in the middle distillate range. The aniline point of the 390-500°F cut improved from 85.5°F to 98°F and from 84.5°F to 106°F for the 500-650°F cut. The °API gravity improved by about three units. These changes mean a higher cetane number for these cuts.

The run showed that on-line hydrotreating can be effective in reducing the heteroatom content of the distillate product. The hydrotreater conditions were probably not at their optimum, and no attempt was made to tune these conditions to target a specific end result. It is quite possible that the performance can be improved. It was not possible to assess the deactivation of the hydrotreating catalyst in this short run. Also, no effect of potential catalyst poisons or inhibitors that would exist in hydrotreater feed (viz. ammonia or water) has been quantified. This run was conducted with continuous H₂S injection. This probably had a mitigating effect on catalyst deactivation. These factors need to be further quantified and optimized.

DETAILS OF OPERATION

COAL FEED

New Mexico sub-bituminous coal (McKinley mine), HRI-5709 was used as the feedstock. As reported in "Microautoclave Studies" (in the concurrently published Report #3), this coal had performed satisfactorily in microautoclave screening studies. Also, it had performed quite well in a preceding co-processing bench run. The coal analyses are shown in *Table 12*. The coal was pulverized to -70 mesh prior to use.

START-UP OIL

The run was started using HRI-5757, a Wyodak-coal-derived heavy distillate obtained from Wilsonville. The analyses of the start-up oil are shown in *Table 13*.

FRESH CATALYST

The same Shell S-317, HRI-394, $\frac{1}{32}$ -inch extrudate NiMo catalyst that had been used throughout the program was used in both liquefaction stages. Shell-424 NiMo catalyst was used in the hydrotreater. The analyses of Shell-424 are shown in *Table 14*. The Shell S-317 analyses are shown in *Table 11* in the section on Run 227-55(CC-1). The catalysts were sulfided during the start-up by doping the start-up oil with TNPS (ditertiary nonyl polysulfide).

RECOVERED CATALYST

The analyses of the recovered catalysts are shown in *Table 15*. The carbon accumulation on both reactor catalysts, 8.45 W% and 14.22 W% were on the low end of the ranges of carbon on catalysts from previous runs with Wyoming coal. The iron and sodium contaminants on the first stage catalyst were relatively high at 1.59 W% and 1.11 W%, respectively. The pore volumes of the first and second stage catalysts had decreased significantly to 0.37 and 0.27 cc/gram.

The carbon content of the hydrotreater catalyst was 3.97 W%, and the nitrogen content was a relatively high 0.76 W%. The pore volume had decreased from 0.47 cc/g for the fresh catalyst to 0.22 cc/g for the recovered hydrotreater catalyst.

TABLE 1

RUN PLAN - (CC-10)

RUN 227-68

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
PERIOD	<u>1-7</u>	<u>8-9</u>	<u>10-12</u>	<u>13-14</u>	<u>15-16</u>
<u>SPACE VELOCITY</u> Lbs Coal/Hr/Ft ³ Catalyst	<u>67</u>				
<u>TEMPERATURE, °F</u>					
First Stage	<u>760</u>				
Second Stage	<u>815</u>				
Hot Separator	550	550	625	625	625
Hydrotreater	650	---	650	---	675
Recycle Ratio, (PFL/Coal)	<u>1.1</u>				
H ₂ S Rate, W% Coal	<u>2.0</u>				

NOTE: Hydrotreater was off line in Conditions 2 and 4. In condition 5, all ASOH and VSOH obtained from PFL was injected into the hydrotreater.

TABLE 2

LIQUEFACTION PERFORMANCE

RUN 227-68 (CC-10)

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
PERIODS	<u>4-7</u>	<u>9</u>	<u>11-12</u>	<u>14</u>	<u>16</u>
Liquefaction Reactors					
Cat. Age (Per Stage)	230	381	489	598	683
(Lb Coal/Lb Cat)					
Space Velocity	68.0	68.4	68.1	68.4	66.9
(Lb Coal/Hr/Ft ³ Cat)					
Temp., °F					
1st Stage Temp	760	759	761	760	760
2nd Stage Temp	815	815	816	816	816
Hydrotreater					
Cat. Age	206	---	325	---	492
(Lb Liq. Prod./Lb. Cat)					
Space Velocity	1.62	---	1.72	---	2.17
(Lb Liq. Prod./Lb Cat/Hr)					
Injected VS:OH (W% Coal)	---	---	---	---	11.0
Temperature, °F	650	---	650	---	675
Hot Sep. Temp., °F	550	550	625	625	625
<u>NORMALIZED YIELDS (W% COAL)</u>					
C ₁ -C ₃	6.36	6.19	6.98	5.77	6.68
C ₄ -390°F	15.68	12.84	14.92	13.17	14.26
390-500°F	8.79	8.23	9.49	8.08	8.74
500-650°F	18.52	18.27	16.51	16.30	15.66
650-850°F	12.87	13.96	8.80	15.64	13.81
850-975°F	3.11	3.40	1.73	3.84	3.04
985°F Liquid	3.67	4.47	5.28	6.09	5.79
IOM	12.21	12.75	15.18	13.20	12.70
ASH	11.00	11.00	11.00	11.00	11.00
CO + CO ₂	0.59	0.74	1.04	0.99	1.06
NH ₃	1.06	0.96	0.99	0.91	1.02
H ₂ S	0.18	0.48	0.45	0.44	0.45
H ₂ O	12.65	13.20	14.57	10.69	12.14
TOTAL (100+H ₂)	106.93	106.48	106.91	106.31	106.37
<u>PERFORMANCE (W% MAF)</u>					
Coal Conversion	86.3	85.7	83.0	85.2	85.7
Resid Conversion	82.2	80.7	77.1	78.3	79.2
HDS	75.7	75.0	70.1	69.1	71.0
HDN	77.9	70.4	72.6	67.2	74.7
C ₄ -975°F Yield	66.2	63.7	57.8	64.1	62.4

TABLE 3

ANALYSES OF PFL

RUN 227-68 (CC-10)

Period Number	<u>5</u>	<u>7</u>	<u>9</u>	<u>12</u>	<u>14</u>	<u>16</u>
TOTAL PFL						
API Gravity	9.0	8.6	7.2	6.9	7.2	7.1
Carbon, W%	89.58	89.03	89.07	89.03	88.91	88.67
Hydrogen, W%	10.42	10.36	10.31	10.53	10.56	9.82
Nitrogen, W%	0.27	0.36	0.39	0.36	0.37	0.34
Sulfur, W%	0.01	0.00	0.00	0.02	0.00	0.02
H/C Ratio	1.40	1.40	1.39	1.42	1.43	1.33
IBP-650°F, W%	9.73	10.01	11.66	8.90	6.86	9.21
650-850°F, W%	55.32	52.67	50.69	51.57	51.27	50.83
850-975°F, W%	16.78	17.72	16.28	16.83	16.18	15.08
975°F, W%	18.17	19.60	21.37	22.70	25.69	24.88
IBP-650°F CUT						
API Gravity	20.4	17.8	18.0	18.0	18.0	18.5
Carbon, W%	88.00	88.14	87.70	87.86	87.23	87.48
Hydrogen, W%	11.34	11.74	11.71	11.63	11.59	11.56
Nitrogen, W%	0.15	0.20	0.20	0.25	0.24	0.22
Sulfur, W%	0.01	0.00	0.00	0.00	0.00	0.03
H/C Ratio	1.55	1.60	1.60	1.59	1.59	1.59
650-850°F CUT						
API Gravity	13.0	11.8	11.6	11.8	13.7	12.1
Carbon, W%	88.68	88.45	89.21	89.13	88.67	88.40
Hydrogen, W%	11.15	11.04	11.39	11.39	11.34	10.80
Nitrogen, W%	0.19	0.21	0.25	0.24	0.29	0.21
Sulfur, W%	0.00	0.00	0.00	0.01	0.00	0.00
H/C Ratio	1.51	1.50	1.53	1.53	1.53	1.47
850-975°F CUT						
API Gravity	4.1	3.9	3.4	3.1	4.6	4.2
Carbon, W%	88.94	89.00	89.48	89.54	89.30	89.15
Hydrogen, W%	10.04	9.97	10.28	10.22	10.35	9.68
Nitrogen, W%	0.30	0.45	0.37	0.36	0.36	0.34
Sulfur, W%	0.02	0.00	0.02	0.00	0.00	0.01
H/C Ratio	1.35	1.34	1.38	1.37	1.39	1.30
975°F CUT						
API Gravity	-4.6	-5.6	-7.2	-6.0	-6.9	-6.6
Carbon, W%	90.43	89.92	90.04	89.16	89.55	88.96
Hydrogen, W%	9.03	8.47	8.70	8.67	8.72	8.05
Nitrogen, W%	0.52	0.62	0.65	0.62	0.66	0.68
Sulfur, W%	0.06	0.11	0.06	0.04	0.04	0.04
H/C Ratio	1.20	1.13	1.16	1.17	1.17	1.09

TABLE 4
ANALYSES OF THF-WASHED FILTER CAKE
RUN 227-68 (CC-10)

Period Number	<u>5</u>	<u>7</u>	<u>9</u>	<u>12</u>	<u>14</u>	<u>16</u>
<u>WEIGHT %</u>						
Carbon, W%	37.54	39.23	39.50	43.76	39.95	39.40
Hydrogen, W%	2.17	2.29	2.32	2.57	2.51	2.39
Nitrogen, W%	0.69	0.73	0.74	0.83	0.76	0.75
Sulfur, W%	0.85	0.76	0.78	0.87	0.76	0.72
Ash	48.47	48.10	48.21	43.42	48.21	49.16
<u>WEIGHT % (ASH-FREE)</u>						
Carbon, W%	72.85	75.59	76.27	77.34	77.14	77.50
Hydrogen, W%	4.21	4.41	4.48	4.54	4.85	4.70
Nitrogen, W%	1.34	1.41	1.43	1.47	1.47	1.48
Sulfur, W%	1.65	1.46	1.50	1.53	1.46	1.41
Oxygen (Diff)	19.95	17.13	16.32	15.12	15.08	14.91

TABLE 5
ANALYSES OF FIRST-STAGE SLURRY SAMPLE (PERIOD 17)
RUN 227-68 (CC-10)

SOLIDS (THF-INSOLUBLES)	
Content (W%) of Filter Cake)	49.40
SOLIDS ANALYSIS	
WEIGHT %	
Carbon, W%	48.72
Hydrogen, W%	3.20
Nitrogen, W%	1.01
Sulfur, W%	0.69
Ash, W%	36.89
WEIGHT % (ASH-FREE)	
Carbon, W%	77.20
Hydrogen, W%	5.07
Nitrogen, W%	1.60
Sulfur, W%	1.09
LIQUID ANALYSIS	
API	5.4
Carbon, W%	88.00
Hydrogen, W%	9.90
Nitrogen, W%	0.43
Sulfur, W%	0.05
H/C Ratio	1.35
IBP-650°F, W%	7.64
650-850°F, W%	41.88
850-975°F, W%	17.21
975°F, W%	33.27
IBP-650°F CUT	
API	17.5
Carbon, W%	87.52
Hydrogen, W%	11.42
Nitrogen, W%	0.24
Sulfur, W%	0.01
H/C Ratio	1.57
650-850°F CUT	
API	12.9
Carbon, W%	88.01
Hydrogen, W%	10.83
Nitrogen, W%	0.22
Sulfur, W%	0.02
H/C Ratio	1.48
850-975°F CUT	
API	5.2
Carbon, W%	87.99
Hydrogen, W%	9.69
Nitrogen, W%	0.37
Sulfur, W%	0.03
H/C Ratio	1.32
975°F CUT	
API	-3.5
Carbon, W%	87.48
Hydrogen, W%	8.37
Nitrogen, W%	0.79
Sulfur, W%	0.16
H/C Ratio	1.15

TABLE 6
QUALITY OF SEPARATOR OVERHEAD
RUN 227-68 (CC-10)

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Period Number	<u>7</u>	<u>9</u>	<u>12</u>	<u>14</u>	<u>16</u>
Hot Separator Temp, °F	550	550	625	625	625
Hydrotreater Temp, °F	650	---	650	---	675
API Gravity	39.9	36.2	36.7	34.3	29.1
Carbon, W%	86.33	86.58	86.36	86.87	87.29
Hydrogen, W%	13.71	13.33	13.54	12.63	12.48
Nitrogen, PPM	9	1280	89	1600	72
Sulfur, PPM	14	230	6	240	2
VABP, °F	401	421	442	449	525
H/C Ratio	1.91	1.85	1.88	1.74	1.72
Watson K	11.25	11.25	11.12	11.02	10.91

All ASOH and 11.0 W% (of Coal Feed) VSOH charged to hydrotreater (in addition to all SOH).

TABLE 7
QUALITY OF ATMOSPHERIC - STILL OVERHEAD/KNOCKOUTS
RUN 227-68 (CC-10)

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Period Number	<u>7</u>	<u>9</u>	<u>12</u>	<u>14</u>
Hot Separator Temp, °F	550	550	625	625
Hydrotreater Temp, °F	650	---	650	---
API Gravity	24.6	24.4	25.9	25.6
Carbon, W%	87.60	87.77	86.99	87.48
Hydrogen, W%	12.34	12.35	12.52	11.99
Nitrogen, PPM	1720	2160	2410	2330
Sulfur, PPM	56	37	210	360
VABP, °F	551	550	515	523
H/C Ratio	1.69	1.69	1.73	1.64
Watson K	10.95	10.95	10.92	10.93

TABLE 8

**ANALYSES OF VACUUM STILL OVERHEAD INJECTED
INTO THE ON-LINE HYDROTREATER (PERIODS 15-16)**

RUN 227-68 (CC-10)

API Gravity	13.1
Carbon, W%	88.32
Hydrogen, W%	10.61
Nitrogen, W%	0.16
Sulfur, W%	0.06
D1160 DISTILLATION	TEMPERATURE, °F
IBP	511
5 V%	595
10 V%	645
20 V%	673
30 V%	705
40 V%	728
50 V%	733
60 V%	750
70 V%	772
80 V%	800
90 V%	830
95 V%	875
FBP	888

TABLE 9
COMPARISON BETWEEN HYDROTREATED AND UNTREATED
TOTAL DISTILLATE (850°F)
RUN 227-68 (CC-10)

TBP CUT	HYDROTREATED (PERIOD 16)	UNTREATED (PERIOD 14)
IBP-180°F		
API Gravity	61.9	62.2
Carbon, W%	84.83	84.99
Hydrogen, W%	14.66	14.88
Nitrogen, WPPM	20	41
Sulfur, WPPM	126	23
Oxygen, W%	<0.05	<0.05
H/C Ratio	2.07	2.10
180-390°F		
API Gravity	48.0	45.7
Carbon, W%	86.02	85.60
Hydrogen, W%	13.67	13.55
Nitrogen, WPPM	25	60
Sulfur, WPPM	13	108
Oxygen, W%	<0.05	<0.05
H/C Ratio	1.31	1.90
Paraffins, V%	19.00	19.64
Olefins, V%	0.80	1.00
Monocycloparaffins, V%	56.83	51.66
Dicycloparaffins, V%	12.20	15.23
Alkylbenzenes, V%	8.96	9.30
Indanes/Tetralins, V%	1.69	2.54
Naphthalenes, V%	0.52	0.63
390-500°F		
API Gravity	31.3	28.5
Carbon, W%	87.21	88.54
Hydrogen, W%	12.39	12.27
Nitrogen, WPPM	83	164
Sulfur, WPPM	5	70
Oxygen, W%	<0.05	<0.05
H/C Ratio	1.70	1.66
Aniline Point, °F	98.0	85.5
Paraffins, V%	18.70	16.57
Olefins, V%	1.00	1.00
Monocycloparaffins, V%	28.09	28.41
Dicycloparaffins, V%	20.97	17.51
Alkylbenzenes, V%	9.56	10.85
Indanes/Tetralins, V%	18.89	21.39
Naphthalenes, V%	2.79	4.27

TABLE 9 (Continued)

**COMPARISON BETWEEN HYDROTREATED AND UNTREATED
TOTAL DISTILLATE (850°F-)**

RUN 227-68 (CC-10)

TBP CUT	HYDROTREATED (PERIOD 16)	UNTREATED (PERIOD 14)
500-650°F		
API Gravity	22.2	19.9
Carbon, W%	88.40	88.82
Hydrogen, W%	12.10	11.41
Nitrogen, WPPM	36	237
Sulfur, WPPM	6	60
Oxygen, W%	0.11	<0.05
H/C Ratio	1.64	1.54
Aniline Point, °F	106.0	84.5
Bromine Number	2.39	5.56
Paraffins, V%	13.47	10.01
Monocycloparaffins, V%	2.59	7.40
Dicycloparaffins, V%	22.59	13.67
Tricycloparaffins, V%	14.53	7.35
Alkybenzenes, V%	9.06	11.92
Indanes/Tetralins, V%	11.35	14.04
Indenes, V%	11.00	13.67
Naphthalenes, V%	8.46	12.07
Acenaphthenes, V%	4.12	6.27
Aceneaphthalenes, V%	1.63	2.21
Tricyclic Aromatics, V%	1.20	1.39
650-850°F		
API Gravity	15.4	13.7
Carbon, W%	88.68	88.20
Hydrogen, W%	11.27	10.47
Nitrogen, WPPM	251	142
Sulfur, WPPM	21	89
Oxygen, W%	0.19	0.17
H/C Ratio	1.53	1.42

TABLE 10**GC ANALYSES OF IBP-180
CUT OF HYDROTREATER
(PERIODS 16) PRODUCT****RUN 227-68 (CC-10)**

	<u>W%</u>	<u>V%</u>
Propane	0.02	0.03
Isobutane	0.07	0.09
N-Butane	0.97	1.19
Isopentane	2.18	2.50
N-Pentane	7.74	8.79
2,2-Dimethylbutane	0.09	0.10
Cyclopentane	3.74	3.57
2-Methylpentane	5.76	6.27
3-Methylpentane	5.20	5.57
N-Hexane	19.81	21.38
2,2-Dimethylpentane	0.03	0.03
Methylcyclopentane	13.21	12.56
2,4 Dimethylpentane	0.20	0.21
Benzene	1.28	1.04
Cyclohexane	35.69	32.64
2-Methylhexane	0.94	0.99
2,3-Dimethylpentane	0.29	0.30
1,1-Dimethylcyclopentane	0.04	0.04
3-Methylhexane	1.00	1.04
CIS-1,3-Dimethylcyclopentane	0.30	0.29
Trans-1,3-Dimethylcyclopentane	0.19	0.18
3-Ethylpentane	0.05	0.05
Trans-1,2-Dimethylcyclopentane	0.31	0.29
N-Heptane	0.26	0.27
Nethylcyclohexane	0.57	0.53
Toluene	0.06	0.05

TABLE 11
GC ANALYSES OF IBP-180 CUT
OF HYDROTREATER
(PERIOD 14) PRODUCT
RUN 227-68 (CC-10)

	<u>W%</u>	<u>V%</u>
Isobutane	0.02	0.02
N-Butane	0.40	0.49
Isopentane	1.06	1.18
N-Pentane	3.88	4.40
Trans-2, Pentane	0.04	0.40
CIS-2, Pentane	0.02	0.02
2-Methyl,2-Butene	0.04	0.04
2,2-Dimethylbutane	0.05	0.05
Cyclopentene	0.05	0.05
3-Methyl, 1-Pentne	0.04	0.04
Cyclopentane	2.30	2.19
4-Methyl,1-Pentane	0.03	0.03
2-Methylpentane	4.03	4.38
4-Methyl-CIS-2-Pentane	0.03	0.03
3-Methyl-Pentane	3.78	4.04
1-Hexene	0.31	0.33
N-Hexane	15.31	16.85
Trans-3, Hexene	0.05	0.05
Trans-2, Hexene	0.10	0.10
4,4-Dimethyl-1-Pentne	0.08	0.08
2-Methyl-2-Pentane	0.06	0.06
3-Methyl-CIS-2-Pentane	0.04	0.04
CIS-2-Hexene	0.06	0.06
3-Methyl-Trans-2-Pentane	0.07	0.07
Methylcyclopentane	10.66	10.11
2,2-Dimethylpentane	0.03	0.03
2,3,3-Trimethylbutane/ 2,4-Dimethylpentane	0.27	0.28
Benzene	1.15	0.93
Cyclohexane/3,3-Dimethylpentane	45.21	43.67
2,3-Dimethylpentane	0.60	0.61
2-Ethyl-3-Methyl-1-Butene	0.09	0.09
2-Methyl-Hexane	2.11	2.21
1,1-Dimethylcyclopentane	0.87	0.83
3-Methylhexane	2.34	2.42
CIS-1,3-Dimethylcyclopentane	0.70	0.67
Trans-1,3-Dimethylcyclopentane	0.47	0.45
Trans-1,2-Dimethylcyclopentane	0.72	0.68
3-Ethylpentane	0.17	0.18
2,2,4-Trimethylpentane	0.03	0.03
N-Heptane	0.55	0.57
1-C-2-Dimethylcyclopentane/ Methylcyclohexane	0.97	0.89
Toluene/2,3,3-Trimethylpentane	0.87	0.71

TABLE 12
ANALYSES OF FEED COAL
RUN 227-68 (CC-10)

COAL	New Mexico (McKinley Mine)
HRI NO	<u>5709</u>
<u>W% DRY BASIS</u>	
Carbon, W%	66.87
Hydrogen, W%	4.60
Nitrogen, W%	1.12
Sulfur, W%	0.60
Ash	11.51
<u>ASH ANALYSIS (IGNITED, W% ASH)</u>	
SiO ₂	59.00
Al ₂ O ₃	24.41
TiO ₂	1.14
Fe ₂ O ₃	5.07
CaO	3.77
MgO	1.04
K ₂ O	1.02
Na ₂ O	1.82
SO ₃	2.30
P ₂ O ₅	0.31
Undetermined	0.12

TABLE 13

ANALYSES OF START-UP OIL

RUN 227-68 (CC-10)

HRI NO. TYPE	5757 Wilsonville Heavy Distillate
API Gravity	8.2
Carbon, W%	89.68
Hydrogen, W%	10.17
Nitrogen, W%	0.27
Sulfur, W%	0.02
D1160 DISTILLATION	TEMPERATURE, °F
IBP	700
5 V%	721
10 V%	734
20 V%	745
30 V%	755
40 V%	772
50 V%	790
60 V%	805
70 V%	827
80 V%	850
90 V%	881
95 V%	908
FBP	945

TABLE 14
ANALYSES OF FRESH HYDROTREATING CATALYST
RUN 227-68 (CC-10)

HRI NUMBER	5749
CATALYST TYPE	SHELL-424
CATALYST SIZE	$\frac{1}{10}$ " TRILOBE
Nickel, W%	3.0
Molybdenum, W%	13.0
Surface Area, M ₂ /g	162
Pore Volume, cc/g	0.47
Compacted Bulk Density, cc/g	0.83

TABLE 15**ANALYSES OF RECOVERED CATALYST****RUN 227-68 (CC-10)**

	<u>STAGE 1</u>	<u>STAGE 2</u>	<u>HYDROTREATER</u>
Carbon, W%	8.45	14.22	3.97
Hydrogen, W%	0.46	0.83	0.63
Nitrogen, W%	0.18	0.17	0.76
Sulfur, W%	5.49	5.19	7.17
Molybdenum, W%	8.07	7.80	9.47
Nickel, W%	1.76	1.65	2.22
Iron, W%	1.59	0.15	
Titanium, W%	0.09	0.04	
Calcium, W%	0.20	0.09	
Sodium, W%	1.11	1.28	
COMPACTED BULK			
Density, g/cc	1.04	1.11	0.92
Particle Density, g/cc	1.34	1.45	1.51
PORE VOLUME, cc/g	0.37	0.27	0.22
Loss on Ignition, W%	16.08	24.81	13.28
Pore Volume (Ignited Catalyst), cc/g	0.58	0.57	0.37
Particle Density (Ignited Catalyst), cc/g	1.12	1.08	1.36

CC-10 PROCESS PERFORMANCE COAL / RESID CONVERSIONS

FIGURE 1

CC-10 PROCESS PERFORMANCE

H/C RATIO OF PFL CUTS

FIGURE 2

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SECTION VIII

RUN 227-69 (CC-11) - PREPARATION OF PRODUCT SLURRY FOR FILTRATION TESTS

SUMMARY

The primary objective of this run was to produce about 20 kg of atmospheric bottoms to evaluate an alternative solids-separation technique, namely the pressure filtration technique developed by British Coal Board. Another objective was to obtain data on the on-line hydrotreating of Black Thunder coal.

Black Thunder sub-bituminous coal was liquefied at a space velocity of 67 lb/ hr/ ft³ of catalyst with the first stage temperature maintained at 775°F (except for the last two days when it was lowered to 750°F to lower gas yields) and the second stage temperature maintained at 825°F. The previous Run 227-68(CC-10) with New Mexico sub-bituminous coal had shown on-line hydrotreating to be effective; hence it was also used in this run to obtain similar data with Black Thunder coal. Unfortunately, reliable hydrotreating data could not be obtained due to the failure of a key thermocouple. About 20 kg of atmospheric bottoms were collected and shipped for filtration tests.

The run was conducted with a continuously injected H₂S stream because prior runs had indicated that it might mitigate catalyst deactivation. There was indeed very little decrease in resid conversion in the first 11 days of the run. The heavy liquid products also showed stable H/C ratios. However, hydrodenitrogenation was affected by catalyst deactivation.

Filtration tests were conducted by British Coal Board. They found that the bottoms could be filtered effectively, and they optimized variables such as filtration temperature and pressure. Filter aids to reduce cake resistance were found to be not beneficial. Filter screens with apertures of size larger than the solids size could be used; however, sluicing to remove partial screen blinding was found to be necessary. Washing of filter cake with a light liquid was required to recover trapped liquid product. Their full report is attached as an Appendix.

BACKGROUND

Solids separation operations, where unconverted coal and ash are separated from liquid product, is an important part of direct liquefaction technology. Its efficiency gets an added importance when liquefaction is conducted in an extinction recycle mode. In this mode, the heavy products are eliminated through their preferential recycle to the liquefaction reactors. Its success depends largely upon the efficiency of the solids separation step, which makes the final increment of heavy liquids available for recycle.

British Coal Board has developed a filtration technique for separating unconverted coal and ash from liquid products ⁽¹⁾. The filtration is integrated with their Liquid Solvent Extraction (LSE) process, and they claim the technique can separate solids from liquid with high efficiency and reliability in a cost-effective manner.

British Coal Board was asked to evaluate their filtration technique for CTSLTM application. The quality of filter feed derived from CTSLTM is expected to be quite different from that obtained from the LSE process, which involves thermal, noncatalytic dissolution.

SCOPE OF WORK

Typically, CTSLTM bench runs are in solvent balance, i.e. the entire amount of atmospheric bottoms is used to provide the necessary amount of recycle solvent. In order to obtain 20 kg of bottoms for filtration tests, a large capacity feed vessel was used. The run was started with start-up oil and equilibrated in seven days. At this point, the capacity of the feed vessel was used to supply the feed to the reactors and the bottoms were collected without using any quantity for recycling. The procedure was repeated after six more days.

The run plan for this 13 day run with Black Thunder coal is shown in *Table 1*. The space velocity was 67 lb/hr/ft³ of catalyst per stage and the first and second stage reactor temperatures were 775°F and 825°F, respectively. The first stage temperature was decreased to 750°F in Periods 12 and 13 to lower the observed high gas yields. H₂S was injected continuously at 2 W% (of feed coal). In Conditions 1 and 3, the hydrotreater was on line, with the target temperatures of 640 and 670°F, respectively. The hydrotreater feed was all of the overhead from the hot separator. It was off line in Conditions 2 and 4. As in the previous run, the hydrotreater catalyst was Shell 424 and the reactor catalysts were Shell S-317.

PROGRAM RESULTS AND ANALYSES

RUN 227-69 (CC-11)

Table 2 is the Operating Summary for the run, giving the principal operating conditions for each Period (day) and normalized product distributions for periods that were considered to represent equilibrated results. *Table 3* shows the yields and process performance for the four conditions.

COAL AND 975°F* CONVERSION

Figure 1 shows the coal and resid (975°F*) conversions obtained in the run. Coal conversion ranged from 85.4 to 88.5 W% (maf), and resid conversion ranged from 83.3 to 87.0 W% (maf). No effect of catalyst deactivation on coal and resid conversions was observed in the first 11 days of operation. As seen from *Figure 1*, there was a slight upward trend in coal conversion between Periods 2 and 7 and between Periods 9 and 13. This trend corresponded to the infusion of much start-up solvent during the start-up and again after all atmospheric bottoms were taken for the filtrations tests in Period 7. Apparently the Wyodak-derived start-up oil from Wilsonville was of lower solvent quality, and it took about 6 days for the process-derived solvent to replace it. (This equilibration took longer in this run than in other runs because of the extra-large-volume charge tank used to accumulate material for the filtration-test samples.)

The lack of significant effect of catalyst deactivation on resid conversion was at least partly due to the presence of the H₂S stream, but the resid conversion was partly influenced by the coal conversion as discussed above. The actual resid yield did increase from 0.8 W% (of coal) in Condition 1 to 1.3 W% in Condition 3, but the run was too short to extrapolate these trends to more-typical equilibrium catalyst ages. There was a sharp decrease in resid conversion when the first stage temperature was decreased from 775°F to 750°F, but there was relatively little decrease in coal conversion. However, note that there was only one data point at this lower temperature.

NORMALIZED PRODUCT DISTRIBUTION

Figures 2 through 4 show distillate yield and distillate selectivity. The distillate (C₄-975°F) yield ranged from 54 to 58 W% (maf coal). It was quite stable during the course of the run. There was a slight shift in selectivity, with a slightly higher fraction of naphtha (C₄-390°F) obtained in the early part of the run. The run was marked by high gas (C₁-C₃) yields, averaging about 9.7 W% (coal) for Conditions 1 and 2. The relatively high gas yield caused a correspondingly lower distillate yield. The effect of the 25°F decrease in the first stage temperature in Condition 4 is not clear. The gas yield had already decreased to 8.1 W% in Condition 3 before the temperature was changed, and it was 7.6 W% and 8.3 W% for the last two periods of the run with the first stage at the lower 750°F temperature. For

comparison, the only similar previous operation was Condition 6 of Run 227-55 (CC-1), which had the same coal rate and reactor temperatures as Condition 4 of Run 227-69(CC-11). Using a kinetic model based on all of the gas yield data from Run 227-55(CC-1), the gas yield for this condition was 7.5 W%, slightly lower than in Run 227-69(CC-11).

HETEROATOM REMOVAL

Figure 5 shows hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) for Run 227-69(CC-11). The extent of HDN was quite high through most of the run. The effect of catalyst deactivation was smaller than usually encountered. Again, the presence of the H₂S stream is the likely cause. When the first-stage temperature was lowered during the final two days, HDN decreased significantly. It may be that the decrease in HDN was a combination of catalyst deactivation and the lowered temperature. The extent of HDS was less than that of HDN. Some of the coal mineral matter probably picked up sulfur from the H₂S stream. Most of the unconverted sulfur remained in the solid product. Whereas the feed coal had a sulfur content of 0.46 W%, the sulfur content of the THF-washed solid product was greater than 1 W%.

PRODUCT QUALITY

The analyses of the products are shown in *Tables 4 through 7*. The hydrotreater was effective in reducing the heteroatom content of the SOH, but not to the very low level that had been expected. The hydrotreater data on New Mexico coal (Run 227-68(CC-10)) had shown that it is possible to reduce the nitrogen content to below 10 ppm. The nitrogen content of the hydrotreated SOH was 50 ppm and 60 ppm in Periods 5 and 11 respectively, compared with 500 ppm and 1680 ppm for the unhydrotreated SOH in Periods 7 and 13. The sulfur contents were similarly low. The higher heteroatom content of the Run CC-11 SOH might be due to the loss of the middle hydrotreater thermocouple and subsequent inaccurate temperature estimation.

Figures 6 through 8 show °API gravity, H/C ratio and nitrogen content of the PFL distillation fractions. The H/C ratio and °API gravity were very stable while the nitrogen content steadily rose. Again, the presence of H₂S is perhaps responsible for maintaining the hydrogenation activity of the liquefaction catalyst. The deactivation effect on the PFL nitrogen content might appear contradictory to the earlier reported data on consistently high overall HDN. However, the net PFL yield was quite low, and hence its increasing nitrogen content does not contribute greatly to the overall HDN. The analyses of the unconverted coal did not show a trend relative to catalyst age. The sulfur content was quite high and indicated that sulfur was being picked by the unconverted coal and ash.

FILTRATION TESTS

Atmospheric Still Bottoms (ASB's) from Conditions 2 and 4 were sent to British Coal Board (BCB) for small-scale pressure filtration tests. The compositions of the ASB's are listed in *Table 8*. The results of these tests and BCB's recommendations for optimal operating conditions are presented in the Appendix to this section. These recommendations were previously summarized in the Summary at the beginning of this section.

DETAILS OF OPERATION

A large capacity feed vessel, which could hold more than a 12-hour supply of feed coal plus recycle solvent, was installed for this run. The run was started using a relatively large amount of start-up oil to slurry the coal in this feed vessel. The operation reached an equilibrated solvent composition over the next seven days by recycling the process solvent. After Period 7, the entire Atmospheric Still Bottoms were collected over the next eight hours for use in the filtration tests. The capacity of the feed tank was used during this period to supply the process feed. In Period 8 the feed tank was again filled by using start-up oil to slurry the feed coal. The process was reequilibrated over Periods 8 through 13 by recycling PFL. At the end of Period 13, the entire Atmospheric Still Bottoms were collected as before.

The hydrotreater was equipped with three thermocouples along its length, the middle thermocouple being the primary sensor. However, when the middle thermocouple failed soon into the run, the average of the top and bottom thermocouple was used to maintain the specified hydrotreater temperature. There could have been a significant difference between this average temperature and the previously used middle temperature.

COAL FEED

Black Thunder mine (Wyoming) sub-bituminous coal (HRI-5713) was used as feedstock. The coal analyses are shown in *Table 9*. The coal was ground to -70 mesh and dried under nitrogen to reduce the moisture content to about 6 W%.

START-UP OIL

The run was started using HRI-5757, a heavy distillate obtained from Wilsonville. It had a boiling range of 700-950°F. The analyses are shown in *Table 10*. A lot of this start-up oil was used to build the initial charge tank inventory and to build this inventory again after the tank was emptied in Period 7 to obtain the first half of the 20 kg Atmospheric Still Bottoms sample. Additional small supplements of start-up oil were required to slurry the feed coal during the run when the recycle PFL was insufficient. These amounts are shown in the Operating Summary (*Table 2*).

FRESH CATALYST

The same Shell S-317, HRI-5394, $\frac{1}{32}$ " extrudate NiMo catalyst that had been used throughout the program was used in both liquefaction stages. Shell 424 NiMo catalyst, HRI-5749, was used in the hydrotreater. The analyses of the Shell 424 catalyst are given in *Table 11*. The Shell S-317 analyses are shown in *Table 11* in the section on Run 227-55(CC-1). The catalysts were sulfided

during start-up by holding all reactors at several intermediate temperatures for several hours in the presence of H_2S .

RECOVERED CATALYST

Table 12 shows the analyses of the recovered liquefaction and hydrotreating catalysts. The first and second stage catalysts had carbon accumulations of 10.0 and 18.8 W%. These values were not much different than the carbon accumulations on recovered catalyst after other runs with Black Thunder coal, but, considering the short 13-day run length, the second stage catalyst carbon content is relatively high. Considering the short 13-day run length. Sodium was the principal metal contaminant, having accumulated 1.70 W% on the first stage catalyst and 2.26 W% on the second stage catalyst. The pore volume decreased from 0.70 cc/cc (particle) for the fresh catalyst to 0.45 and 0.39 cc/cc (particle) for the first and second stage catalyst, respectively.

The recovered hydrotreating catalyst contained 2.91 W% carbon and retained a pore volume of 0.49 cc/cc (particle). Thus this recovered catalyst was somewhat less contaminated than the hydrotreating catalyst removed after Run 227-68 (CC-10). The sulfur content of the catalyst recovered from Run 227-69(CC-11) was less than required for complete sulfidation of the active metals. Assuming stoichiometry of MoS_2 and Ni_3S_2 , the sulfur content was about 88% of the required amount. Perhaps the partial pressure of H_2S was insufficient to maintain complete sulfidation in the presence of water.

(1) Kimber, G., "The Development of Filtration for Coal Liquefaction, " British Coal Liquefaction Project, EPRI Conference, 1991.

TABLE 1

RUN PLAN - (CC-11)

RUN 227-69

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
PERIOD	1-5	6-7	8-11	12-13
SPACE VELOCITY (Lbs Coal/Hr/Ft ³ Catalyst)	<u>67</u>			
TEMPERATURE, °F				
First Stage	<u>775</u>			
Second Stage	<u>825</u>			
Hot Separator	<u>625</u>			
Hydrotreater	640	---	670	---
Recycle Ratio, (PFL/Coal)	<u>1.1</u>			
H ₂ S Rate, W% Coal	<u>2.0</u>			

NOTES: HYDROTREATER WAS OFF LINE IN CONDITIONS 2 AND 4.
CAS BOTTOMS WERE COLLECTED AFTER PERIODS 7
AND 13.

THE INITIAL RUN PLAN CALLED FOR THE FIRST STAGE
TEMPERATURE AT 775°F THROUGHOUT THE RUN. IT
WAS DECIDED TO LOWER TO 750°F ON PERIOD 12 TO
LOWER THE OBSERVED HIGH GAS YIELDS.

TABLE 2

**OPERATING SUMMARY SOLIDS SEPARATION RUN
RUN 227-69 (CC-11)**

COAL: BLACK THUNDER COAL (HRI-5713)
CATALYST: 1ST & 2ND STAGE-S-317 CATALYST

PERIOD NUMBER	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Date (Start of Period)	11/21/90	11/22/90	11/23/90	11/24/90	11/25/90
Hours of Run (End of Period)	72	96	120	144	168
Catalyst Age, Lb Dry Coal/Lb Cat. (Per Stage)	122	166	207	249	291
1st Stage Temperature (°F)	775	776	774	773	774
2nd Stage Temperature (°F)	827	826	827	827	827
Unit Back Pressure (PSIG)	2531	2529	2530	2531	2526
Space Velocity per Stage, Lb/Hr/Ft ³ Cat.	67.1	70.2	66.0	67.8	68.4

W% DRY COAL

PFL Recycle	105.0	100.6	106.7	98.2	97.5
PFL to Buffer - Stage 1	2.8	2.7	2.8	2.7	2.5
PFL to Buffer - Stage 2	2.5	2.7	2.8	2.4	2.7
Makeup Oil	3.5	7.9	1.8	10.4	11.2
H ₂ S	2.1	1.6	2.3	2.2	1.9
TOTAL MATERIAL RECOVERY (GROSS)	99.99	100.6	104.48	100.53	96.64

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	8.59	11.04	9.43	9.61
C ₄ -C ₇ in Gases	5.08	5.02	4.59	4.61
IBP-390°F in Liquids	14.62	14.42	13.79	13.03
390-500°F in Liquids	9.59	9.67	9.92	9.51
500-650°F in Liquids	18.71	18.27	20.41	19.49
650-850°F in Liquids	5.19	5.62	4.29	5.20
850-950°F in Liquids	-0.74	-0.02	-1.23	-1.33
Toluene Soluble 985°F Oil	1.10	0.45	1.41	1.57
Toluene Insoluble 975°F Oil	0.01	0.00	0.01	0.01
Unconverted Coal	12.67	11.83	11.49	10.55
ASH (SO ₃ -free)	6.72	6.72	6.72	6.72
Water	22.73	20.69	23.06	24.20
CO	0.66	0.73	0.96	1.07
CO ₂	1.62	2.29	1.74	2.25
NH ₃	0.98	0.97	1.00	0.99
H ₂ S	0.37	0.36	0.37	0.36
TOTAL (100+H ₂ Reacted)	107.92	108.07	107.95	107.85

PROCESS PERFORMANCE

C ₉ 975°F Distillates, W% of MAF Coal	56.2	56.8	55.5	54.2
975°F Conversion, W% MAF	85.2	86.8	86.2	87.0
Coal Conversion, W% MAF	67.5	86.4	87.3	87.7
HDS, W%	67.5	67.0	67.7	67.3
HDN, W%	87.7	86.9	89.4	88.9

**OPERATING SUMMARY SOLIDS SEPARATION RUN
RUN 227-69 (CC-11)**

COAL: BLACK THUNDER COAL (HRI-5713)

CATALYST: 1ST & 2ND STAGE-S-317 CATALYST

PERIOD NUMBER	9	10	11	12	13
Date (Start of Period)	11/27/90	11/28/90	11/29/90	11/30/90	12/01/90
Hours of Run (End of Period)	216	240	264	288	312
Catalyst Age, Lb Dry Coal/Lb Cat. (Per Stage)	376	418	460	501	543
1st Stage Temperature (°F)	773	774	773	754	749
2nd Stage Temperature (°F)	826	827	826	827	826
Unit Back Pressure (PSIG)	2527	2525	2521	2522	2520
Space Velocity per Stage, Lb/Hr/Ft ³ Cat.	67.6	68.0	67.8	65.8	68.4

W% DRY COAL

PFL Recycle	108.0	94.4	108.6	104.2	103.7
PFL to Buffer - Stage 1	3.0	2.6	2.9	2.9	2.7
PFL to Buffer - Stage 2	2.6	2.7	2.8	2.5	2.6
Makeup Oil	0.0	14.6	0.0	4.4	4.9
H ₂ S	2.3	1.8	2.2	1.9	2.1

TOTAL MATERIAL RECOVERY (GROSS)	100.99	99.26	100.52	102.57	100.63
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ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases	8.13	7.60	8.28
C ₄ -C ₇ in Gases	4.64	3.97	3.65
IBP-390°F in Liquids	13.24	12.48	11.92
390-500°F in Liquids	9.21	8.90	8.82
500-650°F in Liquids	16.61	16.44	15.99
650-850°F in Liquids	9.18	10.07	10.64
850-950° in Liquids	1.10	1.18	1.03
Toluene Soluble 985°F+ Oil	1.30	2.71	3.47
Toluene Insoluble 975°F+ Oil	0.02	0.01	0.02
Unconverted Coal	11.03	10.52	12.09
ASH (SO ₃ -free)	6.72	6.72	6.72
Water	23.26	21.59	20.28
CO	0.72	0.95	0.94
CO ₂	1.45	2.76	1.93
NH ₃	0.94	0.88	0.84
H ₂ S	0.29	0.30	0.32
TOTAL (100+H ₂ Reacted)	107.83	107.07	106.94

PROCESS PERFORMANCE

C ₄ 975°F Distillates, W% of MAF Coal	57.9	58.1	55.8
975°F+ Conversion, W% MAF	86.8	86.6	83.3
Coal Conversion, W% MAF	87.0	87.9	87.0
HDS, W%	54.3	54.6	58.9
HDN, W%	83.8	78.7	74.9

TABLE 3
LIQUEFACTION PERFORMANCE
RUN 227-69 (CC-11)

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
PERIODS	4/5	7	11	13
Cat. Age (Per Stage) (Lb Coal/Lb Cat)	186	291	460	543
Liquefaction SV (Lb Coal/Hr/Ft ³ Cat)	68.1	67.8	67.8	68.4
<u>TEMPERATURE (°F)</u>				
1st Stage Temp	775	774	773	749
2nd Stage Temp	826	827	826	826
Hot Separator	625	625	625	625
Hydrotreater	640	---	670	---
<u>NORMALIZED YIELDS (W% COAL)</u>				
C ₁ -C ₃	9.82	9.61	8.13	8.28
C ₄ -390°F	19.57	17.64	17.88	15.57
390-500°F	9.63	9.51	9.21	8.82
500-650°F	18.49	19.49	16.61	15.99
650-850°F	5.41	5.20	9.18	10.64
850-975°F*	-0.38	-1.33	1.10	1.03
975°F* Liquid	0.78	1.58	1.32	3.49
IOM	12.25	10.55	11.03	12.09
ASH	6.72	6.72	6.72	6.72
CO + CO ₂	2.65	3.32	2.17	2.87
NH ₃	0.98	0.99	0.94	1.93
H ₂ S	0.37	0.36	0.29	0.32
H ₂ O	21.73	24.20	23.26	20.28
TOTAL (100+H ₂)	108.00	107.85	107.83	106.94
<u>PERFORMANCE (W% MAF)</u>				
Coal Conversion	86.9	88.7	88.2	87.0
Resid Conversion	86.0	87.0	86.8	83.3
HDS	67.3	67.3	54.3	58.9
HDN	87.3	88.9	83.8	74.9
C ₄ -975°F Yield	56.5	54.2	57.9	55.8

During some part of the run, it was necessary to employ make-up solvent (HRI-5757) as a small fraction of the recycle oil requirements. The calculated yields are on a net basis. The small negative yields reflect that the amount of the particular cut produced was less than the amount associated with the make-up oil.

TABLE 4
QUALITY OF SEPARATOR OVERHEAD
RUN 227-69 (CC-11)

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Period Number	5	7	11	13
Hydrotreater Temp, °F	640	---	670	---
First Stage Temp, °F	775	775	775	750
API Gravity	34.5	31.9	34.2	32.6
Carbon, W%	87.38	87.31	86.87	86.93
Hydrogen, W%	12.83	12.35	13.01	12.14
Nitrogen, PPM	50	500	60	1680
Sulfur, PPM	42	0*	42	0*
VABP, °F	457	466	444	457
H/C Ratio	1.76	1.70	1.80	1.68
Watson K	11.03	10.86	10.95	10.88

The sulfur content of this sample was determined using Leco sulfur analyzer and is not accurate at the low sulfur level.

TABLE 5
QUALITY OF ATMOSPHERIC - STILL OVERHEAD/KNOCKOUTS
RUN 227-69 (CC-11)

CONDITION	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Period Number	5	7	11	13
Hydrotreater Temp, °F	640	---	670	---
First Stage Temp, °F	775	775	775	750
API Gravity	25.5	24.3	26.5	26.3
Carbon, W%	88.48	88.44	87.21	87.41
Hydrogen, W%	11.79	11.76	11.88	11.70
Nitrogen, PPM	730	900	1260	1100
Sulfur, PPM	0	0	80	40
VABP, °F	521	533	509	507
H/C Ratio	1.60	1.60	1.63	1.61
Watson K	10.90	10.89	10.93	10.90

The sulfur content of the ASOH stream was determined using Leco sulfur analyzer and is not accurate at the low sulfur level.

TABLE 6
ANALYSES OF PFL
RUN 227-69 (CC-11)

Period Number	<u>5</u>	<u>7</u>	<u>11</u>	<u>13</u>
TOTAL PFL				
API Gravity	8.4	7.7	7.3	6.4
Carbon, W%	90.35	90.31	90.51	90.67
Hydrogen, W%	9.78	9.61	9.50	9.28
Nitrogen, W%	0.15	0.13	0.21	0.25
Sulfur, W%	0.01	0.00	0.00	0.01
H/C Ratio	1.30	1.28	1.26	1.23
IBP-650°F, W%	11.57	11.80	10.79	10.19
650-850°F, W%	61.92	61.36	58.33	55.65
850-975°F, W%	12.86	12.98	14.02	13.40
975°F, W%	13.65	13.86	16.86	20.76
IBP-650°F CUT				
API Gravity	18.4	17.7	18.0	17.8
Carbon, W%	88.90	89.22	88.52	88.47
Hydrogen, W%	11.25	11.01	10.77	10.81
Nitrogen, W%	0.05	0.05	0.12	0.14
Sulfur, W%	0.00	0.00	0.00	0.00
H/C Ratio	1.52	1.48	1.46	1.47
650-850°F CUT				
API Gravity	11.5	11.0	11.0	11.4
Carbon, W%	89.86	89.89	89.28	89.4
Hydrogen, W%	10.34	10.24	10.05	9.98
Nitrogen, W%	0.06	0.08	0.16	0.19
Sulfur, W%	0.00	0.01	0.00	0.00
H/C Ratio	1.38	1.37	1.35	1.34
850-975°F CUT				
API Gravity	1.4	0.6	0.9	1.3
Carbon, W%	90.78	90.73	90.26	90.60
Hydrogen, W%	8.79	8.78	8.88	8.70
Nitrogen, W%	0.20	0.15	0.29	0.29
Sulfur, W%	0.00	0.00	0.00	0.00
H/C Ratio	1.16	1.16	1.18	1.15
975°F CUT				
API Gravity	-7.4	-9.3	-8.8	-8.6
Carbon, W%	90.88	91.03	90.29	90.63
Hydrogen, W%	7.47	7.22	6.94	7.26
Nitrogen, W%	0.30	0.37	0.48	0.52
Sulfur, W%	0.02	0.02	0.02	0.04
H/C Ratio	0.99	0.95	0.92	0.96

TABLE 7
ANALYSES OF THF-WASHED FILTER CAKE

RUN 227-69 (CC-11)

Period Number	<u>5</u>	<u>7</u>	<u>11</u>	<u>13</u>
WEIGHT %				
Carbon, W%	46.42	44.81	43.67	47.83
Hydrogen, W%	2.64	2.40	2.40	2.41
Nitrogen, W%	0.71	0.63	0.68	0.72
Sulfur, W%	1.04	1.19	1.42	1.18
Ash	39.57	42.39	41.99	38.46
WEIGHT % (ASH-FREE)				
Carbon, W%	76.82	77.78	78.73	77.72
Hydrogen, W%	4.37	4.17	4.14	3.92
Nitrogen, W%	1.17	1.09	1.17	1.17
Sulfur, W%	1.72	2.07	2.45	1.92
Oxygen (Diff)	15.92	14.89	13.51	15.27

TABLE 8
COMPOSITION OF CAS BOTTOMS USED FOR FILTRATION TESTS

RUN 227-69 (CC-11)

SAMPLE ID	<u>LO-5687</u>	<u>LO-5688/89</u>
CAS BOTTOMS COMPOSITION		
Distillate (975°F-), W%	76.92	69.96
Residual Oil (975°F-), W%	12.38	18.32
IOM, W%	6.54	7.52
Ash, W%	4.16	4.18
LIQUID COMPOSITION		
API Gravity	7.7	6.4
Residual Oil (975°F-), W%	13.86	20.76
Distillate (975°F-), W%	86.14	79.24
VISCOSITY, CP		
At 75°F	953	1967
At 125°F	80	103
At 150°F	34	46

TABLE 9
ANALYSES OF FEED COAL
RUN 227-69 (CC-11)

COAL	Black Thunder
HRI NO	<u>5713</u>
PROXIMATE ANALYSIS, (W%)	
MOISTURE	6.56
VOLATILE MATTER (MAF)	54.6
FIXED CARBON (MAF)	45.4
ULTIMATE ANALYSIS, (W% DRY BASIS)	
Carbon, W%	67.57
Hydrogen, W%	4.75
Nitrogen, W%	0.91
Sulfur, W%	0.46
Ash	7.66
(SO ₃ -Free)	6.76
SULFUR TYPES (W%, DRY BASIS)	
Sulfate	0.01
Pyritic	0.07
Organic	0.48
ASH ANALYSIS (W%, IGNITED BASIS)	
Silicon Dioxide	36.16
Alumina	17.54
Titanium Dioxide	1.24
Iron Oxide	5.01
Calcium Oxide	19.69
Magnesium Oxide	3.99
Potassium Oxide	0.43
Sodium Oxide	0.39
Sulfur Trioxide	12.93
Phosphorous Pentoxide	0.89
Strontium Oxide	0.95
Barium Oxide	0.64
Manganese Oxide	0.11

TABLE 10
ANALYSES OF START-UP OIL
RUN 227-69 (CC-11)

HRI NO.	5757
TYPE	Wilsonville Heavy Distillate
API Gravity	8.2
Carbon, W%	89.68
Hydrogen, W%	10.17
Nitrogen, W%	0.27
Sulfur, W%	0.02
D1160 DISTILLATION	TEMPERATURE, °F
IBP	700
5 V%	721
10 V%	734
20 V%	745
30 V%	755
40 V%	772
50 V%	790
60 V%	805
70 V%	827
80 V%	850
90 V%	881
95 V%	908
FBP	945

TABLE 11
ANALYSES OF FRESH HYDROTREATING CATALYST
RUN 227-69 (CC-11)

HRI NUMBER	5749
CATALYST TYPE	SHELL-424
CATALYST SIZE	1/10 " TRILOBE
Nickel, W%	3.0
Molybdenum, W%	13.0
Surface Area, M ² /g	162
Pore Volume, cc/g	0.47
Compacted Bulk Density, cc/g	0.83

TABLE 12

ANALYSES OF RECOVERED CATALYST

RUN 227-69 (CC-11)

	<u>STAGE 1</u>	<u>STAGE 2</u>	<u>HYDROTREATER</u>
Carbon, W%	10.04	18.82	2.91
Hydrogen, W%	0.39	0.60	0.35
Nitrogen, W%	0.07	0.11	0.03
Sulfur, W%	6.34	5.48	6.87
Molybdenum, W%	8.25	7.78	10.41
Nickel, W%	1.66	1.51	2.31
Iron, W%	0.57	0.07	
Titanium, W%	0.02	0.00	
Calcium, W%	0.07	0.12	
Sodium, W%	1.70	2.26	
COMPACTED BULK			
Density, g/cc	0.82	0.95	0.94
Particle Density, g/cc	1.29	1.45	1.43
PORE VOLUME, cc/g	0.35	0.27	0.34
cc/cc	0.45	0.39	0.49
Loss on Ignition, W%	17.13	26.02	10.96
Particle Density (Ignited Catalyst), cc/g	1.09	1.09	1.43
Pore Volume (Ignited Catalyst), cc/g	0.50	0.51	0.34
cc/cc	0.55	0.56	0.49

SOLIDS SEPARATION RUN (CC-11)

COAL / RESID CONVERSIONS

FIGURE 1

□ COAL + RESID

FIGURE 2

SOLIDS SEPARATION RUN (CC-11) DISTILLATE YIELD

SOLIDS SEPARATION RUN (CC-11)

DISTILLATE YIELD

FIGURE 3

SOLIDS SEPARATION RUN (CC-11)

DISTILLATE SELECTIVITY

FIGURE 4

5 of 7

SOLIDS SEPARATION RUN (CC-11)

HDS / HDN

FIGURE 5

SOLIDS SEPARATION RUN (CC-11)

API GRAVITY OF PFL CUTS

FIGURE 6

SOLIDS SEPARATION RUN (CC-11)

H/C RATIO OF PFL CUTS

FIGURE 7

SOLIDS SEPARATION RUN (CC-11)

NITROGEN CONTENT OF PFL CUTS

FIGURE 8

APPENDIX I
BCB REPORT

BRITISH COAL LIQUEFACTION PROJECT
POINT OF AYR 2.5 TPD LSE PILOT PLANT FACILITY

Filtration of CTSL
Atmospheric Still Bottoms

FINAL REPORT

to

HYDROCARBON RESEARCH INCORPORATED

Report No: ECR 001

Prepared by: S A Moore

Approved by: G M Kimber

Date: July 1991

SUMMARY

British Coal has tested materials supplied by Hydrocarbon Research Incorporated in laboratory and bench-scale filters. The results indicate that the removal of solids from CTSL atmospheric column bottoms produced with Black Thunder coal presents no technical problems.

On a commercial scale, filtration should be carried out at a temperature of at least 300°C and at a differential pressure of at least 4 bar. It is expected that in situ screen cleaning by high pressure sluicing would be required. The filter cake should be washed in situ to recover heavy product which would otherwise be rejected.

The estimated total erected cost for the filtration package required on a 10,000 stpd (coal) CTSL plant is UK £31.8 million at June 1989 prices.

It is recommended that consideration be given to filtering the CTSL product before atmospheric distillation.

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1. INTRODUCTION

Under an Agreement dated 12 March 1991, British Coal has tested materials supplied by Hydrocarbon Research Incorporated (HRI) in laboratory and bench-scale filters. The purpose of this work was to determine the practicability of using filtration as the solids separation step in HRI's CTSL coal liquefaction process.

The work programme was divided into four 'phases', as outlined below, although these did not follow sequentially.

- Phase 1 (Laboratory tests) - simple qualitative tests were carried out on screen bridging and screen blinding, followed by a more extensive series of quantitative tests in a small laboratory filter.
- Phase 2 (Comparative plant test) - a sample of coal provided by HRI was extracted and filtered at conditions typical of those used in British Coal's Liquid Solvent Extraction (LSE) process.
- Phase 3 (Plant tests) - two filtration tests of the material provided by HRI were carried out in a bench-scale pilot plant to confirm the results obtained in Phase 1.
- Phase 4 (Assessment) - the results obtained were reviewed in order to make comment on the technical feasibility of filtering HRI's materials and to make recommendations on suitable filter operating conditions. An estimate was made of the cost of filtration on a conceptual CTSL commercial plant, scaled from cost data recently obtained by British Coal.

2. MATERIALS

HRI provided two samples of atmospheric column bottoms from their bench-scale pilot plant, identified as LO-5687 and LO-5688/89, and one sample of Black Thunder coal representing their process feed. The analytical information provided by HRI on these materials is given in Tables 1 and 2.

British Coal carried out a series of viscosity measurements on samples of the filtrate from the atmospheric bottoms as received and after concentration by distilling off approximately 20% w/w. The results are given in Table 3, including the extrapolated viscosities required for data assessment at practical filtration temperatures.

The samples used for the laboratory test work were taken at the start of the programme as sub-samples from the bulked primary samples, which were mixed at 100°C.

3. EQUIPMENT

The Phase 1 tests were carried out in a small laboratory plate filter, for which a simple schematic is given in Figure 1. For the quantitative tests, a disposable glass fibre filter paper was used as the filter medium, supported horizontally on a perforated plate. The cakes produced were not generally washed or dried. Similar equipment was used for the preliminary qualitative tests on metal screens. The maximum working temperature and pressure are 300°C and 8 bar, respectively. The principal advantages of this equipment are its relatively low sample requirement and its low operating labour costs.

The Phase 2 tests were carried out in a larger plant known as the Integrated Solvent Extraction Plant (ISEP), shown in schematic form in Figure 2. This operates on a batch basis. Coal (usually 5 - 10 kg) and solvent are mixed and pumped to a digester, where they are heated to the desired extraction temperature. Gases and light distillates produced during the reaction are metered and condensed, respectively, allowing an accurate mass balance to be constructed. The digester contents are cooled to the desired temperature and filtered through one of two horizontal plate filters. The filtrate passes to a hold vessel in which it can optionally be concentrated by distillation under vacuum. This technique is also used to produce the wash oil used for cake washing, which is therefore a purely internal recycle stream. Finally, the filter cake is dried in situ under vacuum. Cake discharge is manual, following disassembly of the filter housing, and cake weights can therefore be obtained with high accuracy. This equipment has now been used to prepare over 1700 batches of coal solution and gives excellent reproducibility in its results.

The Phase 3 tests were also carried out in ISEP, using the digester as a simple stirred hold tank for the feed. A diagrammatic section through one of the two filter housings is shown in Figure 3. The screen itself was a flat sheet of Conidur, a commercially available punched stainless steel screen medium, supported on a perforated plate. The nominal screen aperture size was 100 μ . There is no recycle of slurry through the filter housing during filtration. During cake drying, vacuum is applied to both sides of the screen.

4. RESULTS

Table 4 gives experimental and calculated results for all the quantitative tests in Phase 1 - 3. 'Cake QI' is the quinoline insoluble content of the filter cake, expressed as a percentage of the total cake weight, and is assumed to be the sum of the insoluble organic matter and the coal mineral matter. 'Cake CyI' is the cyclohexane insoluble content on the same basis.

Filter cake specific resistivities and the system medium resistances were calculated by the application of Darcy's Law. In practice, the calculated medium resistance, which should theoretically be constant for a given filter assembly, varies markedly and usually correlates well with the cake resistivity. Practically speaking, however, this is of little importance since the contribution of medium resistance to overall resistance is very small when filtering coal liquefaction products. Darcy plots and other experimental data are given in Appendix 1 for all the

Optimised filtration rates were calculated using a computer model developed by British Coal. The primary model output is an optimum rate expressed in kg of filtrate per m² of filter area per hour. The factor required to convert these figures to kg coal(db) per m² per hour was derived by an ash tracer method from HRI's figures for the ash content of the coal and the atmospheric column bottoms, assuming no loss or gain of ash precursors during processing. This gave the 'coal content' of the atmospheric column bottoms, which was modified to give the 'coal content' of the filtrate by using British Coal's figure of 10.3% for the solids content (quinoline insolubles) of the atmospheric bottoms. The ratio of coal to filtrate is 0.695 for all cases except POA 8, where it is 0.898, and CRE 3, where it is proprietary. The optimised filtration rates are calculated on the assumption that cake washing will not be required but that the cake will be dried in situ.

The results for run POA 1 are anomalous, since the cake resistivity was determined over only the first five minutes of filtration, but are included in Table 4 for completeness.

5. DISCUSSION

5.1 Laboratory Tests

5.1.1 Screen bridging

Screen bridging tests were carried out on a selection of screen materials which might be used in a commercial filter design. A nominal 200 μ aperture woven wire screen could not be bridged, but both 100 μ woven wire and 100 μ Conidur were bridged successfully.

5.1.2 Screen blinding

A simple light transmission test through the Conidur screen used in the bridging test indicated a substantial reduction in open area after washing and drying the screen, indicating that an effective method of in situ screen cleaning would be required in commercial operation. In British Coal's experience, the only suitable technique for this is high pressure sluicing.

5.1.3 Filtration temperature

Temperatures in the range 200 - 300°C were examined. Increasing the filtration temperature reduced the cake resistivity significantly at both 2 bar and 4 bar, in addition to reducing the filtrate viscosity. The combined effect was to increase the optimised filtration rate at 2 bar by 13% on increasing the temperature from 250°C to 300°C (POA 7 and POA 3). At 4 bar, the optimised rate was increased by 43% between 200°C and 300°C (POA 10 and POA 5/6). The implication of these results is that filtration should be carried out at as high a temperature as practicable, the limiting factors being filter metallurgy, filter construction and the extent of filtrate vapourisation on the low pressure side of the filter.

5.1.4 Heat treatment

A possible explanation for the temperature effect on cake resistivity noted above was that 'heat treatment' of the slurry in the feed vessel during the warm-up period was beneficial. To test this, the slurry was heat treated for one hour at 380°C prior to filtration at 300°C (POA 9). There was no significant effect on the cake resistivity.

5.1.5 Filtration pressure

Filter differential pressures of 1, 2, 4 and 8 bar were examined at 300°C. Cake resistivities increased with increasing pressure, showing that the cakes were compressible. Furthermore, the cake compressibility itself increased with pressure. The resulting effect on the optimised filtration rate is shown in Figure 4. Clearly, operation at pressures above 8 bar is unlikely to give significantly improved filtration rates and British Coal's experience suggests that it could actually be deleterious. Indeed operation at any pressure above 4 bar might not be cost-effective, due to increased pumping costs. The optimisation of filtration pressure is highly case-specific, however, and depends also on the pressure at which the feed is available.

5.1.6 Body aid

The filtration of materials with high specific cake resistivities can often be improved by the addition of body aid to the slurry. This may be particularly effective if the solids are very fine or the cake is highly compressible, since the body aid then acts to keep the cake structure more open. In run POA 2, coker cyclone fines at a level of 1% by weight were added to the atmospheric column bottoms, which were filtered at 250°C and 2 bar. In comparison to POA 7, the cake resistivity was reduced by 19%. However, the benefit of this was largely negated by the increased solids loading and the optimised filtration rate was increased by only 4%. The use of body aid is therefore unlikely to be cost effective in this application.

5.1.7 Precipitation

Some coal-derived filtrates are prone to precipitation on cooling and standing, particularly if they have been filtered at high temperature. To check on this point, filtrate produced at 300°C and subsequently cooled and stored at ambient temperature was reheated to 100°C and refiltered (POA 12). Approximately 1½% by weight of material was retained, of which approximately two-thirds was cyclohexane soluble. In British Coal's experience, this amount and type of precipitation would not be likely to cause operability problems in continuously operating equipment. It must be remembered, however, that the test samples had previously been cooled and stored for a prolonged period before receipt by British Coal. This may have had the effect of permanently taking out of solution any precipitable material originally present.

5.1.8 Feed concentration

It is common for cake resistivities to reduce as the solids loading of the slurry is increased, a phenomenon ascribed to a change in the packing of the particles in the cake produced. Concentrating the slurry also reduces the amount of filtrate to be removed per unit of solids, which again is beneficial. A sample of atmospheric column bottoms was therefore concentrated by distillation, removing 20.3% by weight at an effective cutpoint of 420°C. The concentrated slurry was filtered at 300°C and 4 bar (POA 8). Although the filter cake resistivity was reduced by 15%, the filtrate viscosity was increased from 0.9 cP to 1.7 cP, more than negating any advantage, and the optimised filtration rate was reduced by 9% based on coal.

The corollary to the above conclusion is that it may be attractive to filter a less concentrated slurry for HRI's application. It is suggested that HRI should consider filtering the CTSL product before it is fed to the atmospheric column. Whether this is advantageous in terms of filtration rates will depend on the extent to which the liquid viscosity is reduced by the retention of light ends and the effect on the cake resistivity. Potential operating advantages may, however, be equally important and include the reduction of pumping costs, since in this configuration the filters could be used as the final pressure let-down stage.

5.1.9 Cake washing

Washing the filter cake in situ increases the length of the filtration cycle, and hence the filter area requirement, but recovers product which would otherwise be discharged with the cake. A washing test was carried out 300°C and 4 bar on filter cake produced in situ at the same conditions (POA 6). The wash oil was the -420°C material produced by distilling the atmospheric column bottoms for the concentration test described above. The washings were collected at intervals and their hydrogen contents determined by an nmr method which is accurate to $\pm 0.02\%$ absolute. The results are plotted in Figure 5, where the number of wash volumes used is calculated from the solids loading of the slurry and the assumption that the initial cake density, excluding liquids, was 600 kgm^{-3} .

The hydrogen content of the wash oil itself is represented by the dashed horizontal line in Figure 5. (The higher hydrogen content of the tail is due to exhaustion of the wash oil in the reservoir with the consequence that lighter material, which had previously been refluxing above the liquid level, now condensed and passed through). The initial point is the hydrogen content of the filtrate prior to washing. Integration of the area between the curve and the dashed line allows the efficiency of washing up to any given wash volume to be calculated. It should be noted that 100% efficiency on this definition does not mean that the cake is free from heavy liquids, but only that no more can be washed out with this solvent at these conditions.

It is clear that increasing the wash oil volume produces rapidly diminishing returns. Washing with 0.5 cake volumes recovered 55% of the available material and would increase the required filtration area by 10%. The corresponding figures for 1.0 cake volumes are 78% and 15%, respectively, and for 2.0 cake volumes are 89% and 24%. The amount of wash oil which is recovered during cake drying is generally around 0.5 cake volumes and any wash oil usage in excess of this entails a distillation penalty for its production. It is unlikely, therefore, that washing with more than 1.0 cake volumes would be cost effective.

5.2 Comparative Plant Tests

An 8 kg sample of Black Thunder coal was extracted in the Integrated Solvent Extraction Plant (Section 3) at typical LSE processing conditions using hydrogenated anthracene oil as the solvent. Relative to a typical UK coal, there were higher yields of undissolved coal, but the product distribution of the coal which did dissolve was lighter, with high yields of CO₂ and water, increased yields of hydrocarbon gases and light distillates and a substantial reduction in the make of material boiling above 450°C. This product distribution was not unexpected, given the low rank of Black Thunder.

Filtration results for this run are included in Table 4 (CRE 3). The cake resistivity was reduced by a factor of five when compared with atmospheric column bottoms filtered at similar conditions, reducing the required optimised filtration area by around 60%, and lay within the usual range for coals extracted with hydrogenated anthracene oil. LSE process-derived recycle solvents generally produce filter cakes of substantially lower specific resistivity.

5.3 Plant Filtration Tests

Two 12 kg batches of atmospheric column bottoms were filtered in larger scale horizontal plate filters, as described in Section 3. The results (CRE 1 and CRE 2) confirmed those obtained in the laboratory, but also provide further insight into the advantages of washing the filter cake.

In CRE 1 the cake was washed with 1.3 volumes of oil and after drying contained 16.9% of quinoline soluble material, assumed to be heavy product. This represents 3.2% on db coal, using the factors derived in Section 4. In CRE 2 the cake was not washed and contained 31.8% quinoline solubles after drying, equivalent to 7.0% on db coal. From the discussion in Section 5.1.9, it can be estimated that the irreducible minimum of quinoline soluble material in the filter cake would be around 2.2% on db coal, a figure which in British Coal's experience is within the usual range for good in situ washing.

6. COMMERCIAL PLANT CAPITAL COST ESTIMATE

Based upon the data obtained at 300°C and a differential pressure of 4 bar, the required filtration area to filter the atmospheric column bottoms from a 10,000 (short) tpd coal commercial plant is estimated at 8400m². This calculation assumes a coal:filtrate ratio of 0.695, as outlined in Section 4. The maximum filtration area per individual filter currently offered by the manufacturers of suitable equipment is 465m². Thus, 20 filters would provide a contingency of 10.7% additional area, 21 filters would provide 16.3% and 24 filters would provide 32.9%. It is expected that the optimum number of filters per train would be four, although a detailed cycle analysis has not been carried out, and the filter layouts to be considered are therefore five or six trains of four filters.

British Coal's cost data for commercial scale filtration is based upon vendor quotations for filters operating at higher temperatures and pressures than the 300°C and 4 bar on which the above area calculation is based. It is understood that this overspecification has little impact on the unit cost of filters. It is therefore reasonable to specify five trains of four filters, to be operated at a temperature above 300°C such that the contingency is 25% or one spare train. Based upon viscosity estimates, the necessary temperature would be approximately 330°C. Alternatively, of course, a combination of higher temperature and higher pressure could be used.

British Coal's estimate for the capital costs of filtering the atmospheric bottoms from a 10,000 stpd CTSL plant, based upon the 5 x 4 layout suggested above, is UK £31.8 million at June 1989 prices.

These costs are derived from a study carried out by a major UK chemical engineering contractor on the capital costs of a commercial coal liquefaction plant utilising British Coal's LSE process technology and constructed at a national UK greenfield coastal site. The contractor believes that the accuracy of the estimating techniques used is such that the final cost estimate is ±25%. Supply costs were derived from a mixture of vendor quotations and estimates from the contractor's in-house data. The remainder of the costs which make up the total erected cost (which excludes interest during construction) are based on estimates by the contractor. Note that buffer capacity outside the filtration unit battery limits is excluded from this cost estimate, but that the wash oil recovery system and filtrate export pump are included. All pumps are duplicated by installed spares of 100% capacity.

The only utilities required are instrument air, steam and cooling water for the vacuum ejector packages, cooling water for the cake cooler conveyors and electric power. British Coal has no specific information on the steam and water requirements for the ejectors, which are likely to vary considerably between possible designs. (As a guide, however, calculations should be based on a required system pressure of 20mbar and an operating volume of 70m³). The total cooling required for the cake cooler conveyors is estimated at 1.6MW per operating train, although some of this duty could be satisfied by steam raising from boiler feed water. The total electrical power requirement is estimated at 1.6MW, based on four operating trains.

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CONCLUSIONS

1. On the basis of the tests reported here, filtration of CTSL atmospheric column bottoms would be technically and technologically feasible on a commercial scale. A variety of screen materials could be used, although it is expected that high pressure in situ sluicing would be required to prevent screen blinding.
2. Filtration on a commercial scale should be carried out at as high a temperature as is compatible with filter metallurgy and construction and certainly at at least 300°C. A differential pressure of at least 4 bar should be used; the benefits of operating at higher differential pressures are likely to be relatively small, however, and will depend on the pressure at which feed is available.
3. Despite the relatively high specific cake resistivities found in this study, the use of body aid is unlikely to be cost effective.
4. The filter cake should be washed in situ with a fraction of the process solvent to recover heavy product. The optimum wash oil:filter cake ratio is unlikely to be greater than 1:1 by volume.
5. Consideration should be given to filtering the CTSL product before atmospheric distillation, although an evaluation of the potential benefits would require further study.
6. The estimated total erected cost for the filtration package required on a 10,000 stpd (coal) CTSL commercial plant is UK £31.8 million at June 1989 prices.

Table 1 Analytical Information on CTSL Atmospheric Bottoms

Sample No.:	LO-5687	LO-5688/89
Distillate <975°F	76.92%	69.96%
Residual Oil >975°F	12.38%	18.32%
IOM	6.54%	7.52%
Ash	4.16%	4.18%
Quinoline Insolubles (British Coal)	10.3%	

Table 2 Analytical Information on Black Thunder coal

Volatile Matter	47.6 %maf
Fixed Carbon	52.4 %maf
Carbon	67.64 %db
Hydrogen	4.62 %db
Nitrogen	0.98 %db
Sulphur	0.36 %db
Ash	6.69 %db
Ash (SO ₃ free)	5.92 %db
Oxygen (diff.)	20.48 %db

Table 3 Viscosity Data (cP)

Temperature		Filtrate	Concentrated Filtrate
120 °C	(m)	4.4	7.4
150 °C	(m)	2.4	4.4
200 °C	(m)	1.4	2.8
250 °C	(e)	1.1	2.0
300 °C	(e)	0.9	1.7

(m) = measured

(e) = extrapolated

Table 4
Mass Balance and Filtration Data

Run Number	PoA 1 ★	PoA 2 ★	PoA 3	PoA 4	PoA 5	PoA 6 ★	PoA 7	PoA 8 ★	PoA 9 ★	PoA 10	PoA 11	PoA 12 ★	PoA 13 ★	CRE 1	CRE 2	CRE 3
Temperature	250	250	300	300	300	300	250	300	300	200	300	100	300	300	300	250
Pressure	2	2	2	1	4	4	2	4	4	4	8	8	8	2	4	1.5
Slurry	145.7	103.5	98.7	103.0	99.2	98.8	98.4	101.5	98.0	100.6	98.1	96.5	96.7	12135	12160	-
Filtrate	106.0	79.5	75.1	80.3	76.4	78.7	77.6	75.6	73.9	77.8	75.3	93.0	74.2	10577	10011	-
Cake	26.3	19.8	16.9	18.6	16.0	14.1	19.5	20.0	18.8	19.6	18.6	1.5	15.4	1587	1872	-
Recovery	90.8	95.9	93.2	96.0	93.1	93.8	98.6	94.2	94.6	96.8	95.7	98.0	92.6	100.2	97.7	-
Cake QI	55.5	60.0	64.6	63.4	65.1	76.4	58.2	54.5	60.7	51.5	59.4	-	78.0	83.1	68.2	-
Cake Cyl												37.3	78.3			
Cake resistivity	243	149	164	138	220	214	183	185	227	276	367	-	339	161	202	30
Med. resistance	58	147	174	55	214	183	129	121	168	207	328	-	225	244	243	102
Optimum rate (filtrate)	48.8	54.8	59.7	49.3	75.4	77.5	52.7	54.1	75.9	53.5	83.9	-	89.5	57.2	77.2	-
(coal)	33.9	38.1	41.5	34.3	52.4	53.9	36.6	48.6	52.7	37.2	58.3	-	62.2	39.7	53.6	54.6

★ = special case

PoA 8 - concentrated by distillation

PoA 6 - washing test

PoA 2 - body aid added

PoA 1 - short filtration

PoA 13 - washing test

PoA 12 - re-filtration

PoA 9 - heat treated

Figure 1 47mm Laboratory Plate Filter

Figure 2 Flow Diagram of the Extraction and Filtration Plant

Figure 3 Diagrammatic Section Through 0.1 m² Plate Filter

Figure 4 Effect of Pressure on Optimised Filtration Rate

Figure 5 Washing Recovery Curve

APPENDIX 1

DARCY PLOTS

The Darcy Equation, which is a simple descriptor of cake filtration, can usefully be written in the form:

$$\frac{dt}{dV} = \frac{\alpha \mu c V}{A^2 P} + \frac{R \mu}{A P}$$

where α = specific cake resistivity
 R = medium resistance
 μ = filtrate viscosity
 c = slurry solids loading (in Kg m^{-3})
 V = filtrate volume
 A = filter area
 P = pressure drop across filter

If the filtrate density is known, V can be replaced by m/ρ , where m is the mass of filtrate and ρ its density.

Integration and insertion of boundary conditions then gives:

$$\frac{t - t_0}{m - m_0} = \frac{\alpha \mu c (m + m_0)}{2A^2 P \rho^2} + \frac{R \mu}{A P}$$

expressing $t - t_0$ as Δt , $m - m_0$ as Δm and $m + m_0$ as $2m - \Delta m$, a plot of $\Delta t / \Delta m$ against $2m - \Delta m$ therefore gives a straight line of slope $\alpha \mu c / 2A^2 P \rho^2$ and intercept μ / AP allowing α and R to be calculated.

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	3.50
20	5.10
30	6.30
40	7.40
50	8.40
60	9.40
80	11.10
100	12.60
120	14.00
150	15.90
180	17.70
210	19.30
270	22.10

Resistivity 2.43E+12 mkg(-1)

Medium Resistance 5.78E+11 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	2.39E+00	4.50E-01	1.29E-03	30	1.1	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	2.39E+03	4.50E+05	1.29E-03	2.07E+05	1.10E-03	1.15E+02	1.00E+03

Temperature: 250°C

Pressure: 2 bar

Notes: Run PoA 1

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BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	3.40
20	5.20
30	6.40
40	7.50
50	8.60
60	9.40
80	11.10
100	12.60
120	14.00
150	15.90
180	17.60
210	19.20
270	22.10
300	23.20
360	26.20
420	28.70
480	31.00
540	33.20
600	35.40
720	39.50
840	43.50
960	47.10
1080	50.50
1200	53.80
1320	57.00
1440	60.00
1560	63.20
1680	65.70
1800	68.30
1920	70.80
2040	73.20
2160	75.50
2280	76.20
2400	76.90
2700	77.70
3000	78.10
3300	78.30

Resistivity 1.49E+12 mkg(-1)

Medium Resistance 1.47E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	6.07E+00	3.02E-01	1.29E-03	30	1.1	11.2	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	6.07E+03	3.02E+05	1.29E-03	2.07E+05	1.10E-03	1.26E+02	1.00E+03

Temperature: 250°C

Pressure: 2 bar

Notes: Run PoA 2
1% Body Aid

British Coal
Liquefaction Project

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	3.30
20	5.00
30	6.40
40	7.60
50	8.70
60	9.70
80	11.60
100	13.10
120	14.60
150	16.70
180	18.50
210	20.30
270	23.60
300	25.10
360	28.00
420	30.70
480	33.20
540	35.70
600	38.10
720	42.70
840	46.90
960	51.00
1080	54.80
1200	58.40
1320	61.90
1440	65.20
1560	68.30
1680	71.30
1800	73.30
1920	74.10
2040	74.40
2160	74.60
2280	74.70
2400	74.80
2700	74.90
3000	75.10
3300	75.20
3600	75.30

Resistivity 1.64E+12 mkg(-1)

Medium Resistance 1.74E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	5.90E+00	2.49E-01	1.29E-03	30	0.9	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	5.90E+03	2.49E+05	1.29E-03	2.07E+05	9.00E-04	1.15E+02	1.00E+03

Temperature: 300°C
Pressure: 2 bar

Notes: Run PoA 3

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	3.00
20	4.70
30	6.00
40	7.10
50	8.20
60	9.30
80	10.90
100	12.30
120	13.70
150	15.50
180	17.10
210	18.70
270	21.50
300	22.70
360	25.10
420	27.50
480	29.60
540	31.60
600	33.50
720	37.20
840	40.50
960	43.70
1080	46.60
1200	49.30
1320	52.00
1440	54.50
1560	56.90
1680	59.10
1800	61.30
1920	63.50
2040	65.70
2160	67.70
2280	69.60
2400	71.50
2700	76.20
3000	78.00
3300	78.50
3600	78.80

Resistivity 1.38E+12 mkg(-1)

Medium Resistance 5.51E+11 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	3.73E+00	4.18E-01	1.29E-03	15	0.9	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	3.73E+03	4.18E+05	1.29E-03	1.03E+05	9.00E-04	1.15E+02	1.00E+03

Temperature: 300°C

Pressure: 1 bar

Notes: Run PoA 4

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BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	4.20
20	6.50
30	8.40
40	9.90
50	11.30
60	12.60
80	14.90
100	17.20
120	19.20
150	21.90
180	24.40
210	26.60
270	31.10
300	33.20
360	37.10
420	40.60
480	43.70
540	46.60
600	49.50
720	55.50
840	60.90
960	66.30
1080	71.00
1200	75.20
1320	76.60

Resistivity 2.20E+12 mkg(-1)

Medium Resistance 2.14E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Q1%	gcm(-3)
values	3.62E+00	1.67E-01	1.29E-03	60	0.9	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	3.62E+03	1.67E+05	1.29E-03	4.14E+05	9.00E-04	1.15E+02	1.00E+03

Temperature: 300°C
Pressure: 4 bar

Notes: Run PoA 5

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BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	4.40
20	6.90
30	8.80
40	10.40
50	11.90
60	13.20
80	15.50
100	18.10
120	19.60
150	22.40
180	24.90
210	27.20
270	31.40
300	33.40
360	37.10
420	40.60
480	43.90
540	46.90
600	50.00
720	55.40
840	60.60
960	65.40
1080	69.80
1200	74.10
1320	77.30
1440	78.40
1500	78.70

Resistivity 2.14E+12 mkg(-1)

Medium Resistance 1.83E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Q1%	gcm(-3)
values	3.10E+00	1.78E-01	1.29E-03	60	0.9	11.2	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	3.10E+03	1.78E+05	1.29E-03	4.14E+05	9.00E-04	1.26E+02	1.00E+03

Temperature: 300°C

Pressure: 4 bar

Notes: Run PoA 6
Washing Test

British Coal
Liquefaction Project

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	3.20
20	4.90
30	6.20
40	7.40
50	8.30
60	9.20
80	10.90
100	12.40
120	13.30
150	15.60
180	17.30
210	19.10
270	21.70
300	23.10
360	25.60
420	28.00
480	30.30
540	32.50
600	34.60
720	38.50
840	42.20
960	45.70
1080	49.00
1200	52.10
1320	55.01
1440	57.77
1560	60.45
1680	63.00
1800	65.44
1920	67.75
2040	70.05
2160	72.24
2280	74.62
2400	75.57
2700	76.75
3000	77.10
3300	77.36
3600	77.49

Resistivity 1.83E+12 mkg(-1)

Medium Resistance 1.29E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Q1%	gcm(-3)
values	5.34E+00	3.38E-01	1.29E-03	30	1.1	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	5.34E+03	3.38E+05	1.29E-03	2.07E+05	1.10E-03	1.15E+02	1.00E+03

Temperature: 250°C

Pressure: 2 bar

Notes: Run PoA 7

British Coal
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BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	3.90
20	6.10
30	7.40
40	8.70
50	9.80
60	10.80
80	13.10
100	14.10
120	15.60
150	17.50
180	19.20
210	20.80
270	23.70
300	25.10
360	27.70
420	30.00
480	32.40
540	34.50
600	36.60
720	40.50
840	44.10
960	47.50
1080	50.80
1200	53.80
1320	56.70
1440	59.50
1560	62.20
1680	64.80
1800	67.20
1920	69.60
2040	72.00
2160	74.20
2280	75.20
2400	75.50
2520	75.60

Resistivity 1.85E+12 mkg(-1)

Medium Resistance 1.21E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	3.88E+00	3.42E-01	1.29E-03	60	1.7	12.9	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	3.88E+03	3.42E+05	1.29E-03	4.14E+05	1.70E-03	1.48E+02	1.00E+03

Temperature: 300°C

Pressure: 4 bar

Notes: Run PoA 8
Slurry Concentrated by 20%

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	5.30
20	7.90
30	9.70
40	11.40
50	12.90
60	14.20
80	16.60
100	18.70
120	20.60
150	23.30
180	25.80
210	28.10
270	32.40
300	34.40
360	38.10
420	41.60
480	45.00
540	48.20
600	51.20
720	56.90
840	62.30
960	67.30
1080	71.80
1200	73.50
1320	74.00
1440	74.50

Resistivity 2.27E+12 mkg(-1)

Medium Resistance 1.68E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Q1%	gcm(-3)
values	2.85E+00	1.72E-01	1.29E-03	60	0.9	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	2.85E+03	1.72E+05	1.29E-03	4.14E+05	9.00E-04	1.15E+02	1.00E+03

Temperature: 300°C

Pressure: 4 bar

Notes: Run PoA 9
Slurry Heat-Treated 1hr at 380°C

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Liquefaction Project

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	3.40
20	5.10
30	6.50
40	7.70
50	8.70
60	9.70
80	11.30
100	12.80
120	14.00
150	15.90
180	17.60
210	19.30
270	22.20
300	23.40
360	26.20
420	28.60
480	30.90
540	33.10
600	35.20
720	39.10
840	42.80
960	46.30
1080	49.60
1200	52.70
1320	55.80
1440	58.60
1560	61.40
1680	64.05
1800	66.60
1920	69.05
2040	71.47
2160	73.71
2280	76.28
2400	77.40
2700	77.75

Resistivity 2.76E+12 mkg(-1)

Medium Resistance 2.07E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	5.45E+00	3.25E-01	1.29E-03	60	1.4	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	5.45E+03	3.25E+05	1.29E-03	4.14E+05	1.40E-03	1.15E+02	1.00E+03

Temperature: 200°C

Pressure: 4 bar

Notes: Run PoA 10

British Coal
Liquefaction Project

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	5.60
20	8.60
30	10.90
40	12.70
50	14.40
60	15.60
80	18.20
100	20.50
120	22.50
150	25.50
180	28.20
210	30.70
270	35.30
300	37.50
360	41.70
420	45.60
480	49.40
540	53.00
600	56.40
720	62.90
840	69.00
960	73.60
1080	74.80
1200	75.18

Resistivity 3.67E+12 mkg(-1)

Medium Resistance 3.28E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	2.78E+00	1.39E-01	1.29E-03	120	0.9	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	2.78E+03	1.39E+05	1.29E-03	8.27E+05	9.00E-04	1.15E+02	1.00E+03

Temperature: 300°C
Pressure: 8 bar

Notes: Run PoA 11

British Coal
Liquefaction Project

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	6.40
20	9.40
30	11.70
40	13.80
50	15.60
60	17.20
80	19.90
100	22.50
120	24.90
150	28.10
180	31.10
210	33.90
240	36.60
270	39.10
300	41.50
360	46.80
420	50.30
480	54.30
540	58.20
600	61.80
720	68.50
840	72.50
960	73.50
1080	74.15

Resistivity 3.39E+12 mkg(-1)

Medium Resistance 2.25E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	QI%	gcm(-3)
values	1.91E+00	1.28E-01	1.29E-03	120	0.9	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	1.91E+03	1.28E+05	1.29E-03	8.27E+05	9.00E-04	1.15E+02	1.00E+03

$\Delta t / \Delta m$

Temperature: 300°C
Pressure: 8 bar

Notes: Run PoA 13

British Coal
Liquefaction Project

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	110.00
20	250.00
30	360.00
40	470.00
50	580.00
60	650.00
80	810.00
100	960.00
120	1060.00
150	1240.00
180	1400.00
210	1540.00
240	1850.00
300	2020.00
360	2250.00
420	2460.00
480	2670.00
540	2860.00
600	3110.00
720	3460.00
840	3850.00
960	4150.00
1080	4440.00
1200	4750.00
1320	5030.00
1440	5310.00
1560	5560.00
1680	5820.00
1800	6050.00
2100	6620.00
2400	7140.00
2700	7620.00
3000	8130.00
3300	8600.00
3600	9120.00

Resistivity 1.61E+12 mkg(-1)

Medium Resistance 2.44E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	9.63E-02	3.30E-05	1.10E-01	30	0.9	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ma)(-1)	kgm(-3)	kgm(-3)
S.I. values	9.63E+01	3.30E+01	1.10E-01	2.07E+05	9.00E-04	1.15E+02	1.00E+03

Temperature: 300°C

Pressure: 2 bar

Notes: Run CRE 1

BLACK THUNDER

TIME(s)	MASS(g)
0	0.00
10	150.00
20	320.00
30	440.00
40	540.00
50	680.00
60	810.00
80	1060.00
100	1260.00
120	1430.00
150	1710.00
180	1920.00
210	2160.00
270	2590.00
300	2770.00
360	3110.00
420	3430.00
480	3740.00
540	4040.00
600	4300.00
720	4790.00
840	5230.00
960	5670.00
1080	6060.00
1200	6420.00
1320	6760.00
1440	7140.00
1560	7490.00
1680	7820.00
1800	8110.00
2100	9080.00

Resistivity 2.02E+12 mkg(-1)

Medium Resistance 2.43E+12 m(-1)

	intercept	gradient	area	delta P	viscosity	solids load	density
units	sg(-1)	sg(-2)	m(2)	psi	cP	Ql%	gcm(-3)
values	4.79E-02	2.07E-05	1.10E-01	60	0.9	10.3	1
S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)	kgm(-3)
S.I. values	4.79E+01	2.07E+01	1.10E-01	4.14E+05	9.00E-04	1.15E+02	1.00E+03

Temperature: 300°C

Pressure: 4 bar

Notes: Run CRE 2

British Coal
Liquefaction Project

BLACK THUNDER

TIME(s)	MASS(g)	Resistivity 2.48E+11 mkg(-1)			Medium Resistance 8.07E+11 m(-1)			
0	0.00	intercept	gradient	area	delta P	viscosity	solids load	density
60	930.00	units	sg(-1)	sg(-2)	m(2)	psi	Q1%	gcm(-3)
120	1540.00	values	5.30E-02	1.07E-05	1.10E-01	22	1.1	12.7
180	2340.00	S.I. units	skg(-1)	skg(-2)	m(2)	Nm(-2)	kg(ms)(-1)	kgm(-3)
240	2860.00	S.I. values	5.30E+01	1.07E+01	1.10E-01	1.52E+05	1.10E-03	1.45E+02
300	3380.00							
420	4210.00							
540	4970.00							
720	6060.00							
900	7070.00							
1200	8530.00							
1500	9750.00							
1800	10830.00							
2100	11780.00							
2400	12740.00							

0.35	
0.3

Temperature: 250°C
Pressure: 1.5 bar

Notes: Run CRE 3

British Coal
Liquefaction Project

SECTION IX

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SECTION IX

RUN 227-70 (CC-12) EVALUATION OF REJUVENATED CATALYST

SUMMARY

The objective of Run 227-70 (CC-12) was to evaluate the performance of rejuvenated catalyst that had been recovered after earlier CTSL™ bench unit operations on Black Thunder Mine (Wyoming) coal. The rejuvenation process, developed by HRI for H-Oil catalysts, removes contaminant metals by acid washing and recovers the surface area by carbon burnoff. Laboratory H-Oil results indicate that 975°F resid and RCR conversions using a four-time rejuvenated catalyst was comparable with that of fresh catalyst. This rejuvenation process is being commercialized for H-Oil applications.

Most previous rejuvenation process development involved cobalt molybdate catalysts. This run was the first operational test of a rejuvenated nickel molybdate catalyst and the first use of rejuvenated catalyst for coal liquefaction. The rejuvenation procedure is detailed in *Appendix A*.

The 12-day run included a single condition of 750°F first stage temperature, 800°F second stage temperature, and 45 lb/hr/ft³ (each reactor) catalyst space velocity. These conditions were identical to those in Run 227-55(CC-1) Condition 1, with which the results were compared.

The rejuvenated catalyst had residual oil conversion activity, hydrogenation activity, and denitrogenation activity essentially that of fresh catalyst and markedly greater than that of catalyst aged in CTSL™ operations. There were slightly lower yields of distillate product with the rejuvenated catalyst because of lower coal conversion and higher carbon oxides yields, factors which might not be associated with the catalyst performance.

The rejuvenated catalyst was of much lower physical strength, and very much shortened particle length, than fresh catalyst, and a more durable initial catalyst might be more appropriate if rejuvenated catalysts are to be used commercially. The fact that the rejuvenated catalyst showed superior performance despite its diminished physical and chemical properties indicates that the rejuvenation process has potential. Modifications of the rejuvenation process to decrease this degradation could lead to even better performance.

SCOPE OF WORK

Table 1 lists the conditions for Run 227-70 (CC-12). The 12-day run included a single condition of 750°F 1st stage temperature, 800°F 2nd stage temperature, and 45 lb/hr/ft³ (each reactor) catalyst space velocity. With these constant conditions the rate of deactivation of the rejuvenated catalyst could be observed and the results could be compared to previous results. Condition 1 of Run 227-55 (CC-1) had identical conditions except there was no H₂S feed and it was a different batch of Black Thunder coal feed. First-stage samples were taken following Periods 6 and 12 to quantify the relative performance of the two stages.

PROGRAM RESULTS AND ANALYSES

RUN 227-70 (CC-12)

This section discusses the conversion, product yields, process performance, and product quality data for Run 227-70 (CC-12). *Table 2* presents the operating conditions, product yields, and conversions for each of the periods for which detailed normalized yields were calculated. Periods 1, 2, and 3 are not shown because of startup effects, and Period 7 is not shown because of the disruption of external oil added in the process of taking the first stage sample.

COAL AND 975°F CONVERSION

The coal and 975°F conversions presented in *Table 2* are plotted in *Figure 1*. Coal conversion for this relatively low-severity operation varied between 83.0 W% and 85.9 W% of maf coal, averaging 84.9 W%, with a slight decreasing trend as the run progressed. This average coal conversion was 1.6 W% lower than the average coal conversion for Run 227-55 (CC-1) Periods 3 through 6. To assign this difference to catalyst performance is uncertain, since in other operations coal conversion, while improved by the presence of catalyst, has shown virtually no change as the catalyst deactivated as indicated by other performance parameters, viz. residual oil formation, hydrogenation, and denitrogenation. Also, by these measures of catalyst activity, the rejuvenated catalyst was of high activity (see below). It is possible these differences are due to differences in the coal shipments, with the CC-12 feed containing about 0.72 W% more ash and 0.35 W% less hydrogen than in the CC-1 feed. (See *Table 6*). Also, the actual reactor average temperatures could have deviated slightly.

For Periods 4 through 6, the 975°F conversion averaged 83.1 W% of maf coal for Run 227-70 (CC-12) vs. 84.6 W% for Run 227-55 (CC-1). As indicated in *Figure 1*, essentially all of the difference in 975°F conversion was due to the lower coal conversion in Run 227-70 (CC-12), and the actual 975°F oil formation actually changed little during the run, increasing from 1.9 W% in Period 4 to 3.6 W% in Period 12.

NORMALIZED PRODUCT DISTRIBUTION

C₁ - C₃ Gas

Figure 2 shows the C₁ - C₃ gas yields for Run 227-70 (CC-12) and Run 227-55 (CC-1) Condition 1. The gas rates were very steady throughout the run, averaging 6.75 W% Dry Coal. In good agreement, the average gas yield for Run 227-55 (CC-1) Condition 1 was 6.97 W%.

C₄ - 975°F Distillate

The distillate oil yield for Run 227-70 (CC-12), shown in *Figure 3*, declined slowly from an average of 60.0 W% of maf Coal for Periods 5 and 6 to an average of 58.2 W% for Periods 11 and 12. The value for Periods 5 and 6 is significantly lower than the 63.2 W% for the corresponding Condition 1 of Run 227-55 (CC-1). However, if the yields of the two runs were normalized to a common yield of carbon oxides and water to compensate for the 1.4 W% dry coal higher carbon oxides yield in Run CC-12, the yield of C₄ - 975°F distillate would then be about 61.5 W%. Then most of this 1.7 W% maf coal difference in distillate yield would be due to the 1.4 W% maf coal difference in coal conversion.

The yields of three distillate fractions are presented in *Figures 4, 5, and 6*. The C₄ - 390°F naphtha yield, *Figure 4*, declined from 18.0 W% dry coal at the beginning of the run to 15.6 W% at the end of the run. The 390 - 650°F middle distillate yield, *Figure 5*, remained steady at an average of 23.7 W% dry coal. This yield is lower than the 28.5 W% that had been attained in Run 227-55 (CC-1) Condition 1. The 650 - 975°F heavy distillate yield, *Figure 6*, showed a very slight upward trend. If the deviant Period 9 value is ignored, it increased slowly from 13.9 W% to 15.1 W% and averaged 14.7 W% of dry coal.

975°F Residuum

The 975°F residuum yield, *Figure 7*, increased slowly from 1.9 W% Dry Coal in Period 4 to 3.6 W% dry coal in Period 12. The residuum yields at the beginning of the run were similar to the yields for Run 227-55 (CC-1). A comparison of the rates of residuum yield increase for the later portions of the two runs, even though the severity was higher in CC-1, indicates that the catalyst deactivation with respect to resid formation was somewhat slower in Run CC-12. In the six day interval between Period 6 and 12 of Run CC-12 the resid yield increased by 1.55 W% of dry coal; whereas the nine days from Period 10 to Period 19 were required for a similar 1.59 W% of dry coal increase in Run CC-1. In both runs the yield of toluene insoluble oil remained below 0.04 W% dry coal through Period 12.

Figure 8, a plot of residual oil concentration in the product slurry versus time of operations, summarizes another aspect of the catalyst performance. In this figure, the trends with time are virtually identical during the two runs. Actually, in the first operations of the two runs, at common operating conditions, there was a lower residual oil concentration in Run CC-12 than in Run CC-1. This difference, along with the similar conversions, indicates better kinetic performance for the rejuvenated catalyst than for the fresh catalyst.

Hydrogen Consumption

The hydrogen consumptions for Run 227-70 (CC-12) and Run 227-55 (CC-1) Condition 1 are shown in *Figure 9*. In Run 227-70 (CC-12) the hydrogen consumption averaged 7.24 W% Dry Coal versus 7.49 W% for Run 227-55 (CC-1) Condition 1.

Heteroatom Removal

Denitrogenation, *Figure 10*, showed an overall decline during Run 227-70 (CC-12). It is generally higher than in Run 227-55 (CC-1) Condition 1, but the comparison may not be very valid because the amount of nitrogen measured in the respective coals were significantly different (1.05 W% Dry Coal for Run 227-55 (CC-1) vs. 0.87 W% for Run 227-70 (CC-12)). Most of the unremoved nitrogen remained in the solids. The removal of nitrogen from the liquid products is discussed in the "Product Quality" section.

The desulfurization is not plotted because, with only 0.54 W% sulfur in the coal, it is not a very significant number. Almost all of the remaining sulfur is in the solid product. Interestingly, the solids in Run 227-70 (CC-12) retained much more sulfur than did the solids in Run 227-55 (CC-1). In Run 227-70 (CC-12) the desulfurization remained approximately constant at about 46%; whereas in Run 227-55 (CC-1) the desulfurization was 70%.

Although deoxygenation determination is generally not very accurate, the water yields in this run were relatively constant, implying more accuracy than usual. Using 19.47% oxygen in the coal (calculated by difference), the deoxygenation, based on measured water yield was 91.8%.

PRODUCT QUALITY

The distillate and resid products from Run 227-70 (CC-12) were analyzed for specific gravity and elemental composition. Additionally, the 975°F oil fraction was analyzed for cyclohexane insolubles, toluene insolubles, carbon residue, and viscosity. These data are presented below. Analyses of the second stage solids is presented along with the analyses of the first stage solids in the "First Stage Performance" section.

Separator Overhead and Atmospheric Still Overhead Products

The Separator Overhead (SOH) and Atmospheric Still Overhead (ASOH) had constant properties throughout the run, indicating little catalyst deactivation with respect to hydrogen and nitrogen content of the light products. The SOH gravity averaged 37.0 °API, the hydrogen averaged 12.87 % (1.77 H/C ratio), and the Kjeldahl nitrogen averaged 0.04 %. 5 V% boiled by 200°F and 95 V% boiled by 640°F. The ASOH gravity averaged 31.3 °API, the hydrogen averaged 12.46%

(1.70 H/C ratio), and the Kjeldahl nitrogen averaged 0.09%. 5 V% boiled by 307°F and 95 V% boiled by 538°F.

Pressure Filter Liquid Properties

The Pressure Filter Liquid (PFL) was distilled into four separate product fractions for analyses. These fractions were IBP-650°F Light Gas Oil (LGO), 650-850°F Vacuum Gas Oil (VGO), 850-975°F Heavy Vacuum Gas Oil (HVGO), and 975°F+ Residuum. The properties of these products give generally better indications of the catalyst activity than do the overall product yields. Most of the unremoved heteroatoms are in the solid products where they are not as susceptible to catalytic conversion, and in the overall yields the solid-phase heteroatoms obscure the more important heteroatom content of the liquid products. Also, these analyses provide good indications of catalyst activity because properties like hydrogen content are more sensitive to catalyst activity than is the shift in boiling range.

The analyses of these fractions are listed in *Table 3* and are compared with the same analyses for Runs 227-55 (CC-1) and 227-69 (CC-11) in *Figures 11 through 16*. Runs 227-55 (CC-1) and 227-69 (CC-11) did not, in general, have identical conditions as Run 227-70 (CC-12), but they are presented for comparison. Note that the generally higher temperatures in the two comparison runs probably increased the rate of catalyst deactivation. The inclusion of Run 227-69 (CC-11), with hydrogen sulfide addition, demonstrates that the hydrogen sulfide was not solely responsible for the lower rate of catalyst deactivation for Run CC-12 than for Run CC-1.

Hydrogen to Carbon Ratio - *Figures 11, 12, and 13* show the H/C ratio for the VGO, HVGO, and residuum fractions, respectively. In all cases, the H/C ratio improved slightly during the course of the run. Although the initial H/C ratios of the fractions were less than the identical Run 227-55 (CC-1) Condition 1, in both Runs 227-55 (CC-1) and Run 227-69 (CC-11) the H/C ratio declines. The rate of this decline may have been larger due to the generally higher temperatures in the comparisons runs, and it is likely that the addition of H₂S aided the performance of Run 227-70 (CC-12) and 227-69 (CC-11). However, despite these qualifications, the excellent hydrogenation activity and the slow rate of deactivation of the rejuvenated catalyst have been definitively established. The °API gravity of these fractions and the °API gravity and H/C ratio of the LGO fraction, although not shown, also confirm the high and sustained catalyst activity.

Nitrogen Content - During the 12-day run, the nitrogen content of the VGO and HVGO product fractions, *Figures 14 and 15*, increased at a rate only slightly less than in the comparison runs. After increasing at a faster rate than the comparison runs between Periods 6 and 9, the nitrogen content decreased somewhat between Periods 9 and 12. This nonmonotonicity and the increasing

H/C ratio suggest that the catalyst is undergoing some activation, possibly by the hydrogen sulfide, during the run.

Considering the previously discussed differences between Run CC-12 and the comparison runs, the approximate similarity of the nitrogen contents of the vacuum gas oil and the heavy vacuum gas oil may indicate slightly lower inherent denitrogenation activity for the rejuvenated catalyst. However, the nitrogen in the residuum, *Figure 16*, was significantly less for Run CC-12 than for the comparison runs initially, and it was relatively unaffected by catalyst age, increasing only from 0.25 to 0.28 W%.

As an indication of the effect of the rejuvenation process on an aged catalyst, the nitrogen contents in the first operations of Run CC-12 were only one-fourth to one-third of those in the final operations of Run CC-1.

975°F* Additional Properties - *Table 3* includes the toluene insolubles, cyclohexane insolubles, Conradson Carbon Residue (CCR), and viscosity of the residuum. The low levels of these 975°F* properties again demonstrate the quality of the products and activity of the catalyst. The cyclohexane insolubles and the CCR's were lower throughout this run than the lowest of the available data for all of the two comparison runs. The CCR and cyclohexane insolubles averaged a steady 27.9 and 2.58 W%, respectively, and the viscosity actually declined from 61 cp at 300°F in Period 6 to 26 cp in Period 12. The stability of the cyclohexane insolubles content was quite a contrast to the pattern of Run CC-1 where there was a 6- to 7-fold increase between the sixth and the nineteenth days.

FIRST STAGE PERFORMANCE

First stage reactor samples were taken at the ends of Periods 6 and 12 to help distinguish the performance of each stage. Boiling-range determinations and distillation fraction elemental analyses permit a comparison of fraction formation, conversion, hydrogenation, and nitrogen removal in the two stages.

Distillation Fraction Analyses

The fraction analyses of the first stage liquids are presented in *Table 3* along with the PFL fraction analyses previously discussed. *Figures 17 through 27* show the °API gravity, H/C ratio, and nitrogen content for the four first and second stage fractions. Data from the identical Run 227-55 (CC-1) Condition 1 are shown for comparison.

°API Gravity - As indicated in *Figures 17 through 20*, the first stage liquid fractions showed the same trends as the PFL fractions. The fractions became slightly lighter as the run progressed. The increase was 14.6 to 15.5 °API for the VGO, 4.8 to 6.0 °API for the HVGO, and -0.9 to -0.1 °API for the residuum.

These increases paralleled the increases in the PFL gravity. It is noteworthy that the first stage fraction gravities were much closer to the PFL fraction gravities than they were in Run 227-55 (CC-1) Condition 1. The first stage gravities were significantly higher for Run 227-55 (CC-1), indicating that less hydrogenation was occurring in the Run 227-70 (CC-12) first stage, but less dehydrogenation was occurring in the second stage.

Hydrogen to Carbon Ratio - The first stage fraction H/C ratios, *Figures 21 - 24*, show similar trends as did the first stage °API gravity. All fractions had very slightly higher H/C ratios in Period 12 than in Period 6, and although the differences are small for the lighter fractions, each of the first stage fractions had a higher H/C ratio than the corresponding PFL product fraction. This difference demonstrates the equilibrium shift to more hydrogenation in the lower temperature first stage. However, the relatively small differences between the hydrogen contents of the first and second stage fractions indicate that the second stage catalyst is very effective at adding hydrogen to the lighter products as they form, and the hydrogenation equilibrium must still significantly favor these reactions at 800°F.

Nitrogen Content - *Figures 25 - 27* show the nitrogen content of the three 650°F+ distillation fractions. In all cases the nitrogen contents of the first stage fractions are lower for Run 227-70 (CC-12) Period 6 than for Run 227-55 (CC-1) Period 6. During the run, the nitrogen content of the first stage VGO increased slightly from 0.13 to 0.18 W%, whereas the nitrogen content of the first stage HVGO and residuum decreased slightly (0.29 to 0.27 W% and 0.43 to 0.39 W%, respectively). Thus it appears that the first stage catalytic activity for denitrogenation began high relative to Run 227-55 (CC-1) and did not decline for the two heavier fractions. For all fractions, the catalyst deactivation for the first stage was less than for the second stage.

Solids Analyses

Table 4 lists the analyses of the first and second stage solids from Run 227-70 (CC-12). As had been true with most of the liquid fractions, there was no indicated degradation of the first and second stage solids during the run. For both the first and second stage, the hydrogen content was slightly higher in Period 12 than in Period 6, the sulfur content was slightly lower, and the nitrogen remained essentially constant. The level of the sulfur content is noteworthy, because it is significantly higher than in previous operations. In Run 227-55 (CC-1) Condition 1 the sulfur/SO₃-free-ash ratios were only 0.036 W% for the first stage solids and 0.027 W% for the second stage solids compared to an average of 0.060 W% and 0.039 W%, respectively, for Run 227-70 (CC-12). It is not clear how the rejuvenated catalyst would cause this difference. Possibly, the addition of 2 W% hydrogen sulfide contributed, but this high sulfur ratio was not noted in any of the other runs with hydrogen sulfide addition. For example, the

sulfur ratio for 2nd stage solids in Run 227-69 (CC-11) (at different conditions) averaged about 0.031 W%.

As the quantity of unreacted solids decreased by 54 W% (rel) in the second stage, the hydrogen content of the solids remained constant at about 4.0 W% for Period 6 and 4.3 W% for Period 12. In previous operations the product from the higher temperature stage had a significantly lower hydrogen content. The lack of dehydrogenation of the solids in the second stage indicates that the most carbonaceous of the first stage solids are still reactive and the second stage catalyst is very active at providing hydrogen donors. As in Run 227-55 (CC-1), the nitrogen-containing solid compounds were somewhat more reactive than were the total organic solids. In Run 227-70 (CC-12), the nitrogen content of the organic solids decreased from an average of 1.33 in the first stage to 1.07 W% in the second stage, or about 63 W% ash-balanced nitrogen removal. However, also as in Run 227-55 (CC-1), the sulfur-containing solid compounds were less reactive than were the total organic solids. If all of the pyrite (0.09 W% dry coal) is assumed to become pyrrhotite and the iron sulfate (0.02 W% dry coal) is assumed unreactive, the organic-sulfur reduction of the solids in the second stage of Run 227-70 (CC-12) averaged about 44 W%.

First and Second Stage Yields and Conversions

The first and second stage flows, product fraction formations, and conversions were calculated for Periods 6 and 12, during which first stage samples were taken. These quantities are shown in *Table 5*. The first stage reactor composition was calculated by ash-balancing the solids component and assuming the vapor quantities were proportional to the amount of coal reacted. The quantity of liquids was then the remainder necessary for 100 % material balance. This assumption is used to smooth out the variable amount of vapors that escape while taking the first stage sample. In this run the first stage liquid flow calculated in this manner was 133.0 W% dry coal for Period 6 and 135.7 W% dry coal for Period 12. The actual ash-balanced liquid yields would have been 140.3 W% and 103.2 W%, respectively.

The first and second stage flows, formations, and conversions listed in *Table 5* indicate some small differences between Period 6 and Period 12 even though these two periods were at the same condition and had fairly similar overall yields and conversions. Part of these differences could be due to the higher catalyst attrition in the second stage. The first stage coal conversion was 66.3 W% maf in Period 6 and 69.2 W% maf in Period 12. Total first stage 975°F+ residuum formations were 14.5 and 10.3 W% dry coal, respectively, and there were very little asphaltenes or preasphaltenes formed in either stage. The fraction yields do not indicate any first stage catalyst deactivation.

These first stage formations correspond fairly closely with the first stage formations from Periods 10 and 19 of Run 227-55 (CC-1), which also had 750°F first stage temperatures. If the Run CC-1 fraction formations are calculated using the same vapor-rate assumption, the formation of 975°F residuum in the first stage of Periods 10 and 19 of Run CC-1 would be 10.8 and 11.7 W% dry coal, averaging only 1.1 W% less than for Run CC-12. The lower overall coal conversion in Run 227-70 (CC-12) appears to be due to lower conversion in the second stage. Periods 6, 10, and 19 of Run 227-55 (CC-1) had first stage coal conversions of 65.4, 68.9, and 66.8 W% MAF, respectively. Because this average of 67.0 W% MAF is 0.7 W% less than the first stage coal conversion for Run 227-70 (CC-12), the 1.6 W% higher overall coal conversion in Run 227-55 (CC-1) was achieved with a 2.3 W% higher second stage coal conversion. As discussed previously in the "Coal and 975°F Conversion" section, possible explanations for the difference in second stage coal conversion include small differences in exact average reactor temperature or coal characteristics.

DETAILS OF OPERATION

Run 227-70 ran very smoothly after three aborted start-ups. Operationally, recurrent first-stage differential pressure surges of 10 to 50 psi were notable. The frequency and magnitude of these surges did not increase as the run progressed. Constant feed was maintained at the constant specified rate, and product rates were steady after the atmospheric still was made functional in Period 1B. There were no significant pump failures, control valve blockages, or vessel level changes to cause product rate and composition variations.

COAL FEED

Black Thunder Mine (Wyoming) sub-bituminous coal (HRI-5713) was the feedstock for Run 227-70 (CC-12). The coal was ground to -70 mesh and dried to about 6 W% moisture before being slurried with recycle oil and charged to the 227 Unit. *Table 6* shows the analyses of the coal used in this run. Previous analyses of this same batch of coal and analyses of the Black Thunder sub-bituminous (HRI-5630) used in Run 227-55 (CC-1) are also given for comparison. The analyses of the HRI-5713 coal used in this run indicated lower hydrogen (4.19 W% vs. 4.54 W%) and higher ash (6.73 W% vs. 6.01 W% (SO³-free)) than the analyses for the HRI-5630 coal used in the companion run. These differences would have affected the reported hydrogen consumption and ash yield.

START-UP OIL

The startup oil for Run 227-70 (CC-12) was distillate oil boiling between 700 and 950°F, identified as HRI-5757. The analyses of the startup oil is given in *Table 7*. It was used during catalyst presulfiding with H₂S and to bring the unit up to run conditions. After Period 1, makeup oil was not needed except for charging the first stage reactor sample bomb in Periods 7A and 13A. Run conditions and recycle solvent cut point had been selected so that makeup oil would not be required.

CATALYST CHARGE

The catalyst rejuvenated for use in Run CC-12 had been recovered after Runs CC-4 and CC-7, both of which had been operated with Black Thunder Mine coal and had reused catalysts recovered after Runs CC-1, CC-2, and CC-5. In these previous operations, the blended catalysts for rejuvenation had processed 1120 lbs coal/lb fresh catalyst. *Table 8* includes the analyses of this blended recovered catalyst, the acid-washed catalyst, and the final rejuvenated catalyst.

The acid washing phase of the rejuvenation procedure was an agitated batch operation for 30 minutes at 150°F using 5 weights of 3.5 W% sulfuric acid.

solution per weight of catalyst. The regeneration of the acid-washed catalyst was carried out in two fixed beds in series--first at 750°F for 4 hours with flowing gas containing 2.5 W% oxygen, then at 800°F for another 4 hours at 800°F, and then with progressively increased oxygen contents of 5 W%, 7.5 W%, and 21 W% over a 6-hour period.

The metals content of the acid washed and regenerated catalysts are compared in *Table 8A*. Of the contaminants, over 95 W% of the calcium, 95 W% of the sodium, and 60 W% of the iron was removed in the acid-washing step. There were also some losses of the promoting metals. About 20 W% of the molybdenum and 60 W% of the nickel were removed by the acid-washing. Apparently some of the catalyst support dissolved as well. The aluminum found in the acid-washing liquor corresponded to about 5 W% of the Al_2O_3 content of the original recovered catalyst.

The rejuvenated catalyst had a crush strength considerably lower than that of fresh catalyst, 1.23 lb/mm versus 1.94 lb/mm. Also, the rejuvenated extrudates were only half as long, on average, as the fresh extrudates, 1.9 mm versus 4.2 mm, although the extrudate diameters were essentially the same. There were a very large number of very short particles, less than 1mm, in the rejuvenated catalyst. This factor caused several false starts for Run CC-12, even before coal feed was started, when the smaller particles became enmeshed in the catalyst support. Successful operation was achieved after the shorter particles were removed by screening.

The details of this catalyst rejuvenation procedure are given in *Appendix A*, and microautoclave tests to determine how some of the rejuvenation steps affected catalyst activity are presented in *Appendix B*.

RECOVERED CATALYST

A significant amount of catalyst was lost during the run, presumably by attrition. While the recovery of catalyst from the first stage reactor after Run CC-12, 89 V%, was in the range of values of recovery after operations with fresh catalyst, the recovery of catalyst from the second stage after Run CC-12 was relatively low, 63 V%, perhaps a consequence of the low crush strength.

The analyses of the recovered catalysts are shown in *Table 9*. The first stage catalyst contained 11.4 W% carbon and the second stage catalyst contained 15.4 W% carbon. The additional deposited carbon resulted in very little surface area or pore volume change for the first stage catalyst. The surface area of the second stage catalyst decreased from 189 m^2/cc for the rejuvenated catalyst charge to 131 m^2/cc particle for the recovered catalyst, and the pore volume similarly decreased from 0.569 to 0.337 cc/cc particle.

The most significant contaminant metal increase was for sodium, which increased from 0.046 W% to 0.533 W% for the first stage catalyst and to 0.847 W% for the second stage catalyst. The calcium content increased from 0.051 W% to 0.092 W% and 0.197 W% for the respective stages. The small changes indicated for iron content were probably not significant.

The molybdenum and nickel promoter-metal contents, although reduced by the addition of contaminant metals and carbon, remained in about the same ratio as for the rejuvenated catalyst charged. These molybdenum nickel ratios were 7.4 W% for the rejuvenated catalyst, 7.4 W% for the recovered first stage catalyst, and 7.6 W% for the recovered second stage catalyst.

TABLE 1

RUN PLAN - (CC-12)

RUN 227-70

Catalyst: Rejuvenated Shell S-317

PERIOD (DAYS)

1A to 13A

NOMINAL CONDITIONS

Unit Pressure, psig	2500
Coal Feed, Lb/hr/ft ³ (Catalyst)	45
Filter Liquid Recycled, W% Dry Coal	116
Oil/Solids in Feed	1.1
Hydrogen Sulfide Feed, W% Dry Coal	2
Atmospheric Still Reboiler Temp, °F	525

REACTOR TEMPERATURES, °F

First Stage	750
Second Stage	800

TABLE 2

OPERATING SUMMARY - RUN 227-70 (CC-12)

CTSL™ WITH REJUVENATED CATALYST

COAL: Black Thunder Coal (HRI-5713)

CAT: 1st & 2nd Stage-Rejuvenated S-317 Catalyst

Period Number	4	5	6	8	9	10	11	12
Date (Start of Period)	12/30/90	12/31/90	01/01/91	01/03/91	01/04/91	01/05/91	01/06/91	01/07/91
Hours of Run (End of Period)	94	118	142	190	214	238	262	286
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	100	127	154	207	234	261	288	315
1st Stage Temperature (°F)	750	750	751	751	750	751	751	750
2nd Stage Temperature (°F)	802	801	800	800	800	800	800	799
SMT Temperature (°F)	165	160	160	160	163	165	166	165
Hot Separator Temperature (°F)	610	609	609	609	609	609	609	609
Unit Back Pressure (PSIG)	2496	2504	2514	2512	2513	2513	2510	2509
1st Stage DP (PSI)	4.6	4.9	4.9	5.0	4.6	4.7	4.9	4.8
2nd Stage DP (PSI)	2.8	2.8	3.0	2.9	3.4	3.0	3.0	3.1
Overall DP (PSI)	12.3	12.4	12.5	12.6	12.3	12.2	12.4	12.2
Cat. Space Velocity per Stage, Lb/Hr/Ft³	45.4	44.8	45.7	45.3	46.3	45.1	45.4	45.4
MISC STREAMS, W% OF DRY COAL								
PFL Recycle	108.6	108.6	108.6	108.6	108.6	108.6	108.6	108.6
PFL to Buffer - Stage 1	4.1	3.8	3.8	4.0	3.7	5.1	3.6	3.6
PFL to Buffer - Stage 2	4.4	4.0	3.7	3.6	3.7	4.3	3.9	3.9
Makeup Oil (HRI-5757)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H ₂ S	1.5	1.7	1.7	1.8	1.7	1.7	1.6	1.7
TOTAL MATERIAL RECOVERY (GROSS)	99.29	99.79	98.78	100.20	98.67	99.15	99.26	98.81
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED								
C ₁ -C ₃ in Gases	7.27	6.74	6.84	6.70	6.66	6.76	6.87	6.19
C ₄ -C ₇ in Gases	4.07	4.04	4.05	3.85	3.71	3.86	3.64	3.24
IBP-390°F in Liquids	13.91	13.91	13.74	12.65	13.22	12.78	12.08	12.38
390-500°F in Liquids	10.28	9.97	9.87	9.65	9.75	9.79	9.07	9.04
500-650°F in Liquids	13.28	13.50	13.69	13.82	14.08	14.02	14.44	14.99
650-850°F in Liquids	11.66	12.19	12.08	12.42	10.85	12.26	12.3	12.59
850-975°F in Liquids	2.21	2.20	2.34	2.62	2.20	2.72	2.86	2.56
Toluene Soluble 975°F* Oil	1.91	2.19	2.26	2.88	2.91	2.95	3.88	3.56
Toluene Insoluble 975°F* Oil	0.01	0.00	0.00	0.01	0.00	0.02	0.01	0.03
Unconverted Coal	13.16	13.93	13.84	14.42	15.84	14.05	14.35	14.42
Ash (SO ₃ -Free)	6.72	6.97	6.97	6.96	6.96	6.39	6.39	6.39
Water	19.41	18.60	18.54	18.20	18.05	18.83	18.92	18.96
CO	0.84	0.73	0.74	0.73	0.73	0.71	0.65	0.63
CO ₂	1.48	1.13	1.15	1.28	1.23	1.10	0.93	1.13
NH ₃	0.86	0.85	0.84	0.76	0.75	0.75	0.78	0.78
H ₂ S	0.28	0.26	0.25	0.27	0.26	0.26	0.26	0.25
TOTAL (100+ H ₂ REACTED)	107.36	107.22	107.20	107.24	107.21	107.25	107.27	107.15
PROCESS PERFORMANCE								
C ₄ -975°F Distillates, W% of MAF Coal	59.4	60.0	59.9	59.1	57.9	59.2	57.9	58.5
975°F* Conversion, W% MAF	83.8	82.7	82.7	81.4	79.9	81.8	80.5	80.8
Coal Conversion, W% MAF	85.9	85.0	85.1	84.5	83.0	85.0	84.7	84.6
HDS, W%	48.6	45.0	44.2	47.6	45.4	46.1	44.8	44.2
HDN, W%	81.1	80.1	79.8	71.8	71.0	71.3	73.9	73.6

TABLE 3
COMPARISON OF FIRST AND SECOND STAGE PRODUCT ANALYSES
RUN 227-70 (CC-12)

	--FIRST STAGE--		----SECOND STAGE----		
PERIOD NUMBER	6	12	6	9	12
CATALYST AGE (LB COAL/LB CATALYST)	154	316	154	208	316
TOTAL LIQUID					
*API Gravity	10.6	11.4	12.5	12.6	12.8
ELEMENTAL ANALYSES, W%					
Carbon, W%	89.24	89.38	89.11	89.31	89.35
Hydrogen, W%	10.44	10.57	10.32	10.43	10.72
Sulfur, W%	0.02	0.00	0.01	0.00	0.00
Nitrogen, W%	0.19	0.26	0.05	0.21	0.16
TOTAL	99.89	100.21	99.49	100.00	100.23
650°F, W%	12.07	12.02	19.23	19.76	19.16
650-850°F, W%	53.42	49.80	55.75	51.63	51.48
850-975°F, W%	12.78	16.16	12.31	12.02	11.83
975°F+, W%	20.92	21.31	11.90	15.89	16.62
LOSS, W%	0.81	0.71	0.81	0.70	0.91
LGO (IBP-650°F)					
*API Gravity	19.6	19.9	20.0	20.0	19.6
Carbon, W%	87.47	87.25	87.73	88.26	88.27
Hydrogen, W%	11.45	11.52	11.43	11.39	11.35
Sulfur, W%	0.01	0.01	0.00	0.01	0.00
Nitrogen, W%			0.05	0.06	0.06
VGO (650-850°F)					
*API Gravity	14.6	15.5	14.4	14.9	15.5
Carbon, W%	89.23	89.10	89.17	89.28	83.79
Hydrogen, W%	10.76	11.19	10.52	10.90	10.94
Sulfur, W%	0.00	0.00	0.00	0.01	0.01
Nitrogen, W%	0.13	0.18	0.03	0.20	0.16
HVGO (850-975°F)					
*API Gravity	4.8	6.0	5.1	5.5	5.6
Carbon, W%	89.74	89.68	89.88	89.59	89.81
Hydrogen, W%	9.99	10.18	9.40	9.82	9.91
Sulfur, W%	0.02	0.01	0.00	0.00	0.00
Nitrogen, W%	0.29	0.27	0.11	0.28	0.18
RESIDUUM 975°F					
*API Gravity	-0.9	-0.1	-3.0	-2.8	-2.1
Carbon, W%	89.36	89.41	89.78	90.39	90.16
Hydrogen, W%	8.98	9.12	7.92	8.62	8.59
Sulfur, W%	0.09	0.11	0.06	0.07	0.00
Nitrogen, W%	0.43	0.39	0.25	0.32	0.28
Cyclohexane Insolubles, W%	1.96	0.74	1.83	3.83	2.09
Toluene Insolubles, W%	0.72	0.53	0.14	0.04	0.92
Ash, W%	0.00	0.00	0.00	0.00	0.00
Viscosity, cps					
at 300°F	---	---	238	180	165
at 350°F	---	---	61	49	26
CCR, W%	---	---	29.1	26.2	27.4

TABLE 4**COMPARISON OF FIRST AND SECOND STAGE PRODUCT THF-WASHED SOLIDS ANALYSES****RUN 227-70 (CC-12)**

	<u>FIRST STAGE</u>		<u>SECOND STAGE</u>		
PERIOD NUMBER	6	12	6	9	12
CATALYST AGE (LB COAL/LB CATALYST)	154	316	154	208	316
SAMPLE ANALYSES					
Ash, W%	(20.40)	(20.70)	(36.78)	(34.87)	(34.37)
Sulfur in Ash, W%	(4.33)	(4.95)	(3.41)	(3.53)	(3.47)
Ash (SO ₃ -Free), W%	18.29	18.14	33.64	31.79	31.39
ELEMENTAL ANALYSES, ASH (SO₃-FREE)-FREE BASIS					
Carbon, W%	71.64	74.08	73.12	73.14	76.07
Hydrogen, W%	3.97	4.35	4.04	4.05	4.30
Sulfur, W%	1.38	1.34	1.94	1.79	1.81
Nitrogen, W%	1.31	1.34	1.07	1.07	1.08
TOTAL	78.30	81.11	80.17	80.05	83.26
Sulfur/Ash (SO ₃ -Free)	0.059	0.061	0.038	0.038	0.040
H/C Ratio	0.66	0.70	0.66	0.66	0.67
SAMPLE FILTRATION					
Filter Cake, Percent of Sample	39.29	41.30	22.01	22.83	22.05
THF Insolubles, W% of Filter Cake	54.30	61.63	57.69	56.70	58.39

TABLE 5**FIRST AND SECOND STAGE FLOWS AND PRODUCT FRACTION FORMATION**

RUN 227-70 (CC-12)

FLOWS - PERCENT OF DRY COAL FEED

	<u>6</u>	<u>12</u>
PERIOD	45.7	45.4
Coal Rate, Lbs/Hr/Ft ³	108.6	108.6
Recycle PFL, W% of Dry Coal Feed	0.0	0.0
Makeup Oil, W% of Dry Coal Feed	154	315
Catalyst Age, Lb/Lb	751	750
First Stage Temperature, °F	800	799
Second Stage Temperature, °F		
FIRST STAGE FEED		
650°F, W%	21.61	22.52
650-850°F, W%	62.66	57.76
850-975°F, W%	14.75	13.27
975°F*, Oil	13.13	18.26
975°F* Asphaltene	0.23	0.22
975°F* Preasphaltene	0.02	0.17
Quinoline IOM	93.03	93.61
Ash	6.97	6.39
TOTAL	212.40	212.20
SECOND STAGE BUFFER		
650°F, W%	0.71	0.78
650-850°F, W%	2.06	2.01
850-975°F, W%	0.49	0.46
975°F*, Oil	0.43	0.63
975°F* Asphaltene	0.01	0.01
975°F* Preasphaltene	0.00	0.00
Quinoline IOM	0.00	0.00
Ash	0.00	0.00
TOTAL	3.70	3.90
FIRST STAGE PRODUCT		
650°F, W%	16.06	16.31
650-850°F, W%	71.06	67.57
850-975°F, W%	18.08	22.89
975°F*, Oil	27.28	28.70
975°F* Asphaltene	0.35	0.06
975°F* Preasphaltene	0.20	0.15
Quinoline IOM	31.35	28.84
Ash	6.97	6.39
Vapor (estimated)	41.05	41.29
TOTAL	212.40	212.20
SECOND STAGE PRODUCT		
650°F, W%	33.47	34.72
650-850°F, W%	75.31	70.91
850-975°F, W%	17.72	16.29
975°F*, Oil	15.78	22.41
975°F* Asphaltene	0.27	0.27
975°F* Preasphaltene	0.02	0.21
Quinoline IOM	13.83	14.42
Ash	6.97	6.39
Vapor	52.71	50.48
TOTAL	216.10	216.10

TABLE 5

Page 2 of 2

FIRST AND SECOND STAGE FLOWS AND PRODUCT FRACTION FORMATION
RUN 227-70 (CC-12)
FLOWS - PERCENT OF DRY COAL FEED

PERIOD	<u>6</u>	<u>12</u>
Coal Rate, Lbs/Hr/Ft ³	45.7	45.4
Recycle PFL, W% of Dry Coal Feed	108.6	108.6
Makeup Oil, W% of Dry Coal Feed	0.0	0.0
Catalyst Age, Lb/Lb	154	315
First Stage Temperature, °F	751	750
Second Stage Temperature, °F	800	799
FIRST STAGE FORMATION		
Vapors	41.05	41.29
650°F, W%	-5.56	-6.21
650-850°F, W%	8.40	9.81
850-975°F, W%	3.33	9.62
975°F*, Oil	14.15	10.44
975°F* Asphaltene	0.12	-0.16
975°F* Preasphaltene	0.18	-0.02
Quinoline IOM	-61.68	-64.77
Ash	0.00	0.00
TOTAL 975°F	47.23	54.51
TOTAL 975°F* RESIDUUM	14.45	10.27
Coal Converted (W% of maf Coal)	66.30	69.20
SECOND STAGE FORMATION		
Vapors	11.66	9.19
650°F, W%	16.70	17.63
650-850°F, W%	2.19	1.33
850-975°F, W%	-0.84	-7.06
975°F*, Oil	-11.93	-6.92
975°F* Asphaltene	-0.08	0.20
975°F* Preasphaltene	-0.18	0.05
Quinoline IOM	-17.05	-14.42
Ash	0.00	0.00
TOTAL 975°F	29.71	21.09
TOTAL 975°F* RESIDUUM	-12.19	-6.67
Coal Converted (W% of maf Coal)	18.83	15.40
TWO STAGE FORMATION		
Vapors	52.71	50.48
650°F, W%	11.14	11.42
650-850°F, W%	10.59	11.14
850-975°F, W%	2.49	2.56
975°F*, Oil	2.22	3.52
975°F* Asphaltene	0.04	0.04
975°F* Preasphaltene	0.00	0.03
Quinoline IOM	-79.20	-79.19
Ash	0.00	0.00
TOTAL 975°F	41.91	46.76
TOTAL 975°F* RESIDUUM	2.26	3.60
Coal Converted (W% of maf Coal)	85.13	84.60

TABLE 6
FEED COAL ANALYSES FOR RUN 227-70 (CC-12)

Run 227-70 Feed: Black Thunder Mine (Wyoming Coal)

FEED DESIGNATION, HRI NO. RUN NUMBER	5713 <u>227-70</u>	5630 <u>227-55</u>	5713 <u>227-69</u>	5713 <u>*</u>
PROXIMATE ANALYSIS, W%				
Moisture	5.23	6.37	6.56	6.38
Volatile Matter (MAF Basis)		44.2	54.6	
Fixed Carbon (MAF Basis)		55.8	45.4	
ULTIMATE ANALYSIS (W%, DRY BASIS)				
Carbon, W%	68.20	67.70	67.55	67.59
Hydrogen, W%	4.19	4.54	4.23	4.38
Sulfur, W%	0.54	0.48	0.51	0.50
Nitrogen, W%	0.87	1.05	0.92	0.95
Chlorine, W%	--	0.04	--	10.19
Ash, W%	(7.72)	(7.15)	(7.62)	(7.61)
Sulfur in Ash	(5.62)	(6.35)	(4.71)	(5.65)
Ash (SO ₃ -Free)	6.73	6.01	6.72	6.54
Oxygen (By Difference)	19.47	20.18	20.07	20.04
SULFUR FORMS, (W%, DRY BASIS)				
Sulfate, W%	0.01	0.04		0.02
Pyrite	0.07	0.11		0.09
Organic	0.48	0.36		0.46
HEATING VALUE, BUT/LB (DRY)		11797		
BTU/LB MAF		12551		
MINERAL ANALYSIS OF ASH (W%, IGNITED)				
Silica, SiO ₂	36.16	34.61		
Alumina, Al ₂ O ₃	17.54	16.98		
Titania, TiO ₂	1.27	1.30		
Ferric Oxide, Fe ₂ O ₃	5.01	6.94		
Lime, CaO	19.69	21.74		
Magnesia, MgO	3.99	4.40		
Potassium Oxide, K ₂ O	0.43	0.35		
Sodium Oxide, NaO	0.39	0.97		
Sulfur Trioxide, SO ₃	12.93	10.74		
Phosphorous Pentoxide, P ₂ O ₅	0.89	1.01		
Strontium Oxide, SrO	0.95	0.29		
Barium Oxide, BaO	0.64	0.37		
Magnesium Oxide, Mn ₃ O ₄	0.11	0.00		
Undetermined	0.00	0.30		
MICROAUTOCLAVE RESULTS **				
Thermal Coal Conversion	80.3	76.6		
Thermal 975°F Conversion	45.4	44.3		
Catalytic Coal Conversion	89.8	87.9		
Catalytic 975°F Conversion	66.4	72.9		

* Check on coal before Run 227-69

** 1989 & '90 tests - 800°F, 30 minutes, 2000 psig H₂, 4/1/ (1) Solvent/Coal (Shell S-317 Catalyst)
Solvent - Wilsonville coal liquefaction distillate product.

TABLE 7
INSPECTION OF START-UP OIL
RUN 227-70 (CC-12)

DESIGNATION	HRI-5757
Gravity, API	8.2
DISTILLATION, °F	
IBP	700
5 V%	721
10 V%	734
20 V%	745
30 V%	755
40 V%	772
50 V%	790
60 V%	805
70 V%	827
80 V%	850
90 V%	881
95 V%	908
E.P.	945
Recovery, V%	99
Residue, W%	0.6
Carbon, W%	89.68
Hydrogen, W%	10.17
Sulfur, W%	0.03
Nitrogen, W%	0.27

TABLE 8

**REJUVENATED CATALYST CHARGED TO RUN 227-70 (CC-12)
AND FRESH CATALYST PROPERTIES**

HRI NUMBER	<u>1-759</u>	<u>5394</u>
Shell S-317 Treatment	Rejuvenated	Fresh
Nominal Size	¹ / ₃₂ " Extrudates	
CHEMICAL ANALYSIS (W%, DRY BASIS)		
Molybdenum, HRI Analyses	9.82	10.76,11.02, 11.58,12.26
Vendor Specification	---	12.0
Nickel, HRI Analyses	1.33	2.00,2.00, 2.25,2.60
Vendor Specification	---	2.5
Carbon	0.73	---
Hydrogen	0.70	---
Sulfur	1.10	---
Nitrogen	0.00	---
PHYSICAL PROPERTIES		
Bulk Density, Compacted, Lb/Ft ³	40.5	36.7
Particle Density, gm/cc	0.961	0.941
Surface Area (Calc.), M ² /gm	197	267
M ² /cc particle	189	251
Pore Volume, cc/gm	0.592	0.697
cc/cc particle	0.569	0.656
Average Crush Strength, Lb/mm	1.23	1.94
PORE SIZE DISTRIBUTION, CC/GM		
Diameter > 30'A	0.59	0.70
Diameter > 100'A	0.34	0.40
Diameter > 250'A	0.15	0.15
Diameter > 500'A	0.13	0.14
Diameter > 1500'A	0.10	0.11
Diameter > 4000'A	0.02	0.03
PENETRATION TEST		
Average Penetration, % of Diameter	---	34.9

TABLE 8A**Metals Content of Acid Washed and Regenerated Catalysts**

	Charge	Acid Washed	Acid Washed and Regenerated
Analysis, W%			
Molybdenum	7.78	7.13	9.82
Nickel	1.69	0.86	1.34
Sodium	0.89	0.03	0.05
Calcium	0.57	0.02	0.05
Iron	0.48	0.22	0.40
Carbon	17.05	18.71	0.73

TABLE 9
RECOVERED CATALYSTS ANALYSES
RUN 227-70 (CC-12)

STAGE	FIRST	SECOND
CATALYST AGE, LB COAL/LB	323	325
CATALYST RECOVERY, +20 MESH, 0%	88.9	63.3
Bulk Density, Gm/cc	0.775	0.800
ANALYSES OF OIL-FREE		
+20 Mesh Catalyst, W%	98.6	90.7
Carbon	11.41	15.44
Hydrogen	0.63	0.61
H/C Ratio	0.66	0.47
Nitrogen	0.07	0.06
Sulfur	5.13	4.71
Molybdenum	8.43	7.57
Nickel	1.14	0.99
Titanium	0.059	0.044
Iron	0.560	0.305
Calcium	0.092	0.197
Sodium	0.533	0.847
TOTAL METAL CONTAMINANTS	1.244	1.393
Loss on Ignition, W%	19.20	19.96
Particle Density, Gm/cc particle*	1.152	0.953
Pore Volume, (D.30 A), cc/gm	0.434	0.354
cc/cc particle	0.500	0.337
Surface Area (Calc.), M ² /gm	179	137
M ² /cc particle	206	131
Crush Strength, Lb/mm	1.14	1.18
ANALYSES OF IGNITED CATALYST		
Particle Density, gm/cc particle	0.953	0.968
Pore Volume (D>30 A), cc/gm	0.689	0.649
cc/cc particle	0.657	0.628
Surface Area (Calc.), M ² /gm	195	189
M ² /cc particle	186	183
	0.02	0.03
ANALYSES OF 200-100 MESH OIL-FREE SOLIDS		
Weight, Grams	5.6	33.3
Molybdenum, W%	---	1.78
* In mercury at 24 psia.		

COAL AND RESID CONVERSION

Run 227-70 (CC-12) and Run 227-55 (CC-1)

C1-C3 GAS YIELD

Run 227-70 (CC-12) and Run 227-55 (CC-1)

FIGURE 2

C4-975 F DISTILLATE YIELD

Run 227-70 (CC-12) and Run 227-55 (CC-1)

FIGURE 3

C4 - 390 F NAPHTHA YIELD

Run 227-70 (CC-12) and Run 227-55 (CC-1)

FIGURE 4

390 - 650 F MIDDLE DISTILLATE YIELD

Run 227-70 (CC-12) and Run 227-55 (CC-1)

FIGURE 5

650 - 975 F HEAVY DISTILLATE YIELD

Run 227-70 (CC-12) and Run 227-55 (CC-1)

FIGURE 6

975 F+ RESIDUUM YIELD

Run 227-70 (CC-12) and Run 227-55 (CC-1)

FIGURE 7

FIGURE 8

RESIDUUM CONCENTRATION IN PRODUCT SLURRY

CTSL - Rejuvenated and Fresh Catalyst

HYDROGEN CONSUMPTION

Run 227-70 (CC-12) and Run 227-55 (CC-1)

FIGURE 9

DENITROGENATION

Run 227-70 (CC-12) and Run 227-55 (CC-1)

FIGURE 10

H/C RATIO OF VACUUM GAS OIL

Rejuvenated & Fresh Catalyst Comparison

*Conditions deviate where different 1st & 2nd stage temperatures are noted next to data points.

FIGURE 11

H/C RATIO OF HEAVY VACUUM GAS OIL

Rejuvenated & Fresh Catalyst Comparison

*Conditions deviate where different 1st and 2nd stage temperatures are noted next to data points.

FIGURE 12

FIGURE 13

H/C RATIO OF RESIDUUM

Rejuvenated & Fresh Catalyst Comparison

*Conditions deviate where different 1st and 2nd stage temperatures are noted next to data points.

NITROGEN IN VACUUM GAS OIL

Rejuvenated & Fresh Catalyst Comparison

*Conditions deviate where different 1st & 2nd stage temperatures are noted next to data points.

NITROGEN IN HEAVY VACUUM GAS OIL

Rejuvenated & Fresh Catalyst Comparison

*Conditions deviate where different 1st and 2nd stage temperatures are noted next data points.

FIGURE 15

Rejuvenated & Fresh Catalyst Comparison

*Conditions deviate where different 1st and 2nd stage temperatures are noted next to data points.

FIGURE 16

API OF PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage LGO

FIGURE 17

API OF PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage VGO

FIGURE 18

API OF PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage HVG0

FIGURE 19

API OF PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage Residuum

FIGURE 20

H/C RATIO OF PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage LGO

FIGURE 21

H/C RATIO OF PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage VGO

H/C RATIO OF PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage HVG0

FIGURE 23

H/C RATIO OF PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage Residuuum

FIGURE 24

NITROGEN IN PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage VGO

FIGURE 25

NITROGEN IN PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage HVG0

FIGURE 26

NITROGEN IN PRODUCT FRACTIONS

Run 227-70 1st and 2nd Stage Residuum

FIGURE 27

6 of 7

APPENDIX A TO RUN 227-70 (CC-12) REPORT CATALYST REJUVENATION PROCEDURE

The process of catalyst rejuvenation was developed by HRI for restoring the activity of H-Oil catalysts. Most of the development work was done using CoMo catalysts. Basically, the process includes acid washing with sulfuric acid to remove the contaminant metals followed by carbon burnoff to restore the surface area of the blocked pores.

With little recent experience with catalyst rejuvenation and no experience rejuvenating this particular catalyst on this scale, the exact procedures were changed somewhat as we proceeded. Much more work would be needed to optimize these procedures.

Catalyst Source and Previous History

All of the Shell S-317 NiMo catalyst that was rejuvenated had been recovered at the end of bench unit 227 coal liquefaction operations with Black Thunder Coal. The specific runs and quantities are listed below:

<u>Run</u>	<u>Reactor</u>	<u>Volume, cc</u>	<u>Weight, g</u>	<u>Catalyst Age lb coal/lb cat</u>
227-61	1st	770	688	886
227-61	2nd	900	870	1267
227-64	1st	810	722	1170
Total/Avg		2480	2280	1121

All three recovered catalysts had been used in more than one run; so these catalyst ages are cumulative. The catalyst histories are summarized in *Table A-1*. The fresh catalyst used in the first "source" runs was from Batch HRI-5394 in all cases.

The catalysts were mixed and labelled as L-758. The total volume and weight of the mixture were 2350 cc and 1981 grams. The decrease from the quantities in the table above was primarily due to sampling for lab analyses.

All L-758 was rinsed four times with toluene and dried under nitrogen overnight. A 25-gram sample of the washed L-758 was removed. Its analyses are included in *Table 3*.

ACID WASH

The L-758 catalyst was acid-washed in two batches by ebullating in a 2-inch by 6-foot insulated glass column. The temperature of the wash was maintained at the specified temperature by windings on the acid-wash holding tank and a hot plate under the acid-wash holding tank.

Procedure

The target acid-wash procedure was the same for each batch, but because of slightly different volumes and heat-up and cool-down times, both runs are chronicled below.

Batch #1:

1. Charged 1235 cc L-758 catalyst to 2-inch glass tube (level = 24 inches).
2. Charged 4.8 liter deionized water and ebullated catalyst.
3. 0 min With unit at 130°F, charged 1 liter 15 W% sulfuric acid solution to unit.

Began slowly increasing unit temperature to 150°C.
4. 20 min Unit reached 150°F. Start 30 minute wash.
- 4A. 25 min Charged 0.33 liter 15 W% sulfuric acid solution to bring acid concentration of wash to 3.5 W%.
5. 50 min Turned off heat and circulation.
(Temperature slowly declined.)
6. 65 min Drained acid solution.
7. 70 min Added 3.5 liter deionized water and circulated for 15 minutes.
8. After 2nd rinse, pH of rinse water was 6.
9. Catalyst was discharged and dried at 110°C.

Batch #2:

1. Charged 1080 cc L-758 catalyst to 2-inch glass tube (level = 21 inches).
2. Charged 6.0 liter deionized water and ebullated catalyst.

3. 0 min With unit at 130°F, charged 1.66 liter 15 W% sulfuric acid solution to unit. This brought the wash solution to 3.5 W% sulfuric acid.

Began slowly increasing unit temperature to 150°C.
4. 18 min Unit reached 150°F. Start 30 minute wash.
5. 48 min Turned off heat and circulation.
(Temperature slowly declined.)
6. 55 min Drained acid solution.
7. 58 min Added 5.0 liter deionized water and circulated for 10 minutes.
8. After 6th rinse, pH of rinse water was 6.
9. Catalyst was discharged and dried at 110°C.

Recovery:

Batch #1	1200 cc	902 g
Batch #2	1050 cc	785 g

After the charge weight is adjusted for volume losses (2.9%), there is a 212 g (11.2 %) weight decrease. Part of this weight corresponds to metals removed by the sulfuric acid as indicated in the metals balance, *Table 4*.

REGENERATION

In the next part of the catalyst rejuvenation, the majority of the carbon on the catalyst was oxidized by stepwise increasing the temperature and oxygen concentration. Basically, metered air and nitrogen flowed through a heated 3-inch by 3-foot stainless steel pipe which contained two catalyst baskets, each containing 200-cc catalyst. The catalyst baskets had a cross-section almost the same as the pipe.

Six batches of acid-washed L-758 catalyst were regenerated in this apparatus. Because the first regeneration runs resulted in catalyst that contained excessive carbon, progressively more severe procedures were implemented. The temperature and oxygen concentration profiles for the four different procedures are listed in *Table 2*.

Table A-1
L-758 CATALYST HISTORY

<u>Charge</u>	<u>Source</u>	<u>Weight, g</u>	<u>Volume, cc</u>
227-64 R1	227-62 R1	632.5	750
	Fresh	90.5	150
227-61 R1	227-59 R1	670	780
	227-57 R2	104	120
227-61 R2	227-59 R2	752	825
	227-57 R3	43	75
227-59 R1	227-57 R1	380	450
	227-57 R2	300	450
227-59 R2	227-55 R2	608	690
	227-57 R3	183	210

TABLE A-2

CATALYST REGENERATION PROCEDURES AND CARBON ANALYSES

Oxygen (Vol%) and Time (hours) at Indicated Wall Temperature

Run #	1		2		3		4		5		6		7**	
Temperature	O ₂	Time	O ₂	Time	O ₂	Time	O ₂	Time	O ₂	Time	O ₂	Time	O ₂	Time
750°F	1	13	1	13	2.5	11	2.5	4	-----	-----	-----	-----	-----	-----
750°F	2	3	2	3	5	3	-----	-----	-----	-----	-----	-----	-----	-----
750°F	6	2	8	2	7.5	2	-----	-----	-----	-----	-----	-----	-----	-----
750°F	21	0.5	21	1.5	21	1.5	-----	-----	-----	-----	-----	-----	-----	-----
800°F							2.5	4	-----	-----	-----	-----	-----	-----
800°F							5	3	-----	-----	-----	-----	-----	-----
800°F							7.5	2	-----	-----	-----	-----	-----	-----
800°F							21	1.5	-----	-----	-----	-----	-----	-----
825°F							21	4	-----	-----	-----	-----	-----	-----
CARBON, W%														
Top Bskt	9.10		6.21		6.84		1.29		1.42		0.07		---	
Btm Bskt	11.91		3.98		6.48		0.57		1.55		0.01		---	
WEIGHT (G) CHARGED,														
Top Bskt	164		157		---		160		161		127*		37**	
Btm Bskt	156		159		---		152		160		124*		38**	
WEIGHT (G) RECOVERED														
Top Bskt	135		124		122		117		117		109*		27**	
Btm Bskt	129		126		121		110		118		106*		27**	

* Rerun of catalyst from Run #1

** Remainder of catalyst -- 45 cc in each basket

APPENDIX B TO RUN 227-70 (CC-12) REPORT

MICROAUTOCLAVE EVALUATION OF RECOVERED, REJUVENATED, AND REGENERATED CTSL™ CATALYSTS

A microautoclave catalyst evaluation program was undertaken to provide additional information on the effects of regeneration and rejuvenation procedures on catalyst activity. The bench run 227-70 (CC-12) demonstrated the high and sustained activity of rejuvenated catalyst, but these microautoclave tests were designed to further distinguish the benefits produced by the different steps and severities of the rejuvenation process. The program compared the activities of ten catalysts. They were the fresh S-317 catalyst, the recovered CTSL™ catalyst used to prepare the rejuvenated catalyst, the rejuvenated (acid-washed and regenerated) catalyst, the acid-washed catalyst produced in the course of preparing the rejuvenated catalyst, regenerated catalyst (without acid washing), acid-washed catalyst regenerated to three different carbon contents, and recovered first and second stage catalysts from Run CC-12.

PROCEDURES

The microautoclave equipment and general procedures have been described previously in the Laboratory-Scale Studies section of this report. These tests were conducted similarly to previous catalyst microautoclave catalyst evaluation tests. The catalysts, except for the original rejuvenated catalyst and the recovered catalysts from Run CC-12, were first presulfided in the microautoclave using tert-nonyl polysulfide (TNPS) and tetralin. For each 3 grams of catalyst 7.5 g of tetralin and 4.5 g of TNPS, corresponding to 8 times the sulfur required to form the metal sulfides, were charged. The presulfiding conditions were 550°F for 120 minutes at 1500 psig hydrogen. The presulfided catalyst was washed with THF and dried.

The catalyst activity tests were conducted at 825°F and 2000 psig hydrogen for 30 minutes using 1 gram of catalyst per gram of pressure filter liquid (approx. 30% resid) from Run CC-1 Period 23A. The charge of fresh Shell S-317 catalyst was 1.65 grams and the other catalyst charge weights were adjusted, based on particle densities, so that there would be an equivalent amount of contaminant-free catalyst. The analyses for most of these catalysts have been included in the "Recovered Catalyst" and "Catalyst Charge" sections of the Run CC-12 report.

RESULTS

Table 1 summarizes the results from these microautoclave tests. Specific comparisons are discussed below.

- 1) The recovered CTSL catalyst used in preparing the Rejuvenated used in Run CC-12 was less active than fresh (presulfided) Catalyst (compare Runs CE32 and CE36):
 - A) Nominally 56% as active for residual oil conversion (relative first order rate constant - $\ln(C_{\text{feed}}/C_{\text{prod}})$);
 - B) The hydrogen content increased by only 0.26 W% compared to 0.57 W%;
 - C) The nitrogen content was lowered by only 0.20 W% compared to 0.37 W%;
- 2) The activity of the rejuvenated catalyst charged to run CC-12 approached that of fresh catalyst (compare Runs CE33 and CE36):
 - A) The nominal residual conversion activity was 93% that of fresh catalyst;
 - B) Hydrogen content was increased by 0.46 W% (vs. 0.57W%);
 - C) Nitrogen content was lowered by 0.39 W/% (more than by fresh catalyst, 0.37 W%);
- 3) Acid Washing alone gave a relatively small improvement in catalyst performance (Run CE37):
 - A) The nominal residual oil conversion activity increased to 69% of fresh catalyst (from 56%);
 - B) The hydrogen content increase was 0.32 W% (up from 0.26W%);
 - C) The nitrogen content was lowered by 0.23 W% (compared to 0.20 W%);
- 4) Regeneration alone (without acid washing) resulted in catalyst performance very comparable to that of the rejuvenated catalyst (Run CE41):
 - A) The nominal residual oil conversion activity, at 97% of that of fresh catalyst, was slightly higher than that of the rejuvenated catalyst, 93%;
 - B) The increase of hydrogen content, 0.42 W%, was slightly less than that with rejuvenated catalyst, 0.46 W%;

- C) The decrease in nitrogen content, 0.31 W%, was slightly less than that with rejuvenated catalyst, 0.39 W%;
- 5) A series of tests with acid washed catalyst regenerated to various carbon contents indicated the following (Runs CE38, CE39, and CE40):
- A) Lowering the carbon content to 9.0 W%, from 18.7 W%, resulted in only partial recovery of catalytic activity, to 82% of fresh catalyst residual oil conversion activity, and comparable performance with regard to hydrogen uptake and nitrogen removal;
 - B) The regenerated sample with 4.0 W% carbon gave the highest residual oil conversion activity, almost exactly equal to that of the fresh catalyst. However, hydrogen addition and denitrogenation were slightly below that of the fresh catalyst or of the rejuvenated composite, which contained 0.73 W% carbon.
 - C) The regenerated sample containing 1.55 W% carbon had values of the three performance parameters very close to those with the composited L-759 rejuvenated catalyst. This degree of agreement might be regarded as the reproducibility of the test procedure.
- 6) The first and second stage catalysts recovered after CTSL™ Run CC-12 were also evaluated in the microautoclave with the following results (Runs CE34 and CE35);
- A) The second stage catalyst had been appreciably more deactivated than the first stage catalyst to 45% of fresh catalyst residual oil conversion activity compared to 70% for the first stage catalyst, and only 0.19 W% hydrogen addition compared to 0.38% for the first stage catalyst. The product nitrogen contents were the same for these two tests, but very small effects would be expected after considering the results of the other microautoclave tests;
 - B) The averages of the three performance parameters for first and second stage catalysts from Run CC-12 were very close to the performance parameters for the original L-758 recovered catalyst (which was a composite of first and second stage catalysts) used in preparing the rejuvenated catalyst. This result indicates no extraordinarily great rate of deactivation for the rejuvenated catalyst, although the Run CC-12 operation processed 325 lbs coal/lb catalyst/stage, while the operations of the CTSL™ recovered catalyst used in preparing the rejuvenated catalyst charge to Run CC-12 had processed about 1121 pounds coal per pound of catalyst in a sequence of runs.

In summary, this program has duplicated the relative catalyst activity results attained in Run CC-12 and has provided more information on the activity of other treated catalysts. As had been demonstrated in Run CC-12, this program showed that the rejuvenated catalyst had catalytic performance very nearly that of fresh S-317 catalyst. Acid washing alone caused only a partial restoration of catalytic activity while regeneration (without acid washing) was very nearly as effective as the rejuvenation procedure. Optimal regeneration might be at a lower severity than used in preparing the rejuvenated catalyst. The recovered second stage catalyst from Run CC-12 was considerably more deactivated than the first stage catalyst. This difference in activity had also been apparent from the analyses of the first and second stage samples from Run CC-12.

TABLE B-1

MICROAUTOCLAVE TESTING OF REGENERATED AND REJUVENATED CTSL CATALYST										
MA Run	Catalyst Carbon (3)	-----Microautoclave Product, Wt----- Residuum Hydrogen Nitrogen Sulfur	Relative Resid. Rate Constant	Hydrogen Change	Nitrogen Change					
Feed to Microautoclave tests										
Catalyst										
Fresh S-317 (1)	CE36	0.00	14.08	29.34	8.53	0.57	0.04	1.00	0.57	-0.37
L-758 Recovered Catalyst to Rejuvenation	CE32	17.26	19.46	8.79	0.37	0.14	0.56	0.26	-0.20	
L-759 Rejuvenated Catalyst To Run CC-12 (1)	CE33	0.73	14.78	8.99	0.18	0.16	0.93	0.46	-0.39	
Acid Washed L-758 (1)	CE37	18.71	17.63	8.85	0.34	0.18	0.69	0.32	-0.23	
Regenerated L-758 (Not Acid Washed) (1) (2)	CE41	1.38	14.42	8.95	0.26	0.41	0.97	0.42	-0.31	
Acid Washed L-758	CE38	9.00	16.06	8.89	0.28	0.13	0.82	0.36	-0.29	
Regenerated to 9.0% Carbon (1)	CE39	4.08	14.04	8.77	0.22	0.20	1.00	0.44	-0.35	
Regenerated to 4.0% Carbon (1)	CE40	1.55	15.05	8.99	0.20	0.27	0.91	0.46	-0.37	
Regenerated to 1.55% Carbon (1)										
Recovered Catalyst From Run CC-12	CE34	11.41	17.59	8.91	0.32	0.04	0.70	0.38	-0.25	
First Stage	CE35	15.44	21.08	8.72	0.31	0.15	0.45	0.19	-0.26	
Second Stage			19.34	8.81	0.32	0.14	0.57	0.28	-0.25	
Average										

(1) Catalyst Presulfided in Microautoclave: 2 hours, 550 F, 1500 psig (H2)
With 38% TNPS in Tetralin, 4/1 Solvent/Catalyst

(2) Regenerated in Laboratory, 850 F, 2% Oxygen

(3) Carbon on Catalyst to Presulfiding or to Microautoclave Test.

Microautoclave Tests: 825 F, 30 Minutes, 2000 psig (H2),
1 grams CTSL PFL/Gram estimated contaminant-free catalyst

marejuv.tab

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SECTION X

RUN CC-13 (227-71) CO₂ AND LIGHT DISTILLATE SLURRYING

SUMMARY

The objectives of Run 227-71(CC-13) were to evaluate CO₂ or a vaporizable distillates as feed slurring agents for coal to the CTSLTM operation.

Carbon dioxide was added at four different rates, ranging from 0 to 0.6 lb/lb coal. Also, in one condition a naphtha/light gas oil was used to slurry the feed to simulate the effects on the reactor kinetics of the CO₂ vaporizing from a CO₂/coal slurry.

The added CO₂ was largely reacted (about 58%), with hydrogen to form CO, CH₄, and H₂O. As a result, an increase in hydrogen consumption of 3.8 W% dry coal was observed. Also, increased coal conversions, by 1-2%, were obtained during the operations with CO₂ addition. The addition of CO₂ had no clear impact upon the conversion of residual oil to distillates, so that distillate oil yields were increased only by the degree of increased coal conversion. In the final operations with CO₂ addition with the highest proportion of CO₂ addition, the products hydrogen contents, nitrogen contents, sulfur contents, cyclohexane and toluene insolubles contents were poorer than in any other CTSLTM operations with Black Thunder Mine coal.

In the operation using light gas oil as coal slurring oil the coal conversion, 94.0%, was the highest of any CTSLTM operation with the Black Thunder Mine coal. There was probably little impact upon the kinetics of conversion of residual oil to distillates, although there was a relatively high yield of residual oil because of the lack of residual oil recycle. With recycle of some residual oil along with the use of light distillate as the principal coal slurring agent, it is considered that increased coal conversion can be obtained while maintaining low residual oil yield. The type of oil used for this purpose in this run, 480°F volume average boiling point, is probably nearly optimum in maintaining an acceptable slurry environment at reactor conditions.

SCOPE OF WORK

A feed slurrying agent that would vaporize in the reactor would afford less dilution, than with the usual slurrying agents, of the resulting slurry phase in the reactor and promote more complete reaction of the coal and heavy primary liquid products to lighter liquids. CO₂ has been demonstrated as a feasible slurrying agent for pipeline transport of coal and might be applied for this use in CTSL™ liquefaction. However, on the small scale of Bench Unit operations it was not possible to maintain CO₂/slurry feed to the unit, and the test program was modified to study the impact of CO₂ feed to the process while using the conventional CTSL™ practice of slurrying the coal with recycled filtered liquid. Also, there was an attempted operation using a light gas oil as slurrying agent in place of the filtered liquid, which was maintained for 40 hours before problems developed in maintaining feed slurry flow.

Table 1 lists the conditions that were used in Run 227-71(CC-13), in which there were 14 days of coal operations. The operations were with Black Thunder Mine (Wyoming) sub-bituminous coal, and Shell S-317 catalyst that were the same as used in comparable conventional CTSL™ Bench Unit Operations. The CO₂ fed in the operations ranged from 0 to 0.6 lbs/lb of the coal fed, while there was an additional solvent feed of about 1.2 lbs/lb coal, either recycle filtered liquid obtained by filtration of the reactor product slurry, or an extraneous naphtha/light gas oil solvent that had been produced in other coal liquefaction operations.

PROGRAM RESULTS AND ANALYSES

RUN 227-71 (CC-13)

This section discusses the conversion, product yields, process performance, and product quality data for Run 227-71(CC-13). *Table 2* presents the operating conditions, product yields, and conversions for each of the periods for which detailed normalized yields were calculated.

The liquefaction performance during Run CC-13 is summarized in *Table 2*, which gives the detailed product distribution. *Figure 1* summarizes the day-by-day coal conversion. *Figures 2 and 3* graphically compare, for the four principal operating periods of the run, the yield of C₄-975°F distillate product and the yield of 975 °F⁺ residual oil, respectively.

COAL CONVERSION

Coal conversion in Run CC-13 ranged from 90.0 to 94.0 W%, see *Figure 1*. The lowest coal conversion was in the first operation of the run, with no CO₂ addition. The highest coal conversion was in the operation using light gas oil make-up, and is the highest coal conversion obtained in any CTSLTM operation with Black Thunder Coal in the current program. The following tabulation summarizes the average coal conversions for the various operation of the run.

CO ₂ Lb/Lb Coal	PFL Recycle Lb/Lb Coal	LGO Make-up Lb/Lb Coal	Coal Conv. W% maf Coal	Ash Conc.* W%
0.00	1.18	0.00	90.4	4.4
0.08	1.20	0.00	91.4	4.4
0.25	1.28	0.00	92.5	4.4
0.25	0.00	1.18	94.0	5.8
0.56	1.04	0.00	93.0	5.6

* In Hot Separator slurry separated at 600°F.

The very high conversion in the operation with light gas oil make-up conforms to the conception of promoting the coal conversion reaction because of less dilution of slurry phase reactants. As an index of this factor, the concentration of mineral matter (ash) in the product slurry from the hot separator (which is an indicator of slurry phase concentrations in the reactors) summarized above was about 1.3 times as great with light gas oil make-up as in the previous operation with filtered liquid recycle, while unreacted coal concentration was virtually unchanged. The actual increase in solids concentration in reactor environment using the distillate slurring oil was even higher since a considerable amount of mid-distillate condensed from the vapor phase as the reactor product stream was cooled from 825°F. Flash calculations at the hot separator (600°F) and reactor (825°F) temperatures indicate

that the concentration of solids in the reactor were about twice as great in the operation using the light gas oil as slurring agent. These calculations are summarized more fully below, in connection with the residual oil yields.

The increase in coal conversions because of the CO_2 additions did not have a similar relation to apparent changes in slurry phase compositions. Apparently, the CO_2 either had an interaction with the unreacted coal, or improved the liquid/coal contact to promote higher coal conversions.

NORMALIZED PRODUCT DISTRIBUTION

C₄-975 Distillate Yields

C₄-975°F distillate yield was 60.7 W% of MAF coal in the conventional reference operations at the beginning of the run, then 3-6 W% higher in the operations with CO₂, and 5 W% lower in the operations with the light gas oil slurrying agent, see *Figure 2*. The nominal impact of CO₂ addition was greater than the associated 2% increase in coal conversion, indicating a possible ancillary contribution to the change in C₄-975°F distillate yield. Since there was only a small impact of CO₂ addition upon residual oil yield, see below, this leaves the possibility of some hydrocarbon synthesis (Fischer-Tropsch) reaction to produce liquids. While there was almost certainly additional methane formation with the CO₂ addition, see below, there was apparently very little change in C₂ and C₃ hydrocarbon formation so that the synthesis of still heavier hydrocarbons seems unlikely. The difference between the incremental liquid yield and the incremental coal conversion more probably reflects material balance difficulties which were occasioned by the somewhat erratic rate of CO₂ addition during these operations.

The 5 W% lower C₄-975°F distillate yield while using the light gas oil makeup, despite a 2-3% higher coal conversion, was caused largely by the 5 W% higher residual oil yield for that operation. This change was not because of any impact of the light gas oil upon the kinetics of secondary reaction of residual oil, but probably because there was no residual oil recycle, and an appreciable amount of net slurry product was generated, approximately 1 pound per pound of coal fed. The ultimate application of light slurry recycle would have to incorporate a portion of residual oil recycle to limit the formation of residual oil.

975°F Residual Oil Yield

975°F Residual oil yield was 1.3 W% of maf coal in the conventional reference operations without CO₂ addition at the beginning of the run, about this level or slightly lower in the operations with CO₂ addition, and 5.9 W% of maf coal in the operation using the light gas oil slurrying agent, see *Figure 3*. *Figure 4* reflects the apparent kinetics of secondary residual oil conversion reactions, by comparing the residual oil concentrations in the product (hot separator) slurry for the various operations of Run CC-13, and comparable operations of CC-1, in which no CO₂ was added. In general, the residual oil concentrations for the operations with CO₂ addition lie below what would be expected for a comparable operation with no CO₂ addition. However, the differences are small in the first part of Run CC-13, and the larger difference at the end of the run may largely be due to failure to reach an equilibrated condition after the upset at the end of the eleventh day and stabilizing the unit in the twelfth day.

Figure 4 shows, for the operation with the light gas oil slurrying agent, much lower residual oil concentration in the product slurry, by a factor of 2, than in the contemporary operations with CO₂ addition during the run. This nominally indicates

enhanced residual oil kinetics in this mode. However, more detailed flash calculations at the actual reactor conditions (at 825°F against the separator temperature of 600°F) indicate nearly equivalent residual oil concentrations in the reactor environment for the two types of recycle solvent, as follows:

Period	9	11
Recycle, Lb/Lb Coal		
Filter Liquid	1.18	0.08
Light Gas Oil	0.00	1.10
CO ₂ Feed, Lb/Lb Coal	0.24	0.26
Hot Separator Experimental		
Condensables, W% of Dry Coal		
Slurry, W% of Dry Coal Feed	35.7	67.6
Composition, W%	146.0	111.4
Residual Oil		
Unreacted Coal	10.3	5.9
Ash	4.8	5.0
	4.4	5.8
Hot Separator Flash Calc.		
Condensables, W% of Dry Coal	33.0	64.7
Slurry, W% of Dry Coal Feed	148.7	114.3
Composition, W%		
Residual Oil	10.0	5.7
Unreacted Coal	4.7	5.7
Ash	4.4	5.7
Reactor Outlet Flash Calc.		
Condensables, W% of Dry Coal	104.1	146.5
Slurry, W% of Dry Coal Feed	77.6	32.5
Composition, W%		
Residual Oil	19.1	19.8
Unreacted Coal	9.1	20.0
Ash	8.4	20.0

The gas oil components had sufficient hydrogen donor/shuttling capability to effectively convert the coal and support secondary reaction of the residual oil to a degree approaching that of the conventional full range recycle solvent.

The light oil that was used for slurring the coal in this run would appear to be near the optimum volatility for this purpose, since it resulted in a reactor which nominally contained 40 W% solids and appeared to develop no operating problems in the reactors. A more volatile solvent would have resulted in still higher solids

concentration and potential operating problems, while a less volatile solvent would give some additional dilution of the solids with the prospect of lower coal conversion.

Light Gas Yields and CO₂ Reactions

As indicated in *Table 2*, in the operations with CO₂ addition, there were apparent negative yields of CO₂ along with higher yields of C₁-C₃ gases, CO, and water than those obtained in the reference operation at the beginning of the run with no CO₂ addition. *Figure 5* relates the amount of CO₂ in the outlet gases to the amount of CO₂ added to the operation. *Figures 6, 7, and 8* give similar relations for the net yields of H₂O, CO, and CH₄, respectively. Each of these figures contain the linear least squares relations for the factors correlated, all of which were highly significant, statistically, with confidence levels above 99%.

The correlated values for the proportion of CO₂ addition that reacts, and the amounts of additional products were the following:

	Lbs/Lb CO ₂ Added
CO ₂ Reacted	0.583
Incremental H ₂ O formed	0.427
Incremental CO formed	0.105
Incremental CH ₄ formed	0.143
C in CO ₂ reacted	0.159
O in CO ₂ reacted	0.424
C in CO and CH ₄ formed	0.152
O in CO and H ₂ O formed	0.439
H in CH ₄ and H ₂ O formed	0.083

These correlations indicate that 58.3% of the CO₂ was reacted. The elemental balances indicate that CO, CH₄, and H₂O were the only products that were formed from the CO₂.

With respect to the other light gas products that might have been formed, the following tabulation compares their average collected yields for the operations with and without CO₂ addition:

	Yields, W% of Dry Coal		Confidence
	<u>No CO₂</u>	<u>CO₂ Added</u>	<u>Level, %</u>
C ₂ Hydrocarbons	2.61	2.11	83.7
C ₃ Hydrocarbons	3.23	3.06	39.1
C ₄ Hydrocarbons	2.44	2.26	57.1
Total	8.28	7.43	76.5

The confidence levels noted here are a comparison of the averages with and without CO₂ addition. Although in each case the average of the yields with CO₂ addition was lower than that without CO₂ addition, the scatter of the data was such as to result in relatively low statistical confidence levels. The sum of the C₂, C₃, and C₄ yields did have a marginally significant correlation against the amount of CO₂ fed, 92.3% confidence level, as summarized by *Figure 9*. The least squares correlation indicates 1.8 W% of dry coal lower yield of these components when the CO₂ addition was 0.6 lbs/lb dry coal. This relation suggests that CO₂ inhibits the formation of light gases during the liquefaction/conversion of the coal, ostensibly by a chain quenching effect, although the experimental support of such a hypothesis is weak.

Hydrogen Consumption

The elemental balance given above in connection with reaction of CO₂ indicates that additional hydrogen consumption because of the CO₂ corresponds to 14 W% of the amount of CO₂ reacted. The normalized yields given in *Table 2* show an increase in hydrogen consumption of 3.8 W% of dry coal when the CO₂ reacted amounted to 26.2 W% of the dry coal, which is in agreement with this ratio. The correspondence overrides the effect of any ancillary hydrogenation/dehydrogenation effects of the addition of CO₂, or the presence of considerable amounts of CO consequent to the reaction of the CO₂.

Product Properties

Table 3 summarizes the hydrogen, nitrogen, and sulfur analyses of the liquid products and product fractions from Run CC-13.

The hydrogen contents of the product fractions for the final operation of the run, while feeding 0.55 lbs CO₂/lb coal, were 0.18% to 1.23% lower than those of the products in the conventional operation at the beginning of the run, with the difference being the greatest for the heavy liquid product fractions. In Run CC-11, with H₂S added to the feed as in Run 227-71(CC-13), the decrease in hydrogen contents over a comparable interval of the run was 0.09% to 0.44%, so that Run CC-13 operation with CO₂ addition displayed a lower hydrogenation effectiveness. This difference might be due in some degree to dilution of the hydrogen because of the added CO₂ and its products, but the hydrogen partial pressure was only about 100 psi lower in the final operation of Run CC-13 than in the initial operation, because the system pressure had been raised to 2800 psi, from 2500 psi, for the final operation. In the final operations of Run 227-71(CC-12), with 0.56 lbs CO₂/lb coal, the hydrogen contents of the heavy liquid products were lower than in any such CTSL™ products from Black Thunder Mine coal, by 0.6 W% in the 850-975°F product fraction and by 0.8 W% in the 975°F+ residual oil.

The change in nitrogen contents of the products in course of Run CC-13 were approximately the same as during Run CC-11. The level of nitrogen contents were generally the same for these two runs, excepting in the residual oil component, where the Run 227-71(CC-13) nitrogen contents were higher by about 0.2 W% throughout the run.

The sulfur contents of the liquid product fractions were generally low in the range of 0.01-0.06 W%. However, these values are higher than generally obtained in other CTSL™ operations with Black Thunder Mine coal. In Run 227-69(CC-11) sulfur contents of the distillate components were generally less than 0.01 W%, and 0.01-0.04 W% in the residual oil.

Cyclohexane insolubles content of the 975°F+ product for the final operations of Run CC-13 were over twice the amount at the corresponding point of Run CC-11. However, even for the first operations of the two runs the cyclohexane insolubles content for Run 227-71(CC-13) was higher by a factor of 1.5. The toluene insolubles content of the residual for the final operations of Run 227-71(CC-13) was very high, 6.2 W%, compared to less than 1 W% in Run 227-69(CC-11).

There was poor catalytic performance respecting hydrogenation, denitrogenation, and desulfurization throughout Run 227-71(CC-13), and especially in the final operations with the highest proportion of CO₂ feed.

Table 4 summarizes the analyses of the oil-free product solids from Run 227-71(CC-13). There are two notable characteristics of the solids from the

operations in which CO₂ was included in the feed: (1) The nominal oxygen content (by difference) was higher than that when there was no CO₂ in the feed, by a factor of about 1.25; (2) there was a relatively lower hydrogen content by a factor of 0.8. These differences indicate that the added CO₂ suppresses decarboxylation of the coal, and some of the native hydrogen in the coal reacts directly with the higher CO₂ content of the vapor phase.

DETAILS OF OPERATIONS

RUN PLAN AND OPERATING HISTORY

The initial Run Plan was to use CO₂ as the sole feed coal slurrying agent by means of a pressurized, refrigerated slurry preparation system. However, the attempts to prepare a pumpable CO₂/coal slurry on the Bench Unit scale of operations were unsuccessful, principally because high vaporization and vapor-binding of the slurry feed pump. The run plan was then changed to feed CO₂ in addition to a feed slurry incorporating a normally liquid material, recycled filtered liquid or light gas oil make-up (which in process application could be recycled by the distillation of the reactor products).

The final run plan is given in *Table 1*. The run duration was 14 days as Run 227-71(CC-13). After an initial operation of five days, in a normal CTSL™ configuration with recycled filtered liquid slurrying oil and without CO₂ addition, addition of CO₂ was started first at a rate of 0.1 lbs/lb coal, then increasing to 0.25 lbs/lb coal. Then, in the tenth day, filtered liquid recycle was stopped and replaced by an equal amount of light gas oil make-up. The operation with light gas oil make-up was maintained for 40 hours to the end of the eleventh day, when the feed slurry flow failed because of difficulties in keeping the coal in suspension in the light oil. The twelfth day was spent in stabilizing the unit for the final operation with the filtered liquid recycle resumed and the CO₂ addition increased to 0.6 lbs/lb coal to the scheduled end of operations after 14 days.

An elevation in pressure drop from a normal level of about 3 psi to about 20 psi across the second stage reactor first appeared during the twelfth day of the run during the attempted operations using a light distillate (480°F average boiling point) for slurrying the coal in place of recycled filtered liquid. This elevated pressure drop persisted to the end of the run with the return to normal slurrying practice in the thirteenth day.

On inspection, the catalysts were found in the normal settled positions in the reactors, corresponding to about 5% loss of catalyst in the first stage and no loss of catalyst in the second stage, and recovered from the reactors as loose extrudates, although there was a thin plug about half way up in the settled bed in the second stage reactor and a small amount of catalyst in the screen at the top of the reactor.

COAL FEED

The coal feed for Run 227-71(CC-13) was a shipment of Black Thunder Mine coal, HRI 5828, which had been received shortly before the start of the run. The coal analyses are given in *Table 5*. The HRI 5828 shipment had a hydrogen content that was lower than any of those of previous shipments of the Black Thunder Mine coal, by 0.1-0.4 W%. Microautoclave evaluation of the HRI 5828 coal indicated poorer conversion performance than for the earlier shipments, 3-5% lower conversions in the catalytic tests and 3-9% in the thermal tests. Other elemental analyses and the mineral analysis were in the range of those of the earlier shipments.

LIGHT SLURRY OIL

The light slurry oil, HRI 5663, used as coal slurrying oil in a portion of the run was a coal derived distillate obtained from the Wilsonville Coal Liquefaction facility. Their identification was Coal Distillate, SW #94532, UN 1136, I 144850, Sec 50. Its analyses are given in *Table 6*. The boiling range was 148-748°F, with 30 V% as naphtha over at 390°F. The hydrogen content and characterization of the HRI 5663 oil was in the range of those of product/recycle oils that are obtained in conventional CTSLTM operations, and also of the products that were obtained during the Run 227-71(CC-13) using the HRI 5663 oil for coal slurrying. The Watson characterization factor of the HRI 5663 oil was about 0.1-0.2 units lower than the CTSLTM oils, and the hydrogen content was about 0.2 W% higher than in such oils.

CATALYST

Shell S-317 NiMo catalyst, HRI 5394, was used in both stages in 1/32 inch extrudate form. The catalyst was sulfided during the start-up by doping the start-up oil with TNPS (di-tertiary nonyl polysulfide). During coal operations H₂S, corresponding to 2 W% of the coal, was continuously added to maintain the sulfide level of the catalyst. The analysis of the fresh HRI 5394 charged to the run are summarized in *Table 7*.

RECOVERED CATALYST ANALYSES

The analyses of the first and second stage catalysts recovered after the final operations of Run 227-71 are summarized in *Table 8*.

The volume of the +20 mesh recovered catalysts from the first and second stages corresponded to 86% and 76% of the volume charged, respectively. Molybdenum analyses of the recovered 20-100 mesh material corresponded to 2% and 6% of the molybdenum in the charged catalyst.

The catalysts recovered after the run from both stages were highly contaminated, with carbon contents higher than contained on the corresponding catalysts recovered after previous CTSLTM runs with Black Thunder Mine coal. The first stage

catalyst contained 17.6 W% carbon, which compares to values of 15.6%, 11.4%, 8.9%, 13.6%, 10.0%, and 11.4% for recovered first stage catalysts after the earlier runs with Black Thunder Mine coal. The second stage catalyst after Run CC-13 contained 31.4 W% carbon, which is exceptionally high compared to values of 18.9%, 13.1%, 18.2%, 18.8%, and 15.4% for second stage catalysts after those earlier runs. It does not appear that these carbon accumulations Run 227-71(CC-13) were associated with loss of ebullation during the run since the unit was operating in good order with only a slightly elevated pressure drop during the final coal operations and the subsequent shut-down operations.

There were exceptionally high losses in pore volume and surface area associated with the very high carbon accumulation on the recovered second stage catalyst, with a pore volume about one-third, and surface area one-tenth of that of fresh catalyst. The first stage catalyst retained higher proportions of these parameters, with 60% of the pore volume, and 75% of the surface area of the fresh catalyst. These first stage catalyst properties are comparable to those of recovered second stage catalysts from earlier CTSLTM operations, but represent lower proportion of pore volume and surface area compared to the earlier recovered first stage catalysts, which had about half as great a loss in those characteristics.

Table 1

RUN CC-13 (227-71) - OPERATIONAL SUMMARY

Catalyst - Fresh Shell S-317 (HRI 5394)
Coal - Black Thunder Mine (Wyoming)
Thunder Basin Coal Co. (HRI 5828)

CONDITION	1	2	3	4	5
PERIOD (DAYS)	1-5	6-7	8-9	10-11	12-14
<u>NORMAL CONDITIONS</u>					
Unit Pressure, psig	-----		2500	-----	
Coal Feed, Lb/Hr/Ft ³ (Catalyst)	-----		45	-----	
Filtered Liquid Recycle, Lb/Lb Dry Coal	1.2	1.2	1.2	0.05	1.2
Atmospheric Still Reboiler Temp., °F					
Reactor Temperatures, °F					
First Stage					
Second Stage	-----		750	-----	
	-----		825	-----	
CO ₂ Addition, Lb/Lb Dry Coal	0.0	0.1	0.25	0.25	0.6
Light Gas Oil Addition, Lb/Lb Dry Coal	0.0	0.0	0.0	1.1	0.0

Table 2

LIQUEFACTION PERFORMANCE RUN 227-71(CC-13)

Black Thunder Mine Coal - CO₂ Addition and Light Solvent Slurry Oil

Condition	1	2	3	4	5
Period (Day)	5	7	9	11	14
Catalyst Age, Lb Dry Coal/Lb Catalyst (Stage)	143.	201.	259.	318.	401.
Coal Feed Rate, Lb/Hr/Ft ³ Catalyst (Stage)	44.2	44.7	44.9	44.9	43.3
CO ₂ Addition, Lb/lb Dry Coal;	0.0	0.074	0.245	0.255	0.556
Oil Addition (HRI-5663), Lb/Lb Dry Coal	0.0	0.0	0.0	1.10	0.0
Filtered Liquid Recycle, Lb/Lb Dry Coal	1.18	1.20	1.18	0.08	1.04
Temperature, F					
First Stage	752.	750.	752.	752.	751.
Second Stage	829.	827.	828.	828.	829.
Hot Separator	607.	608.	599.	602.	594.
Atmospheric Still	534.	537.	525.	526.	524.
Pressure, psig	2502.	2596.	2595.	2652.	2806.
Net Yields, W% of Dry Coal					
C1-C3	11.49	12.69	12.76	10.96	16.97
C4-390 F	22.27	19.55	21.30	11.69	17.62
390-650 F	25.51	26.40	33.68	22.73	33.94
650-850 F	7.83	7.79	6.36	11.85	7.53
850-975 F	1.16	1.31	1.07	5.66	0.53
975 F+ Liquid	1.29	1.54	1.15	5.89	0.86
Unconverted Coal	8.63	8.26	7.03	5.64	6.53
Ash (SO ₃ -free)	6.50	6.50	6.50	6.50	6.50
Water	21.31	21.65	37.66	37.44	39.32
CO	0.48	1.29	0.97	3.62	7.31
CO ₂	0.72	0.34	-18.34	-13.71	-26.25
NH ₃	1.02	1.01	0.96	0.92	0.95
H ₂ S	0.37	0.32	0.39	0.44	0.44
Total (100 + H ₂ Consumption)	108.59	108.65	111.51	109.62	112.26
PROCESS PERFORMANCE					
W% of MAF Coal					
Coal Conversion	90.8	91.2	92.5	94.0	93.0
975F+ Conversion	89.4	89.5	91.2	87.7	92.1
C4-975 F Distillate Yield	60.7	58.9	66.8	55.5	63.8
Desulfurization	63.5	55.1	67.3	75.7	75.4
Denitrogenation	90.7	88.9	84.9	81.0	84.3

Run70sum.tab

Table 3

ANALYSES OF PRODUCTS - RUN CC-13

CTSL Operations - CO2 and Light Distillate Feed

Day of Operations	5	9	11	14
CO2 Feed, Lbs/Lb Dry Coal	0.00	0.245	0.255	0.556
Light Gas Oil Feed, Lbs/Lb Dry Coal	0.00	0.00	1.18	0.00
Filtered Liq. Recycle, Lbs/Lb Dry Coal	1.18	1.18	0.00	1.04
Hydrogen Contents, W%				
Separator Overhead	12.73	12.50	12.96	12.06
Atmospheric Overhead	12.27	12.12	12.04	11.90
Filtered Liquid				
IBP-650 F	11.31	11.02	11.02	10.90
650-850 F	10.07	9.81	10.13	9.89
850-975 F	8.50	7.98	8.26	7.73
975 F+	6.96	6.38	6.26	5.73
Nitrogen Contents, W%				
Separator Overhead (Antek)	0.04	0.09	0.07	0.16
Atmospheric Overhead (Antek)	0.04	0.15	0.13	0.21
Filtered Liquid				
IBP-650 F	0.08	0.14	0.13	0.15
650-850 F	0.05	0.11	0.28	0.19
850-975 F	0.23	0.34	0.47	0.42
975 F+	0.50	0.62	0.66	0.68
Sulfur Contents, W%				
Separator Overhead	0.00	0.02	0.02	0.03
Atmospheric Overhead	0.01	0.03	0.00	0.00
Filtered Liquid				
IBP-650 F	0.01	0.01	0.03	0.03
650-850 F	0.03	0.02	0.04	0.03
850-975 F	0.02	0.01	0.02	0.04
975 F+	0.03	0.05	0.06	0.04
975 F+				
Cyclohexane Insoluble, W%	18.1	27.5	41.3	35.3
Toluene Insoluble, W%	1.1	1.0	3.1	6.2

Run71elem.tab

Table 4

THF-WASHED PRODUCT SOLIDS ANALYSES

RUN 227-71(CC-13)

Period Number	5	9	11	14	Feed
Catalyst Age, Lbs Coal/Lb Catalyst	143	259	318	402	
Feed CO ₂ /Coal, Lb/Lb	0.0	0.25	0.25	0.56	
SAMPLE ANALYSES					
Ash, W%	(46.75)	(52.37)	(57.91)	(52.82)	(7.64)
Sulfur in Ash, W%	(2.94)	(3.09)	(2.84)	(2.58)	(5.97)
Ash (SO ₃ -Free), W%	43.31	48.32	53.80	49.41	6.50
Elemental Analyses, Ash(SO ₃ -free)-free					
Carbon, W%	73.16	67.89	67.68	68.87	72.74
Hydrogen, W%	3.67	2.90	2.66	2.77	4.39
Sulfur, W%	2.78	3.82	4.11	2.95	2.90
Nitrogen, W%	0.83	0.75	0.61	0.77	0.99
Total	80.44	75.36	75.06	75.36	78.71
Sulfur/Ash(SO ₃ -free)	0.068	0.064	0.053	0.052	0.085
H/C Ratio	0.60	0.51	0.47	0.48	0.72

Run71sol.tab

Table 5

FEED COAL ANALYSES FOR RUN 227-71 (CC-13)
(OTHER BLACK THUNDER ANALYSES SHOWN FOR COMPARISON)

Run 227-71 Feed: Black Thunder Mine (Wyoming) Coal

FEED DESIGNATION, HRI No.	5713	5630	5713	5713	5828
RUN NUMBER	227-70	227-55	227-69	*	227-71
PROXIMATE ANALYSIS, W%					
Moisture	5.23	6.37	6.56	6.38	4.83
Volatile Matter (MAF Basis)		44.2	51.03		
Fixed Carbon (MAF Basis)		55.8	42.35		
ULTIMATE ANALYSIS (W%, Dry Basis)					
Carbon	68.20	67.70	67.55	67.59	68.01
Hydrogen	4.19	4.54	4.23	4.38	4.10
Sulfur	0.54	0.48	0.51	0.50	0.55
Nitrogen	0.87	1.05	0.92	0.95	0.93
Chlorine	--	0.04	--		
Ash	(7.72)	(7.15)	(7.62)	(7.61)	(7.64)
Sulfur in Ash	(5.62)	(6.35)	(4.71)	(5.65)	(5.97)
Ash (SO ₃ -free)	6.73	6.01	6.72	6.54	6.50
Oxygen (By Difference)	19.47	20.18	20.07	20.04	19.91
SULFUR FORMS (W%, Dry Basis)					
Sulfate	0.01	0.04		0.02	0.02
Pyrite	0.07	0.11		0.09	0.07
Organic	0.48	0.36		0.46	0.52
HEATING VALUE, Btu/lb(Dry)		11797			
Btu/Lb MAF		12551			
MINERAL ANALYSIS OF ASH (W%, Ignited)					
Silica, SiO ₂	36.16	34.61			36.42
Alumina, Al ₂ O ₃	17.54	16.98			15.67
Titania, TiO ₂	1.27	1.30			1.22
Ferric Oxide, Fe ₂ O ₃	5.01	6.94			6.64
Lime, CaO	19.69	21.74			19.83
Magnesia, MgO	3.99	4.40			3.98
Potassium Oxide, K ₂ O	0.43	0.35			0.39
Sodium Oxide, NaO	0.39	0.97			0.76
Sulfur Trioxide, SO ₃	12.93	10.74			12.36
Phosphorous Pentoxide, P ₂ O ₅	0.89	1.01			0.77
Strontium Oxide, SrO	0.95	0.29			0.83
Barium Oxide, BaO	0.64	0.37			0.46
Manganese Oxide, Mn ₃ O ₄	0.11	0.00			0.15
Undetermined	0.00	0.30			0.52
MICROAUTOCLAVE EVALUATION**					
Thermal Coal Conversion	80.3	76.6			
Thermal 975 F+ Conversion	45.4	44.3			
Catalytic Coal Conversion	89.8	87.9			84.2
Catalytic 975 F+ Conversion	66.4	72.9			63.9

* Check on coal before Run 227-69

** 1989, & '90 tests - 800 F, 30 minutes, 2000 psig H₂,
 4/1/(1) Solvent/Coal/(Shell S-317 Catalyst)
 Solvent - Wilsonville coal liquefaction distillate product.

Run71coa.tab

Table 6

INSPECTIONS OF LIGHT SOLVENT SLURRYING OIL FOR RUN 227-71(CC-13)

Designation	HRI 5663
Gravity, API	26.0
Distillation, °F	
IBP	148
10 V%	250
20 V%	323
30 V%	390
40 V%	474
50 V%	520
60 V%	543
70 V%	580
80 V%	615
90 V%	660
E.P.	748
Recovery, V%	100
Residue, W%	0.0
W% @ 650°F	79.9
Volume Average B. P.	480
Watson Character. Factor	10.74
Carbon, W%	87.71
Hydrogen, W%	12.09
Sulfur, W%	0.02
Nitrogen, W%	0.16

Table 7

FRESH CATALYST PROPERTIES - RUN 227-71(CC-13)

HRI No.	5394
Designation	Shell S-317
Nominal Size	1/32" Extrudates
Charge to Reactors	
Chemical Analysis (W%, Dry Basis)	
Molybdenum, HRI Analyses	10.76,11.02,11.58,12.26
Vendor Specification	12.0
Nickel, HRI Analyses	2.00,2.00,2.25,2.60
Vendor Specification	2.5
Physical Properties	
Bulk Density, Compacted, Lb/Ft ³	36.7
Particle Density, gm/cc	0.941
Surface Area (Calc.), M ² /gm	267
M ² /cc particle	251
Pore Volume, cc/gm	0.697
cc/cc particle	0.656
Average Crush Strength, Lb/mm	1.94
Pore Size Distribution, CC/GM	
Diameter > 30 [°] A	0.70
Diameter > 100 [°] A	0.40
Diameter > 250 [°] A	0.15
Diameter > 500 [°] A	0.14
Diameter >1500 [°] A	0.11
Diameter >4000 [°] A	0.03
Penetration Test	
Average Penetration, % of Diameter	34.9

Table 8 Recovered Catalysts Analyses - Run 227-71

RECOVERED CATALYSTS ANALYSES - RUN 227-71

STAGE	First	Second
CATALYST AGE, LB COAL/LB	541	537
CATALYST RECOVERY, 20 Mesh V%		
Bulk Density, Gm/cc	0.821	1.118
ANALYSES OF OIL-FREE		
+20 MESH CATALYST, W%		
Carbon	17.60	31.44
Hydrogen	1.12	0.97
H/C Ratio	0.76	0.37
Nitrogen	0.30	0.23
Sulfur	5.43	5.26
Molybdenum	7.52	5.95
Nickel	1.63	1.28
Titanium	0.03	0.02
Iron	0.45	0.10
Calcium	0.59	0.29
Sodium	0.82	0.85
Total Metal Contaminants	1.89	1.24
Loss on Ignition, W%	20.44	40.98
Particle Density, Gm/cc particle*	1.329	1.655
Pore Volume (D>30 A), cc/gm	0.296	0.124
cc/cc particle	0.393	0.205
Surface Area (calc.), M2/gm	141	15
M2/cc particle	187	25
Modal Pore Diameter, Angstrom		
Macro-pores		1930
Mini-pores	61	
ANALYSES OF IGNITED CATALYST		
Particle Density, gm/cc particle*	1.069	1.080
Pore Volume (D>30 A), cc/gm	0.557	0.563
cc/cc particle	0.595	0.608
Surface Area (calc.), M2/gm	204	190
M2/cc particle	218	205
Modal Pore Diameter, Angstrom		
Macro-pores		2190
Mini-pores	91	96
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS		
Weight, Grams	64	92
Molydenum, W%	1.53	3.52
ANALYSIS OF -100 MESH OIL-FREE SOLIDS		
Weight, Grams	53	50
Molydenum, W%	0.31	1.41

* In mercury at 10 psia.

Run71rcvcat.tab

FIGURE 1

COAL CONVERSION - RUN 227-71(CC-13)

CTSL - With CO2 and Light Distillate

FIGURE 2

C4-975 F LIQUID YIELDS — RUN 227-71(CC-13)

CTSL — With CO2 and Light Distillate

FIGURE 3

RESIDUAL OIL YIELD — RUN 227-71(CC-13)

CTSL — With CO2 and Light Distillate

FIGURE 4

RESIDUUM CONCENTRATION IN PRODUCT SLURRY

CTSL - With CO2 and Light Distillate

FIGURE 5

CO₂ OUT VS CO₂ FED

CTSL Run 227-71(CC-13) - Collected Yields

FIGURE 6

NET H₂O FORMATION VS CO₂ FED

CTSL Run 227-71(CC-13) - Collected Yields

FIGURE 7

CO YIELD VS CO₂ FED

CTSL Run 227-71(CC-13) - Collected Yields

FIGURE 8

CH₄ YIELD VS CO₂ FED

CTSL Run 227-71(CC-13) - Collected Yields

FIGURE 9

C2-C4 GAS YIELD VS CO2 FED

CTSL Run 227-71(CC-13) - Collected Yields

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SECTION XI

RUN 227-75 (CC-15) EVALUATION OF A PRE-DISPERSED IRON CATALYST IN TWO-STAGE LIQUEFACTION

SUMMARY

The objective of this run was to evaluate the performance of the dispersed iron-based catalyst in the liquefaction of Black Thunder Mine Coal in a bench-scale continuous flow unit with a thermal-catalytic configuration.

The iron catalyst precursor was impregnated on the coal matrix using an incipient wetness technique developed by Pittsburgh Energy Technology Center (1). Black Thunder Mine coal was impregnated with hydrated iron oxide (FeOOH) at 5000 ppm of iron using this technique and was liquefied in thermal-catalytic mode. The iron catalyst precursor was activated in a pretreating stage (at 527 or 570°F) prior to the thermal stage at 800°F. The catalytic stage was an ebullated bed reactor at 775°F consisting of Shell S-317 NiMo catalyst. The space velocity was 43 lb/hr/ft³ catalyst. The performance of this system was compared with that obtained without the use of any dispersed iron catalyst.

Run CC-15 (227-75) was successfully completed with three conditions with FeOOH impregnated coals and one condition with untreated Black Thunder Mine coals. At relatively low concentration of 0.5 W%, the dispersed iron additive improved distillate yield, coal and 975°F conversion. Compared to the condition with no dispersed catalyst, the coal conversions were 1.9 W% higher, averaging 92.6 W% (maf), and the resid conversions averaged 3.4 W% higher, declining from 89.1 W% (maf) in Period 5 to 85.3 W% in Period 14. Similarly, the C_4 -975°F distillate yield, which decreased from 66.1 W% (maf) to 60.2 W%, was significantly lower in Condition 3, with no dispersed catalyst. The hydrogenation activity of the dispersed iron catalyst was evident in the lower hydrogen contents of both the first and second stage products. Overall performance was similar to that of the two stage CTSL™ process.

However, the impregnation procedure introduced additional nitrogen to the coal matrix and resulted in a higher nitrogen product. The economics of the improved process performance should be evaluated against the costs for impregnating the iron catalyst precursor as well as additional hydrotreating cost.

- (1) Cugini, A.V., et al, DOE/PETC, "A Highly Active Disposable Iron Catalyst for Coal Liquefaction", 201st National ACS Meeting, Atlanta, GA, April 14-19, 1991.

SCOPE OF WORK

In Run 227-75 (CC-15) an iron-based predispersed catalyst was evaluated in a two-stage mode of operation. The first liquefaction stage was a backmixed, thermal reactor (without supported catalysts) and was controlled at 800°F, while the second stage was a catalytic ebullated bed charged with Shell 317 (1/32" extrudate) catalysts. The volume of both stages is identical. Prior to the first liquefaction stage, the pre-dispersed iron catalyst precursor was activated in a pretreater at temperatures ranging from 527°F to 570°F. The supported catalyst in the second stage was sulfided during the start-up period. Also, hydrogen sulfide was injected continuously at 3 W% of feed coal throughout the run.

The run plan for this 14-period (day) with Black Thunder mine coal, shown in *Table 1*, consists of four process conditions. The coal space velocity (43 lb/hr/ft³) catalyst (2nd stage), temperature of the first (800°F) and second stages (775°F) were held constant throughout the entire run. The catalyst pretreatment temperature was 527°F in Condition 1 and was increased to 570°F for the remaining of the run conditions. Except in Condition 3, which used untreated Black Thunder coal, all other conditions employed an iron-treated coal. The iron catalyst precursor (FeOOH) was impregnated on the coal matrix at a loading of 5,600 ppm of iron. The coal preparation was carried out at HRI according to a recipe supplied by the Pittsburgh Energy Technology Center.

PROGRAM RESULTS AND ANALYSES

Run 227-75 (CC-15)

The operating summary, the conversions and product yields obtained from two stage liquefaction of iron-treated and untreated coals are shown in *Tables 2 and 3*. The last day of each condition (Periods 5, 8, 11 and 14) represented the steady state operations for each of the respective operating conditions, namely Conditions 1, 2, 3, and 4.

PROCESS PERFORMANCE

In operations with the iron-impregnated coal as feed, the coal conversion ranged from 92.1 to 93.2 W% (maf basis) as illustrated in *Figure 1*. There was no major difference in coal conversion due to the two activation temperatures (522 and 565°F) tested in Conditions 1 and 2. In Period 9 the coal feed was changed from iron-treated in Condition 2 to untreated coal in Condition 3, resulting in a 2.7 W% decrease, from 92.7 to 90.0 W%, in coal conversion. However, the decrease in coal conversion was fully regained when the feed was switched back to iron treated coal.

In the absence of iron additive the coal conversion was similar to the 90.8 W% obtained in Run 227-71 (CC-13) with the same batch of coal in catalytic/catalytic mode of operation under similar reaction severity (reactor temperatures at 750 and 825°F; space velocity of 45 lb coal/hr/ft³ catalyst). From these results, it seems that coal conversion was not affected by the activity of the supported catalyst but improved in the presence of finely dispersed iron catalyst.

The 975°F* (residuum) conversion and C₄-975°F distillate yields are shown in *Figure 2*.

In Condition 1, with the pretreating temperature at 522°F, the residuum conversion was 89.1 W% and the distillate yield was 66.1 W%, both on a moisture-ash-free basis. When the pretreating temperature was raised to 568°F in Condition 2, both the residuum conversion and distillate yield decreased slightly to 87.7 and 64.1 W% while the gas make was relatively constant at 10.6-10.8 W% (maf coal).

When the feed was changed from iron treated coal to untreated coal (Condition 3), the distillate yield dropped by 7.7 W% as the yields of unconverted coal, residuum and water went up substantially. The gas make was practically at the same level as in Conditions 1 and 2.

In Condition 4, iron-treated coal was reintroduced. Both the residuum conversion and distillate yield recovered significantly, though to levels below those of

Condition 2. The distillate yield increased to 60.2 W% in Condition 4 (from 56.4 W% in Condition 3) but was 3.9 W% (maf coal) lower than in Condition 2. This decreased distillate yield reflects the deactivation of the second stage supported catalyst, which appeared to be deactivating at a steady rate from Conditions 1 and 2 into Condition 4. However, with the limited number of consecutive days using the separate coals, it cannot be determined whether the iron additive had a positive or negative effect on the deactivation rate of the supported catalyst. The above results indicate positive effect of iron catalyst on distillate yield as on well as coal and residuum conversions.

Figures 3 and 4 compare the distillate yield (distribution) and selectivity obtained during the run. In ascending order, the yields were in the order of:

500-650°F > IBP-390° > 390-500° >> 650-850° >> 850-975°

when iron catalyst was added. In the case of untreated coal there was more material in the IBP-390° than the 500-650° cut. The remaining cuts were in the same order as the former case. The thermal/catalytic mode of operation produced mostly light distillate; more than 80 W% of the distillates boiled below 650° F in the first three conditions. Due to the aging of the second stage catalyst, the selectivity of the IBP-650°F cut dropped to 76.8 W% in Condition 4.

Figure 5 shows the hydrodenitrogenation observed during the run. In the presence of iron catalyst (Conditions 1,2, and 4), HDN ranged from 82.6 to 90.0 W% (maf coal) and decreased linearly with the age of the second stage catalyst at an average rate of 0.0289 W% per lb dry coal/lb catalyst. In Condition 3, no iron catalyst, HDN was significantly below (18 W%) the level projected by using the estimated average aging rate. Most likely, the lower HDN was due to the presence of different types of nitrogen compounds in the iron-treated and untreated coals. As discussed in the "coal" section, additional nitrogen compounds were added to the iron-treated coal during the impregnation procedure. It is a strong possibility that these "foreign" nitrogen compounds were loosely bonded to the coal structure, hence could be removed easily. On the other hand, the inherent coal nitrogens are bonded mostly through a ring structure and therefore are much more difficult to be removed.

Overall hydrodesulfurization, HDS, is defined as the quantity of sulfur removed from the feedstock and converted to hydrogen sulfide. Due to reaction of sulfur with calcium and iron present in the ash, as evidenced by the consumption of H₂S and the high concentration of sulfur reported in the solid residuals, results on HDS were not very clear. HDS were in fact negative in Condition 1, 2, and 4, in which iron-impregnated coal was used. Although HDS was positive in Condition 3 (untreated coal as feed), the value was considerably lowered than results from catalytic/catalytic mode of operations.

QUALITIES OF INTERSTAGE AND TWO-STAGE PRODUCTS

The three liquid product streams from the Bench Unit are the Separator Overheads (SOH), the Atmospheric Still Overheads (ASOH), and the Pressure Filter Liquids (PFL). The API gravity, ultimate analysis, initial boiling point, as well as the boiling point distribution of each individual product stream were determined. In addition, the filter liquid was further separated into four boiling point fractions (IBP-650°, 650-850°, 850-975°F and 975°F*) according to the ASTM D1160 distillation procedure. Analyses of SOH, ASOH, PFL, and Pressure Filter Cake are shown in *Tables 4 to 8*.

Four samples were taken from the ebullating line of the first liquefaction stage (thermal reactor). These samples were collected at Periods 6A, 9A, 11C and 14C, just after the completion of each condition. The solid residuals were separated from the liquid portion by pressure filtration. The distribution between PFL and PFC is given in *Table 9*. An analytical scheme similar to that of the two-stage products was used to analyze the solid residual (filter cake) and filter liquid from the first stage samples. Analyses of the pressure filter cake and liquid of each first stage sample are given in *Tables 10 and 11*, respectively.

Analysis of Separator Overheads (SOH)

Inspections of the Separator and Atmospheric Still Overheads are presented in *Tables 4 and 5*, respectively.

The Separator Overheads are light distillates obtained by flashing the second stage products at 555°F under system pressure. The API gravity of these distillates ranged from 37.4 to 39.8°. The majority of the Separator Overheads, more than 95 W% as determined by ASTM D-1160 Distillation procedure, boiled below 650°F. Using the specific gravity (60/60) and the volume averaged boiling point, a Watson characterization factor for each of the Conditions was calculated and reported in *Table 4*. The calculated Watson factors ranged between 11.3 and 11.5. These values were slightly higher than previously obtained values of 10.7-11.1 for Black Thunder Mine coal when processed under either thermal/catalytic or catalytic-catalytic mode of operations. This suggested products from this run were less aromatic.

The sulfur contents were less than 200 ppm. In fact the sulfur content of this stream was below 105 ppm up to Condition 2 (Period 8) and took a step increase to 196 ppm in Condition 3 when untreated coal was used. In spite of switching the feed back to iron treated coal in Condition 4, the sulfur content remained at a high level of 186 ppm.

The nitrogen content of the SOH obtained from Conditions (1, 2 and 4), when iron impregnated coal was used as feed, ranged from 1470 to 2920 ppm and

varied linearly with catalyst age, as shown in *Figure 6*. This increase was equivalent to 5.5 ppm nitrogen per hour over Condition 1 to 4. The corresponding nitrogen content of SOH from the untreated coal (Condition 3) was 30 W% below the projected level for iron-treated coal. This is a direct reflection of the higher level of nitrogen in the iron impregnated coal. The additional nitrogen was due to the inclusion of ammonium nitrate during the impregnation procedure. Similar nitrogen differences were also found in all other product fractions.

Analysis of Atmospheric Still Overheads (ASOH)

ASOH was obtained by fractionating the hot separator bottoms using a continuous pipe still. The vapor outlet temperature of the Continuous Atmospheric Still (CAS) was about 550°F. ASOH had a higher initial boiling but lower end point than SOH. Its initial boiling points ranged from 201-224°F while the final boiling points varied from 554 to 568°F. On average, the volume averaged boiling point of ASOH was 70°F higher than that of SOH. The API gravity of ASOH decreased gradually with on stream time, from 31.6 in Condition 1 to 27.1 toward the end of the run. The estimated Watson characterization factors, averaging about 11.1, were slightly less than those of SOH.

Nitrogen contents were 20 to 80 W% higher in the ASOH than in the SOH. As indicated in *Figure 6*, the impact of catalyst deactivation on nitrogen content in ASOH was not as high as that in the SOH. The average increase was 4.0 ppm nitrogen per hour over the entire run.

Analysis of Pressure Filter Liquids (PFL)

The bottoms from the CAS was filtered using a 12" pressure filter to give a solid-free liquid stream. Most of the PFL was recycled back to the slurry-mix tank as vehicle oils and a small portion of the remaining PFL was also used as a buffer oil for the operation of the ebullating pumps. The quality of the PFL is important in sustaining stable operations of the liquefaction reactors. For this reason substantially more analyses were performed on the PFL stream. The API gravity, boiling point, distribution, ultimate analysis and toluene insolubles of PFL are reported in *Table 6*. In addition, PFL's from Periods 5, 8, 11, and 14 were further fractionated into four different boiling point fractions (IBP-650°, 650-850°, 850-975° and 975°F+ fractions). Ultimate analysis and API gravity of each cut was performed, as shown in *Table 7*.

The API gravity of PFL decreased steadily from 19.4° in Period 2 to 3.8° as the run proceed. The increase in specific gravity was mainly due to the gradual building up of 975°F+ residuum, as illustrated in *Figure 7*. The amount of preasphaltenes in the PFL, as indicated by the level of toluene insoluble materials, remained below 0.25 W% of the PFL until Condition 3 (untreated coal)

when it increased to 1.6 W%. Furthermore, the H/C molar ratio was also decreased with on-stream time from 1.35 in Period 5 to 1.19 in Period 14.

When untreated coal was used, both the CCR content and viscosity of the PFL were substantially higher than in other conditions in which iron impregnated coal was used suggesting the iron additive had an important role in reducing the buildup of asphalthenic compounds.

Analysis of Pressure Filter Cake (PFC)

Since no solid was being recycle to the process, the pressure filter cake was a net product from this mode of operations. The PFC sample from each of the periods was analyzed for ash content, sulfur in ash and quinoline soluble oils. Ultimate analysis and iron content were also determined for selected periods (Period 5, 8, 11, and 14). Results of these analyses are summarized in *Table 8*.

When iron impregnated coal was used (Condition 1, 2, and 4), the sulfur content of PFC was considerably higher than when untreated coal (Condition 3) was involved. The additional sulfur was probably present as iron sulfide. The inclusion of sulfur in PFC may prohibit its utilization as combustion feedstocks.

Analysis of First Stage Samples

Since the first stage sample for Condition 1 (Period 6A) was not representative, the discussions in this section are limited to samples from the other conditions.

The first stage samples contained approximately 10 W% of solid materials (THF insolubles), 23.6-25.8 W% of 975°F⁺ residuum and 63-66 W% of distillable oils, as shown in *Table 9*. Similar to the second stage product, the amount of insoluble organic matter (unconverted coal) was the highest when untreated coal was used (Condition 3).

Detailed analyses of filter cake and liquid from the first stage samples *Tables 10 and 11*, respectively.

The characteristics of the first stage and two-stage products are compared in *Table 12*. The average first stage (thermal stage) coal conversion averaged 90.9 W% of maf coal for Conditions 2 and 4 with iron-treated coal versus only 87.0 W% for the untreated coal. However, the incremental coal conversion in the second stage was higher for the untreated coal, by 1.9 W%, probably due to the availability of more reactive coal species from the lower conversion first stage.

As anticipated, while most of the coal dissolution occurred at the first stage, hydrogenation and heteroatoms removal from the liquid products were achieved at the second catalytic stage. As the reaction proceeded from the first to the second stage, the H/C ratio of the filter liquid became higher, while both the S/C

and N/C ratios decreased. The increase in H/C ratio of the PFL is higher in the presence of the finely dispersed iron catalyst, 6-13 W% in Conditions 2 and 4 versus 1.7 W% in Condition 3 as shown in *Figure 8*. However, the 975°F+ fraction showed the opposite trend, having a higher second stage/first stage increase in H/C ratio in the Condition 3 operations with untreated coal. Although the H/C ratio was significantly higher under catalytic/catalytic mode of operations (Run CC-4, Condition 2), the increase in H/C ratio in the second stage product was minimized. This was due to the considerably higher catalyst age and the reversed temperature configuration in this run.

Similar trends in nitrogen removal were observed between the first and second stage products. The improved nitrogen removal rate between the iron treated and untreated coals was mainly due to the easy removal of "foreign" nitrogen compounds in the iron-treated coal. These "foreign" nitrogen compounds were introduced during the impregnation procedure and were loosely attached to the coal matrix, while the "original" coal nitrogens were usually part of the ring structure.

The H/C, N/C, S/C ratios of the filter solids (THF washed filter cakes) are also compared in *Table 12*. Except the 11C sample (Run CC-15 Condition 3), all PFS samples from the second stage had a lower H/C ratio than the first stage sample, reflecting the further conversion of relatively hydrogen rich materials in coal into liquid products. The relative changes in H/C ratio between the two stages are illustrated in *Figure 9*. The increase in H/C in the second stage product with untreated coal warrants further investigation.

As indicated in *Figure 9*, there was substantial sulfur inclusion in all PFS samples when iron additives, both iron oxide powder and impregnated FeOOH were involved.

COMPARISONS WITH OTHER IRON ADDITIVES

The performance of FeOOH as catalyst precursor from this Run (Condition 4) is compared with results obtained from two previous run conditions that used Black Thunder Mine coal and iron additives. The run conditions are Run CC-4 Condition 2 and Run CC-7, Condition 5. Iron oxide was used in both of these run conditions. The former condition was under catalytic/catalytic mode, while the latter was thermal/catalytic. However, the reaction severity as well as catalyst age of the two run conditions were not identical to that of Run CC-15 Condition 4.

The product yields and performance of these run conditions are given in *Table 13*. The catalyst age of the two earlier runs (CC-4 and CC-7) was almost three times that of Run CC-15 Condition 4. Also, the reaction severity was lowest in Run CC-4 Condition 4, while that of the other conditions were similar. The amount of iron additive was 0.56 W% of coal feed in Run CC-15 and 3.0 W% in the other two runs.

The best performance was achieved under catalytic/catalytic mode of operations with 5.2 W% iron oxide as additive. This condition gave the highest C₄-975-F distillate yield (64.6 W% maf coal), lowest gas make and 975°F+ resid yield.

Both thermal/catalytic conditions resulted in lower distillate yields of about 60 W%. However, the iron oxide conditions generated more C₁-C₃ gases and gave lower 975°F+ Resid yield. This most likely was due to the higher thermal severity at the first liquefaction stage.

DETAILS OF OPERATIONS

Three 2,000 cc reactors were used in this run. The configuration was the same as had been used in Run 227-72 (CC-14) with Illinois No. 6 coal. The first reactor was a pretreater for activating the dispersed catalyst precursor. The second reactor, referred to as the first (liquefaction) stage, did not contain any supported catalyst. The third reactor, referred to as the second (liquefaction) stage, was an ebullated bed reactor holding Shell S-317 catalyst. The contents of the pretreater and first stage were circulated at a high rate to obtain complete back-mixing.

OPERATIONS

The unit start-up commenced on October 16, 1992 on filtered liquids (L-769). Coal was introduced into the unit at 4:00 am on October 21 that marked the start of Period 1. After 14 days of smooth operation, the unit was shut down at 4:00 am on November 4.

The bench unit was initially started using L-769 start-up oil. A high differential pressure was developed across the second catalytic stage when the reactor temperature reached 650°F. The unit was shut down and the catalyst bed was drained. Upon inspection, the bubble cap was plugged with supported catalyst, and some solid containing soft paste was found in various transfer lines. It was determined that the start-up oil contained a small amount of solid. The start-up oil was then filtered for the rest of the run.

The second stage reactor was charged with the same catalyst that has been drained out. The unit was re-started using the filtered start-up oil (L-769). The second stage temperatures were kept at several intermediate temperatures for a certain period of time before coal was cut in to presulfide the supported catalyst with ditertiary nonyl poly sulfide (TNPS) in L-769. A steady stream of H₂S was injected after the coal was cut-in. In Period 1, the H₂S injection rate was determined to be double the desired rate. This higher rate was maintained through Period 2 and 3 and was reduced back to the desired level of 3 W% coal in Period 4.

Four samples were taken from the ebullating line of the first liquefaction stage (second reactor) (Periods 6A, 9A, 11C, and 14C). These samples were representative grab samples of the first stage slurry. No attempt was made to quantify the amount light volatiles that were lost during the depressurization of the sample. Also, during the recovery of the Period 6A sample, it was found that the bottom of the collection cylinder was clogged by materials left behind from previous operations. The sample was recovered by flashing through the top outlet of the cylinder. The collection cylinder was disassembled and cleared before the Period 9A sample was taken.

COAL PREPARATION

Black Thunder mine coal was used as feedstock. *Table 1* shows the analyses of the untreated coal (HRI-5828) and iron-treated (L-780) coal.

The iron additive (nominally 5,000 ppm based on dry coal), hydrated iron oxide (FeOOH), was loaded to the feed coal according to an incipient wetness impregnation and precipitation technique developed by Pittsburgh Energy Technology Center. The PETC procedure called for vigorous mixing of powdered coal with a ferric nitrate solution "...to form a wet paste mixture of incipient wetness". The iron additive was precipitated by ammonium hydroxide. The iron treated coal was then recovered from the solution and vacuum dried at 140°F (60°C) to a desired moisture level in an inert atmosphere.

A total of approximately 1,200 lbs of iron treated coals at 5,000-6,000 ppm Fe were prepared in ten batches. The bulk preparation procedure deviated from the PETC recipe slightly. The amount of water required to bring pulverized coal to an incipient wetness state was first determined in the laboratory. Based on this information, the ferric nitrate to water ratio was adjusted from the PETC procedure to achieve the desired level of iron loading at the incipient wetness state. The ferric nitrate (hydrated salt) to water ratio used in this procedure was 3.61 nitrate to 25 water.

The iron nitrate solution was sprayed uniformly onto the coal using a paint sprayer when the coal was being tumbled in a mortar mixer. After all the solution was sprayed onto the coal, the wetted coal was allowed to mix for another five minutes. Excessive mixing was avoided to prevent the formation of large, hard agglomerates which would be difficult to re-slurry during the precipitation stage. This problem was experienced during the initial two batches.

The precipitation step was carried out in the PDU 260 slurry mix tank. A predetermined amount of nitrate treated, wet coal was transferred into the slurry mix tank containing the ammonium hydroxide solution (22.6 lbs of 29% ammonium hydroxide in 565 lbs of water per 100 lb untreated coal). The coal and ammonium hydroxide were allowed to mix for at least 30 minutes. The coal and ammonium hydroxide mixture was then discharged from the slurry mix tank and stored in open top drums. Coal was recovered by decanting as much of the water as possible from the drums after at least 36 to 48 hours of settling time. The wet solids were then dried in a nitrogen atmosphere at 212°F overnight. The dried, iron treated coals were then stored in nitrogen-purged, sealed plaster drums.

The analyses of two preliminary batches of iron treated coal are given in the table below:

Coal	PETC	Treated	Treated	Treated
HRI Samples #	6050	L-780A	L-780B	L-780A (Washed)
Proximate Analysis (by TGA Method)				
Moisture, W%	2.62	7.18	7.12	
Ash, mf W%	8.55	5.75	5.68	
Volatile Matter, mf W%	45.21	44.60	44.71	
Fixed Carbon, mf W%	46.23	49.64	49.60	
ASTM Ash, mf W%	6.38	6.07	6.24	6.06
Fe in Ash, W% Ash	7.95	10.68	9.15	9.35
Fe in Ash, W% mf Coal	0.507	0.648	0.571	0.567
Elemental Analysis, W% mf Coal				
Carbon		66.90	66.89	67.35
Hydrogen		4.53	4.43	4.43
Nitrogen		2.42	2.35	2.40
Sulfur		0.31	0.35	0.36

The total iron loadings of batches L-780A and L-780B were 6,480 and 5,710 ppm of dry coal. A small sample from L-780A was rewashed in the laboratory in an attempt to reduce its nitrogen content. The iron loading on the washed L-780A sample was slightly lower than the unwashed sample. However, there was not much difference in the nitrogen contents of the washed and unwashed coals.

Fourteen days of smooth operation were completed on November 4, 1992. After the shutdown the unit was generally clean and the catalyst was free-flowing.

The analysis shown in *Table 1* corresponds to an iron loading of 2000 ppm for the untreated coal, while that of the impregnated coal feed varied between 5700 to 6500 ppm. Also, the iron treated coal contained 2.8 times more nitrogen than that of the untreated coal. Although not confirmed by direct determination, the additional nitrogen probably occurred in the form of ammonium nitrate.

START-UP/MAKE-UP OIL

The bench unit was started-up using a filtered vacuum gas oil designated (L-769). This oil, generated from Black Thunder mine coal, was a mixture of oil from Wilsonville operations and HRI PDU operations completed in July, 1992. The analyses of this oil is shown in *Table 2*. This oil was also used as make-up

oil during the run to supplement process derived, pressure filter liquid to slurry feed coal. The amount of makeup oil added during each period usually constituted a small fraction (less than 3 W%) of the slurrying oils, in which PFL was the major component. However, due to operating problems, larger amounts were added during Periods 3, 7, and 9. The makeup oil in Periods 3, 7, and 9 corresponded to 13.7, 7.0 and 20.8 W% of the total slurrying oil, respectively. These infusions affected the reactor compositions somewhat but should have had only a minor effect on the yield structure of Periods 5, 8, 11, and 14 of which the process performance of Conditions 1, 2, 3 and 4 were based. There was no make-up oil added in Periods 5 and 14. Periods 8 and 11 had a small amount of make-up oil addition (2.7 and 2.2 W% total slurrying oil), which was subtracted from the appropriate product distillate fractions in the yields normalization.

FRESH CATALYST

The second stage of the liquefaction unit contained fresh Shell 317 NiMo catalyst. The same catalyst had been used in most of the bench runs in this program and its analyses are shown in *Table 11* in the section on Run 227-75 (CC-1). The catalyst was presulfided in-situ in a stream of dimeric disulfide (3.5 W%) in start-up oil (L-769) prior to coal feed. A stream of liquid hydrogen sulfide was fed to the unit during the entire course of the run to maintain the catalyst in the sulfided state.

RECOVERED CATALYST

The analyses of the catalyst recovered from the second stage at the conclusion of Run 227-75, thermal-catalytic mode of operations, are summarized in *Table 16*.

The volume of the +20 mesh recovered catalyst corresponded to 71% of the volume of fresh catalyst charged. The molybdenum content of the +20 mesh and 20-100 mesh recovered catalyst was 7.82 and 6.96 W%, respectively, which corresponded to 69 and 61 W% of that of the fresh catalyst (11.4 W%).

The carbon content of the recovered catalyst was considered high as compared to recovered first stage catalysts from other catalytic-catalytic mode of operations employing a low/high temperature sequence. The carbon content of the recovered catalyst was 17.5 W% (+20 mesh fraction). In spite of similar reactor temperature (775°F) and coal exposure (543 lb dry coal per lb of catalyst), the first stage catalysts from Run 227-69 contained only 10.0 W% of carbon. The difference in carbon accumulation between these two runs was mostly due to the relatively high reaction temperature (800°F) and the absence of supported catalysts to stabilize the thermal product generated from the first stage in Run 227-75. It is likely that these unstable first stage products had a higher rate of carbon deposition than the more hydrogenated product from a catalytic first stage

operation. A similar trend was observed from in Run 227-72 when Illinois No. 6 was liquefied under similar conditions.

There were significantly high losses in pore volume and surface associated with the very high carbon accumulation on the recovered second stage catalyst, with pore volume about 50%, and surface area 66% of that of fresh catalyst. However, most (more than 97%) of these losses were recovered after regeneration under an atmosphere containing 2% oxygen at 850°F. These high recoveries implied low metals contaminations on the recovered catalysts. Apparently, the dispersed catalysts acted as effective scavengers of the contaminant metals, as discussed in Run 227-72.

TABLE 1**Run Plan for 227-75 (CC-15)**

Condition Period* (day)	<u>1</u> 1-5	<u>2</u> 6-8	<u>3</u> 9-11	<u>4</u> 12-14
Coal ID	L780	L780	5828	L780
Additive	Fe	Fe	None	Fe
Nominal Conditions				
Space Velocity (lb coal/ft ³ Cat.)	42	42	42	42
No. of Reactors *	3	3	3	3
Temperature (°F)				
Pretreater	522	565	565	565
First Stage	800	800	800	800
Second Stage	775	775	775	775
Constant Parameters:				
Pressure:	2500 psig			
PFL/Coal Ratio:	1.6			
H ₂ S rate:	3.0 W% dry coal			

- * All three reactors were operated in a fully backmixed mode by recycling of reactor fluid at a rate much higher than the coal/PFL feed rate. In addition, the first reactor (Pretreater) and second reactor (1st stage) were operated as thermal reactor without any supported catalyst. The third reactor, the second stage, was loaded with Shell S-317 Ni/Mo catalyst and was operated as an ebullated bed reactor.

TABLE 2
Evaluation of FeOOH Impregnated Coal (CC-15)

Catalyst: Shell 317 Ni/Mo
Coal: Black Thunder Mine Coal

Condition	1	2	3	4
Mode				
First Stage	Therm.	Therm.	Therm.	Therm.
Second Stage	Cat.	Cat.	Cat.	Cat.
Temperature, °F				
Pretreating	522	568	566	566
First Stage	799	801	801	800
Second Stage	775	774	775	773
Catalyst Age, lb coal/lb cat.				
Second Stage	147	228	316	403
Space Velocity				
lb coal/h/ft ³ cat.	42.3	41.7	43.7	42.7
Additive Rate, W% mf Coal	0.56	0.56	None	0.56
H ₂ S Rate, W% mf Coal	3.5	3.6	3.2	3.0
Performance, W% mf Coal				
C ₁ -C ₃	10.55	10.78	10.35	10.49
H ₂ Used	9.26	9.0	8.14	8.34
C ₄ -975°F	66.1	64.1	56.4	60.2
Coal Conversion				
First Stage	91.1	91.1	87.0	90.7
Second Stage	93.1	92.7	90.0	92.7
975°F+ Conv.	89.1	87.7	84.0	85.3
H ₂ N	90.0	87.1	66.6	82.6
H ₂ S	-3.1	-15.2	48.8	-19.8
Normalized Yields, W% Dry Fresh Feed				
C ₁ -C ₃ in Gas	9.94	10.13	9.94	9.86
C ₄ -C ₇ in Gas	2.80	2.91	3.00	2.57
IBP-390°F	16.26	16.36	15.61	14.69
390-500°F	13.67	13.30	12.22	11.12
500-650°F	14.55	17.59	14.98	15.70
650-850°F	10.04	7.99	6.66	10.08
850-975°F	1.81	2.07	1.66	2.43
975°F+ Resid	3.79	4.67	5.66	6.98
Unconverted Coal	6.50	6.87	9.40	6.85
Ash	6.03	6.03	5.71	6.03
Water	15.52	16.41	19.33	17.43
CO _x	2.11	1.88	2.68	1.71
NH ₃	2.71	2.62	0.73	2.49
H ₂ S	-0.02	-0.07	0.25	-0.10
Total	108.72	108.46	107.82	107.84

TABLE 3
Run 227-75 (CC-15) Operating Summary
Dispersed Iron-Based Catalyst Run
Coal: Black Thunder - L-780 (Fe Treated) Periods 1-8, 12-14)
HRI-5828 (Untreated) Periods 9-11
Catalyst: Second Stage - Shell S-317 NiMo Catalyst (HRI-5394)

PERIOD NUMBER	1	2	3	4	5	6	7	8
Date (Start of Period)	10/21/92	10/22/92	10/23/92	10/24/92	10/25/92	10/26/92	10/27/92	10/28/92
Hours of Run (End of Period)	24.	48.	72.	97.	121.	145.	169.	193.
Stage 2, Cat. Age. Lb Dry Coal/Lb Cat.	26.	57.	85.	115.	144.	172.	200.	228.
TEMPERATURES, °F								
Pretreater Stage Reaction	523.	520.	523.	523.	522.	558.	567.	568.
First Stage	788.	800.	799.	799.	799.	801.	801.	801.
Second Stage	767.	774.	775.	775.	775.	776.	784.	774.
PRESSURES, PSIG								
Unit Back Pressure	2491.	2503.	2506.	2505.	2505.	2501.	2494.	2502.
SPACE VELOCITIES								
Lb Coal/Hr/Ft ³ (cat.)	38.0	45.4	41.7	42.5	42.3	42.0	39.9	41.7
RECYCLES, W% OF DRY COAL								
Pressure Filter Liquid	142.2	164.0	144.1	162.4	167.0	167.0	155.4	162.6
PFL to Buffer - Pretreater	3.3	3.7	4.0	4.0	4.3	4.0	4.4	4.1
PFL to Buffer - Stage 1 & 2	9.9	9.3	12.2	9.9	9.5	9.7	9.3	8.5
Make-Up Oil	39.3	3.1	22.9	4.6	0.0	3.9	11.6	4.5
H ₂ S	6.5	6.5	6.2	2.9	3.5	2.9	3.3	3.6
Total Material Recovery (Gross)	85.81	95.23	97.08	99.30	97.36	98.53	99.42	97.25
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED								
C ₁ -C ₃ in Gases					9.94			10.13
C ₄ -C ₇ in Gases					2.80			2.91
IBP-390°F in Liquids					16.26			16.36
390-500°F in Liquids					13.67			13.30
500-650°F in Liquids					17.55			17.59
650-850°F in Liquids					10.04			7.99
850-975°F in Liquids					1.81			2.07
Toluene Soluble 975°F Oil					3.75			4.61
Toluene Insoluble 975°F Oil					0.04			0.06
Unconverted Coal					6.50			6.87
Ash (SO ₃ -free)					6.03			6.03
Water					15.52			16.41
CO					0.74			0.67
CO ₂					1.37			0.91
NH ₃					2.71			2.62
H ₂ S					-0.02			-0.07
Total (100 + H₂ Reacted)					108.72			108.46
PROCESS PERFORMANCE								
C ₄ -975°F Distillates, W% of MAF					66.1			64.1
Coal					89.1			87.7
975°F Conversion, W% MAF		91.6	92.2	92.1	93.1		93.2	92.7
Coal Conversion, W% MAF					-3.1			-15.2
HDS, W%					90.0			87.1
HDN, W%								

TABLE 3
Run 227-75 (CC-15) Operating Summary
Dispersed Iron-Based Catalyst Run
Coal: Black Thunder - L-780 (Fe Treated) Periods 1-8, 12-14)
HRI-5828 (Untreated) Periods 9-11
Catalyst: Second Stage - Shell S-317 NiMo Catalyst (HRI-5394)

PERIOD NUMBER	9	10	11	12	13	14
Date (Start of Period)	10/29/92	10/30/92	10/31/92	11/01/92	11/02/92	11/03/92
Hours of Run (End of Period)	217.	241.	265.	289.	313.	337.
Stage 2, Cat. Age. Lb Dry Coal/Lb Cat.	257.	286.	316.	345.	374.	403.
TEMPERATURES, °F						
Preheater Stage Reaction	567.	567.	566.	566.	566.	566.
First Stage	801.	800.	801.	801.	801.	800.
Second Stage	773.	774.	775.	775.	773.	773.
PRESSURES, PSIG						
Unit Back Pressure	2499.	2497.	2499.	2496.	2495.	2492.
SPACE VELOCITIES						
Lb Coal/Hr/Ft ³ (cat.)	42.6	43.2	43.7	42.8	42.8	42.7
RECYCLES, W% OF DRY COAL						
Pressure Filter Liquid	143.8	162.1	162.8	165.4	167.0	167.0
PFL to Buffer - Pretreater	4.4	4.3	4.7	4.5	4.4	4.3
PFL to Buffer - Stage 1 & 2	7.7	9.1	10.7	10.1	9.7	10.1
Make-Up Oil	37.7	4.2	3.5	5.5	0.0	0.0
H ₂ S	3.1	3.1	3.2	3.1	3.1	3.0
Total Material Recovery (Gross)	93.31	100.41	98.98	101.26	99.97	100.08
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED						
C ₁ -C ₃ in Gases			9.94		9.68	9.86
C ₄ -C ₇ in Gases			3.00		3.00	2.57
IBP-390°F in Liquids			15.61		14.98	14.69
390-500°F in Liquids			12.22		11.58	11.12
500-650°F in Liquids			14.98		16.25	15.70
650-850°F in Liquids			6.66		9.20	10.08
850-975°F in Liquids			1.66		2.25	2.43
Toluene Soluble 975°F Oil			5.33		6.13	6.81
Toluene Insoluble 975°F Oil			0.33		0.14	0.17
Unconverted Coal			9.40		17.46	6.85
Ash (SO ₃ -free)			5.71		6.03	6.03
Water			19.33		17.08	17.43
CO			0.80		0.75	0.74
CO ₂			1.88		0.95	0.97
NH ₃			0.73		2.49	2.49
H ₂ S			0.25		-0.09	-0.10
Total (100 + H₂ Reacted)			107.82		107.88	107.84
PROCESS PERFORMANCE						
C ₄ -975°F Distillates, W% of MAF Coal			57.4		60.9	60.2
975°F Conversion, W% MAF			84.0		85.4	85.3
Coal Conversion, W% MAF		91.3	90.0		92.1	92.7
HDS, W%			48.8		-19.3	-19.8
HDN, W%			66.6		82.7	82.6

TABLE 4

**Separator Overhead
Run 227-75 (CC-15)**

Condition Period	1 5	2 8	3 11	4 14
API Gravity	39.8	38.8	38.3	37.4
Watson	11.5	11.4	11.4	11.3
Characterization Factor				
Distribution, W%				
IBP-390°F	45	45.5	45.6	46.7
390-500°F	20.2	20.5	20.6	19.8
500-650°F ⁺	30.3	29.2	28.9	28.4
650°F ⁺	3.8	4.1	4	4.4
Loss	0.7	0.7	0.9	0.7
Elemental, W%				
Carbon	86.47	86.33	86.7	86.66
Hydrogen	13.05	12.79	12.73	12.63
Sulfur, ppm	102	103	196	186
Nitrogen, ppm	470	2,100	1,860	2,920
Boiling Point	138	122	124	116
Distribution, °F				
5 V%	187	177	176	176
10 V%	210	201	200	198
20 V%	246	238	238	234
30 V%	286	276	278	271
40 V%	339	330	334	322
50 V%	390	390	390	383
60 V%	446	447	446	431
70 V%	500	500	500	494
80 V%	552	550	548	545
90 V%	596	600	596	596
95 V%	628	628	632	632
FBP	654	654	654	660

TABLE 5**ASOH Inspections
Run 227-75 (CC-15)**

Condition Period	1 5	2 8	3 11	4 14
API Gravity	31.6	29.3	29	27.1
Watson Characterization Factor	11.2	11.2	11.1	10.9
Distribution, W%				
IBP-390°F	22.1	19	20.7	17.4
390-500°F	47.8	51.5	53.5	49.9
500-650°F*	27.1	26.8	23.2	29.9
650°F*	2.3	2.3	2.2	2.4
Loss	0.7	0.4	0.4	0.4
Elemental, W%				
Carbon	86.86	87.07	87.01	87.15
Hydrogen	12.41	12.11	11.89	11.8
Sulfur, ppm	221	181	200	233
Nitrogen, ppm	2,670	3,170	2,800	3,690
Boiling Point	201	222	222	224
Distribution, °F				
5 V%	282	308	305	314
10 V%	315	344	340	350
20 V%	369	386	380	395
30 V%	406	424	412	424
40 V%	436	445	438	446
50 V%	457	463	457	467
60 V%	478	480	474	485
70 V%	495	496	490	500
80 V%	512	512	506	516
90 V%	532	529	524	533
95 V%	544	542	537	544
FBP	568	562	554	562

TABLE 6

**Pressure Filter Liquid
Run 227-75 CC-15**

Condition Period	1	1	1	1	2	2	3	3	4	4
	2	3	4	5	7	8	10	11	13	14
API Gravity	19.4	15.0	12.8	11.1	9.2	8.4	6.5	5.6	4.2	3.8
IBP, °F	462	510	469	442	491	447	447	482	486	503
ASTM Distillation, W%										
IBP-650°F	44.14	32.61	29.66	25.29	31.11	24.67	24.29	21.41	22.63	18.74
650-850°F	39.55	45.55	46.69	45.74	39.17	42.41	41.76	39.49	37.20	39.29
850-975°F	7.14	7.56	7.44	9.22	11.53	11.32	10.54	10.42	10.45	10.71
975°F+	8.32	13.25	15.49	19.20	17.30	20.66	22.93	28.54	29.15	30.78
Loss	0.85	1.03	0.82	0.46	0.89	0.94	0.48	0.14	0.57	0.48
Elemental Analysis, W%										
Carbon				88.95		89.22		89.94		89.55
Hydrogen				10.02		9.76		8.83		8.86
Sulfur				0.029		0.038		0.019		0.031
Nitrogen				0.31		0.57		0.57		0.89
H/C				1.35		1.31		1.18		1.19
Iron Content, ppm				9.10		11.60		1.20		1.19
975°F+ Fraction										
Toluene Insoluble, W%	1.68	0.40	0.56	1.08	0.77	1.15	1.83	5.66	2.23	2.37
W% PFL	0.14	0.05	0.09	0.21	0.13	0.24	0.42	1.62	0.65	0.73
Ash in TI, W%	0.35	0.00	0.00	0.07	0.00	0.01	0.00	0.01	0.00	0.00

TABLE 7**Pressure Filter Liquid Inspection**

Condition Period	1 5	2 8	3 11	4 14
IBP-650°F				
°API Gravity	21.3	19.5	19.1	17.5
Carbon	88.41	88.03	88.9	88.48
Hydrogen	11.63	11.32	11.15	10.99
Sulfur, ppm	29	69	73	79
Nitrogen, ppm	2,300	3,000	2,500	54,000
650-850°F				
°API Gravity	14.7	13.3	11.9	11
Carbon	89.26	88.01	89.03	89.11
Hydrogen	10.75	10.39	9.97	9.92
Sulfur, ppm	46	120	980	940
Nitrogen, ppm	4,000	3,600	3,800	7,400
850-975°F				
API Gravity	1.5	0.5	-1.2	-0.7
Carbon	89.99	89.08	90.44	89.52
Hydrogen	8.83	8.73	8.15	8.28
Sulfur, ppm	180	430	220	220
Nitrogen, ppm	7,100	7,400	6,800	8,800
975°F+				
°API Gravity	-8.8	-10.6	-11	-11.5
Carbon	91.41	89.62	91.1	87.77
Hydrogen	7.17	6.79	6.21	6.35
Sulfur, ppm	500	480	480	400
Nitrogen, ppm	11,100	10,800	9,900	13,500
CCR, W%	41.84	46.82	54.85	48.59
Viscosity, cp	0.7	0.7	0.9	0.7
400°F	78.3	133.6	461.3	170
450°F	28.2	40.2	98.1	45.4
Cyc. Insol, W%	13.98	21.09	32.8	27.77
Tol. Insol, W%	1.08	1.15	5.66	2.37

TABLE 8

Pressure Filter Cake- Run CC-15

Condition Period	1	1	1	2	2	3	3	4	4
	2	3	4	5	7	8	10	11	13
Elemental Analysis, W% PFC									
Carbon				59.43		60.21		68.52	61.34
Hydrogen				5.07		4.91		5.20	4.68
Sulfur				2.47		2.49		0.80	2.34
Nitrogen				0.67		0.70		0.66	0.88
ASTM Ash, W% PFC									
S in Ash, W% Ash	34.05	33.37	31.61	31.91	31.43	29.44	21.45	20.63	28.85
Fe in Ash, W% Ash	5.72	6.29	6.25	5.74	5.53	4.24	3.79	2.42	4.82
SO ₃ -Free Ash, W% PFC	29.18	28.12	26.67	10.21	27.08	5.14	19.42	1.07	25.37
				27.33		26.32		19.38	
Quinoline Filtration									
Insolubles, W% PFC	68.71	62.37	60.55	58.75	55.55	56.67	49.08	51.27	55.01
Ash in QI, W% PFC	35.42	32.96	31.64	32.65	32.04	30.22	22.58	21.88	30.23
S in QI Ash, W% Ash	6.31	5.79	5.61	5.34	6.24	4.91	4.42	4.59	5.90
IOM, W% PFC	39.53	34.25	33.88	31.42	28.47	30.35	29.66	31.89	29.64
THF Washed Sample									
THF Insolubles, W% PFC				57.77		57.15		52.11	55.43
ASTM Ash, W% THFI				57.31		55.46		39.95	53.88
S in THFI Ash, W%				7.14		6.91		4.00	6.57
Elemental Analysis, W%									
Carbon				34.85		36.74		48.64	38.04
Hydrogen				1.54		1.67		2.51	1.77
Sulfur				4.32		4.37		1.64	4.24
Nitrogen				0.69		0.64		0.62	0.81

TABLE 9
INSPECTION OF FIRST STAGE SAMPLES
WHOLE SAMPLE
Run 227-75

Condition Period	1 6A*	2 9A	3 11C	4 14C
Sample Weight, gm	299.1	381.1	403.5	401.9
Pressure Filtration				
Filter Liquid, W%	96.1	85.5	81.9	83.2
Filter Cake, W%	3.9	14.5	18.1	16.8
Distribution, W%				
Distillate	85.6	66.3	64.7	63.4
975°F*	13.2	24.6	25.0	25.8
IOM**	0.6	4.5	6.6	5.6
Ash	0.6	4.6	3.6	5.2
Coal Conversion, W% maf coal				
1st stage	91.1	91.1	87.0	90.7

* Sample receiver was plugged by solid from previous letdown. The interstage was recovered by flashing through the top of the receiver resulting in a partial recovery of the sample.

** THF Insoluble organic matter.

TABLE 10
INSPECTION OF FIRST STAGE SAMPLES
PRESSURE FILTER CAKE
Run 227-75 (CC-15)

Condition Period	1 6A	2 9A	3 11C	4 14C
W% Whole Sample	3.9	14.5	18.1	16.8
TGA Analysis, W% PFC				
-975°F	24.6	26.9	28.4	26.9
975°F*(1)	60.2	41.9	51.2	63.4
Ash	15.2	31.2	20.4	28.1
THF Insolubles, W% PFC	30.7	62.7	56.5	64.6
Elemental Analysis, W%				
Carbon	39.71	41.01	52.25	43.38
Hydrogen	1.90	1.97	2.55	2.35
Sulfur	4.22	3.68	1.64	4.24
Nitrogen	0.92	0.95	0.83	1.06
ASTM Ash, W%	51.5	50.3	35.6	48.0
S in Ash, W%	7.47	6.68	4.28	5.92
Fe in Ash, W%	6.56	8.22	3.71	6.39
Quinoline Extraction				
QI, W% THFI	100	100	95.7	97.3
Ash in QI, W% THFI	53.1	49.8	36.5	48.0
S in QI Ash, W%	7.4	6.1	4.6	5.9

TABLE 11

**INSPECTION OF FIRST STAGE SAMPLES
PRESSURE FILTER LIQUID
Run 227-75 (CC-15)**

Condition Period	1 6A	2 9A	3 11C	4 14C
Whole Sample, W%	96.1	85.5	81.9	83.2
IBP, °F	352	435	420	426
Distribution, W% PFL				
IBP-650°F	47.6	19.2	20.2	16.4
650-850°F	33.8	36.4	37.3	34.1
850-975°F	6.65	11.6	9.9	13.4
975°F+	10.6	31.6	31.9	35.2
Ultimate Analysis, W%				
Carbon	87.75	83.74	89.37	88.69
Hydrogen	11.03	8.09	8.61	8.23
Sulfur	0.149	0.08	0.11	0.079
Nitrogen	0.43	1.09	0.61	1.15
IBP-650°F Fraction				
API Gravity	27.5	20.6	19.7	16.9
Carbon	87.42	87.54	87.46	87.08
Hydrogen	12.40	10.92	11.02	10.54
Sulfur	0.097	0.074	0.104	0.051
Nitrogen	0.18	0.52	0.25	0.051
650-850°F Fraction				
API Gravity	16.6	9.9	10.4	8.6
Carbon	88.15	89.36	89.20	88.30
Hydrogen	11.14	9.78	9.77	9.38
Sulfur	0.113	0.109	0.117	0.101
Nitrogen	0.32	0.63	0.32	0.71
850-975°F Fraction				
API Gravity	1.6	-4.6	-4.5	-4.7
Carbon	89.41	88.45	89.09	89.21
Hydrogen	9.02	7.85	7.59	7.74
Sulfur	0.128	0.112	0.156	0.104
Nitrogen	0.77	1.16	0.71	1.28
975°F+ Fraction				
API Gravity	-9.0	-11.8	-14.3	-13.2
Carbon	88.89	88.20	89.54	88.68
Hydrogen	6.79	6.09	5.52	6.09
Sulfur	0.21	0.185	0.197	0.132
Nitrogen	1.34	1.84	1.16	1.76

TABLE 12
COMPARISON OF FIRST STAGE AND TWO-STAGE PRODUCTS

Run No. Condition	CC-4 2	CC-7 5	CC-15 2	CC-15 3	CC-15 4
Configuration	Cat./Cat	Therm./Cat.	Therm./Cat.	Therm/Cat.	Therm./Cat.
Additive Type	Iron Oxide	Iron Oxide	FeOOH	None	FeOOH
Reactor Temperature, °F 1st/2nd Stage	751/825	825/750	801/774	801/775	800/773
Space Velocity, lb/h/ft ³ Cat.	68.9	43.8	41.7	43.7	42.7
Catalyst Age lb mf coal/lb Cat.	736/1109	1170	228	316	403
Coal Conversion, W% maf coal					
1st Stage	N/A	88.6	91.1	87.0	90.7
2nd Stage	88.1	90.8	92.9	90.6	92.4
1st/2nd Ratio	N/A	0.98	0.98	0.96	0.98
975°F* in PFL					
1st Stage	25.2	38.2	31.6	31.9	35.2
2nd Stage	16.8	28.0	20.7	28.5	30.8
1st/2nd Ratio	1.50	1.36	1.53	1.12	1.14
H/C Ratio					
1st Stage PFL	1.36	0.95	1.16	1.16	1.11
2nd Stage PFL	1.37	1.10	1.31	1.18	1.19
1st Stage PFS*	0.74	0.64	0.58	0.59	0.65
2nd Stage PFS*	0.69	0.55	0.54	0.62	0.56
N/C Ratio					
1st Stage PFL	3.26	8.60	6.24	5.85	11.1
2nd Stage PFL	3.04	8.30	5.48	5.44	8.52
1st Stage PFS*	16.3	13.0	19.9	13.6	20.9
2nd Stage PFS*	14.5	12.8	14.9	10.9	18.3
S/C Ratio					
1st Stage PFL	0.04	0.17	0.49	0.46	0.33
2nd Stage PFL	0.04	0.02	0.09	0.09	0.08
1st Stage PFS*	25.8	89.4	33.6	11.8	36.6
2nd Stage PFS*	90.1	115.0	44.6	12.6	41.8

* THF Washed pressure filter solids.

TABLE 13

Comparison Between Additive Type and Reactor Configuration

Configuration Additive Type	Catalytic/Catalytic Iron Oxide Powder	Thermal/Catalytic Iron Oxide Powder	Thermal/Catalytic FeOOH (Impregnated)
Run	CC-4	CC-7	CC-15
Condition	2	5	4
Catalyst Age (lb coal/lb cat.)			
1st Stage	717	--	--
2nd Stage	1,088	1,170	403
Reactor Temperature			
1st Stage	751	825	801
2nd Stage	825	750	775
Space Velocity (lb coal/hr/ft ³ cat)	68.9	43.8	42.7
Additive Rate (W% mf Coal)	5.2 (3.2 Fe)	5.7 (3.6 Fe)	0.56 Fe
H ₂ S Rate (W% Coal)	1.8	5.4	3.0
Yields Distribution (W% maf coal)			
C ₁ -C ₃	8.75	14.24	10.49
C ₄ -390°F	20.58	23.70	18.37
390-500°F	11.71	12.66	11.83
500-650°F	21.54	16.93	16.71
650-850°F	10.02	7.29	10.73
850-975°F	0.71	-0.92	2.59
975°F+ Resid	0.62	3.52	7.43
Unconverted Resid	11.9	9.25	7.29
Water	20.68	18.74	18.55
CO + CO ₂	2.15	3.70	1.82
NH ₂	0.90	0.65	2.65
H ₂ S	-1.93	-1.35	-0.10
Performance (W% maf coal)			
Hydrogen Consumption	8.60	8.36	8.34
Coal Conversion	88.1	90.8	92.7
975°F+ Conversion	87.5	87.4	85.3
HDN	76.9	53.9	82.6
C ₄ -975°F Liquid	64.6	59.7	60.23

TABLE 14**Feed Coal Analysis
Run 227-75 (CC-15)**

HRI No.	5828	L-780
Moisture Content, W%	8.41	8.81
Ash Content, W% (mf)	6.95	7.15
SO ₃ -free, W% (mf)	5.71	6.03
Ultimate Analysis, W% (maf)		
Carbon	72.51	72.38
Hydrogen	4.08	4.31
Sulfur	0.51	0.49
Nitrogen	0.95	2.64
Oxygen (by diff.)	21.95	20.18
H/C	0.68	0.71
Iron Content, W% mf Coal	0.20	0.56

TABLE 15**Analyses of Start-Up Solvent
Run 227-75 (CC-15)**

HRI No.	L-769
API Gravity	10.1
Elemental Analysis, W%	
Carbon	88.95
Hydrogen	10.08
Sulfur	0.06
Nitrogen	0.34
ASTM D-1160 Distillation, °F	
IBP	605
5 V%	642
10 V%	653
20 V%	676
30 V%	691
40 V%	709
50 V%	725
60 V%	748
70 V%	781
80 V%	840
90 V%	895
95 V%	962
FBP	975*

* Boiling point at 96 V%

TABLE 16

Recovered Catalyst Analyses - Run 227-75
Shell 317 1/32" Extrudate

Stage: Second
 Catalyst Age, lb coal/lb fresh cat. 403

On Oil-Free Catalyst

	<u>+20</u>	<u>20-100</u>	<u>-100 Mesh</u>	<u>Fresh Catalyst</u>
Screen Analysis, W%	72.6	10.2	17.2	
Bulk Density, g/cc	0.921	0.860	0.650	
Elemental, W%				
Carbon	17.51			
Hydrogen	1.01			
Nitrogen	0.25			
Sulfur	-			
Metal, W%				
Molybdenum	7.82	6.96	1.91	11.4
Nickel	1.70	N/A	N/A	2.2
Iron	0.105	0.716	3.51	
Calcium	0.034	N/A	N/A	
Ignition loss, W%	25.7	31.7	23.62	

Physical Properties of +20 Mesh Catalyst

	<u>Oil-Free</u>	<u>Oil-Free Regenerated**</u>	<u>Fresh Catalyst</u>
Apparent Density, g/cc	2.341	3.223	N/A
Surface Area (calc.) m ² /g	134.8	218.1	204
BET Surface, m ² /g	109.7	173.0	N/A
Pore Volume*, cc/g	0.325	0.636	0.652
Modal Diameter, Micropore Å	76	86	95
Macropore Å	2,700	2,700	2,800

- * By Hg intrusion at 60,000 psig; volume with pore diameter >30Å
 ** Regenerated with 2% O₂ @ 850°F.

FIGURE 1

Run CC-15 Process Performance
Coal Conversion

Run CC-15 Process Performance Distillate Yield & 975+deg-F Conversion

FIGURE 2

FIGURE 3

Run CC-15
Distillate Yield

FIGURE 4

Run CC-15
Distillate Selectivity

Run CC-15 Process Performance

Effect of Catalyst Deactivation [W% maf Coal]

■ HDN ♦ Distillate * Resid. Conv.

Run CC-15 Process Performance

Effect of Catalyst Deactivation on Nitrogen Content of Products [Thousands ppm]

■ N_SOH ▲ N-ASOH ♦ N_PFL

Run CC-15 Process Performance

Inspection of Pressure Filter Liquids [W% PFL]

□ 975F+ Resid. ♦ Toluene Insol.

FIGURE 8

Comparison of First-Stage and Two-Stage Products
Pressure Filter Liquid (H/C and N/C Ratios)

Comparison of First-Stage and Two-Stage Products
Pressure Filter Liquid (S/C Ratio)

FIGURE 9

Comparison of First-Stage and Two-Stage Products
Pressure Filter Solid (H/C and N/C Ratio)

Comparison of First-Stage and Two-Stage Products
Pressure Filter Solid (S/C Ratio)

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SECTION XII

RUN 260-03 PDU CATALYTIC TWO-STAGE LIQUEFACTION OF BLACK THUNDER COAL

SUMMARY

The objective of the PDU operation was to scale-up the CTSL™ Process with sub-bituminous coal and to demonstrate resid and heavy gas oil extinction in catalytic two-stage liquefaction with equilibrated catalyst using a commercially viable solids separation process. A 28-day run in HRI's Process Development Unit 260 was planned using Black Thunder mine (Wyoming) coal. The major modification of the PDU for this operation was installation of a vertical-leaf pressure filter for separation of solids from the reactor liquid flash bottoms slurry.

The Wyoming coal CTSL™ process was developed over the period 1985-1992 and included 324 days of Bench-Scale studies. Among these were operations on Wyodak, Clovis Point and Black Thunder coals. Two demonstration runs operating in the extinction recycle mode were carried out in 1985 (227-26) and (227-27)⁽¹⁾ totalling 45 days of operation. Data from this operation and succeeding studies from 1988-1992 consisting of 11 runs covering 200 days at conditions were used to prepare the specifications for PDU 260-03. Included was a Bench Run that produced a slurry for filtration tests by the British Coal Board resulting in the choice of Filtration for Solid Separation.

One significant change from Bench-Scale operations was the choice of catalyst, a $1/16$ " NiMo Criterion 317 formulation, whereas the Bench-Studies used $1/16$ " and $1/32$ " Amoco NiMo and CoMo catalysts and for the demonstration and latter runs a $1/32$ " Shell 317 extrudate. Since a merger of Shell and Cyanamid Catalyst Operations occurred to form Criterion, the Shell version was no longer produced, thus the choice of $1/16$ " Criterion extrudates. Unfortunately, the Criterion C-317 did not resemble the Shell S-317 in pore size and pore distribution and promoter level and may have contributed to some of the scale-up problems experienced in PDU 260-03.

The most outstanding achievement of the PDU operation was the development and operation of the U.S. Filter and the early demonstration of heavy oil extinction.

Pumping and filter-leaf sealing problems with the filtration system caused initial delays in the PDU operations. Later the run was interrupted several times, most often because of catalyst particles in downstream valves. A total of 13 days of coal operations were completed with five interruptions. The original run plan had

specified 28 days of operation with the ultimate conditions of 775°F first stage temperature, 825°F second stage temperature, 44 lb coal/hr/ft³ (ea. stage) catalyst space velocity, and 1.5 lb catalyst/ton dry coal catalyst replacement rate for each stage.

Because of the short duration of continuous operations, accurate product yields could not be calculated. As required for resid extinction, the goal of returning all of the vacuum bottoms to the process was achieved. However in most cases, there was significantly more residual oil net product remaining on the filter cakes than had been expected. The coal conversions varied between 78 W% and 88 W% of maf coal in these abbreviated operations, which had not attained full temperature severity.

After repairs, modifications, and improvements were made to the filtration system, approximately 30 filtrations were completed. All of the filtration steps - filling the filter and building the initial screen coating, filtering the slurry, washing the filter cake, vacuum drying the filter cake, discharging the filter cake, vacuum drying the filter cake, discharging the filter cake, and sluicing the filter leaves - were operational. However, some problems remained with cake integrity which led to low cake solids contents of 45-50 W%. Additional modifications are needed to insure that the cake does not slough-off or crack before the wash and vacuum cycle.

OVERALL ANALYSIS

Since continuous operation of the PDU could not be maintained beyond four days, this scale-up had only limited success. The major operability problem that occurred during the PDU operation was upsetting of the catalyst into the separator and let-down system. This occurred without prior warning or signs of problems with the catalyst bed (except for the early spiral cup problems with obvious solids accumulation in the June start-ups). Several theories, as follows, are postulated for the latter catalyst upsets.

1. The catalyst strength was degraded in the presence of water vapor causing attrition-segregation, and carry-over into the let-down system (see Catalyst Strength Evaluation, page 27).
2. Catalyst carry-over resulted from phase separation of the highly paraffinic structures and wax being produced. (See Control Data page 39, *Table 9*, and summary comparison in *Table 10*). The wax may have agglomerated and segregated in the bed forcing some catalyst into the pump suction and into the reactor discharge line where plugging occurred.

Prior to successful operation, the filtration operation encountered numerous mechanical problems. Among these were:

- ◆ Over amperage draw of the filter feed pump (Disc Flow) drive motor.
- ◆ Failure of the disc casting.
- ◆ Failure of the Disc Flow pump mechanical seal.
- ◆ Pluggage at the Filter Discharge Valve.
- ◆ Bypassing around the filter leaves.
- ◆ Failure of the filter leaf drive motor (the U.S. Filter Unit had been stored outside).
- ◆ A smoldering fire within the filter caused by auto ignition of the cake on exposure to some air (shut down procedures have been changed to achieve a lower temperature prior to opening).

During the several months from the first operation in November 1991 to June of 1992, the mechanical and electrical problems were addressed and corrected so that operations were able to proceed in June. Additional operating problems occurred during the approximately 30 cycles completed from June through July, mostly with regard to insufficient vacuum drying of the filter cake. With further procedural improvements, this operation should be successful.

CONCLUSIONS

- ◆ Scale-up of the CTSL™ extinction recycle process was only marginally successful based on the inability to contain the catalyst within the fluidization zone of the second reactor.
- ◆ Operation of the U.S. Filter for sub-bituminous coal solid separation was demonstrated.
- ◆ Near extinction recycle of the heavy oils was achieved for a short period of time.
- ◆ The feasibility of producing very paraffinic oils from Black Thunder sub-bituminous coal was demonstrated.
- ◆ A more moisture resistant and stronger catalyst substrate is required for controlled ebullated bed operation particularly with high oxygen content coals.

RECOMMENDATIONS

- ◆ As evidenced by the excellent hydrogenation achieved, operation at higher space velocities with sub-bituminous coal in the CTSL™ mode should be considered or conversely a lower activity catalytic system (dispersed catalyst) could be used for the initial dissolution and hydrogenation step.
- ◆ The marginal catalyst strength caused by susceptibility of the C-317 catalyst to moisture indicates that further catalyst development for the CTSL™ processing of sub-bituminous coals is warranted. A more moisture resistant catalyst and one that more closely models the physical and chemical structure of the catalysts used on a Bench-Scale is needed.
- ◆ Consideration should be given to modification of the filter procedure preceding the wash and vacuum cycle. Presently, the large reservoir of filter liquid or wash liquid is pumped out at low suction pressure prior to the vacuum cycle. It is recommended that nitrogen pressure to 100 psig be applied to the filter to force the reservoir liquid through the filter cake, thus ensuring cake integrity prior to the vacuum cycle:
- ◆ Start-up procedure should be reviewed, giving consideration to:
 - @ using a very low inventory of catalyst or aged catalyst during the early operation
 - @ using a more rapid approach to target reactor operating temperatures
 - @ use a high initial coal feed rate to age the catalyst more rapidly and to prevent over-hydrogenation.
- ◆ Prior to a PDU scale-up, a Bench-Scale Demonstration operation with the catalyst and conditions simulating PDU conditions should be conducted.

TASK 4.0 - PDU RUN 260-03

BACKGROUND

Task 4.0 of the Two-Stage Close-Coupled, Catalytic Liquefaction of Coal Project prescribed the incorporation of the process improvements demonstrated on the bench-scale units into a PDU scale-up operation. The most important aspect of this larger scale operation is the capability to add and withdraw catalyst, allowing a true equilibrium catalyst condition. Although resid extinction had been demonstrated for Illinois No. 6 coal in 25 days operation (Demonstration Bench Run I-27)⁽²⁾, the operation was not at steady state. The operating conditions had to be made more severe as the run progressed to maintain the 760°F+ fraction extinction as the catalyst deactivated. Similarly, minimal resid yields were obtained for Wyoming Coal in 44 days of operations in Bench Unit Demonstration Runs 227-26 and 227-27⁽³⁾.

True extinction recycle would also require complete removal of the heavy liquids from the solids-containing product stream. In the bench program, this had been approximated by batch pressure filtrations and toluene extraction of the filter cake, with toluene recovery by distillation. This system could not be economically scaled up. In two of the preceding bench runs, products were produced for testing the feasibility of solids separation by delayed coking (discussed previously with Bench Run CC-9), and by vertical-leaf pressure filtration. Other possible solids-separation methods included centrifugal extraction, Rose-SRTM (Residuum Oil Supercritical Extraction - Solids Rejection), and oil agglomeration. The process of vertical-leaf pressure filtration, similar to that in service at the British Coal Point of Ayr liquefaction facility⁽⁴⁾ and tested at the Wilsonville liquefaction facility producing Solvent Refined Coal⁽⁵⁾ was determined likely to be the most efficient method of solids separation in the PDU and one that could be scaled up to commercial size. The optimization and feasibility of vertical-leaf pressure filtration is discussed in Section IV PDU Unit Description and Modifications.

OBJECTIVES

The main objective of the PDU operation was to Scale-up the CTSLTM Process with sub-bituminous coal and to demonstrate resid and heavy gas oil extinction in Catalytic Two-Stage Liquefaction with equilibrated catalyst using a commercially viable solid separation process. A 40-day run with either sub-bituminous or bituminous coal was deemed appropriate to establish the operability, yield pattern, required catalyst replacement ratio, and exact operating conditions.

Another objective of the PDU operation was to establish the procedures and modifications necessary to effectively use the vertical-leaf pressure filtration system in this application of separating the solids from the CTSLTM product slurry.

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RUN PLAN

The Run plan was designed to meet the run objectives while keeping the estimated costs within budget. It was therefore necessary to approach the final catalyst age distribution as quickly as practicable and to limit the run length to 26 days. *Figure 1* shows three catalyst replacement scenarios for the projected approach to equilibrium (as indicated by the resid concentration in the PFL recycle). The scenario of half-rate catalyst replacement on alternate days up to day 16 and full rate replacement at 3.0 lbs catalyst per ton of coal (two stages) was selected to provide the most meaningful data in the shortest time.

The principal operating variables for PDU Run 260-03 are given in *Table 1*. *Table 2* lists the temperature progressions for the 1st and 2nd stage, O-1 Separator, and the Vacuum Still. These temperatures are raised as the coal concentration is increased to the full rate during the first five days and as the average catalyst age increases. The objective of these temperature progressions is to maintain approximate resid extinction during the entire run. The projected yields are given in *Table 3*. Dimethyl disulfide (DMDS) feed is maintained at 6.0 lb/hr to maintain the catalyst in a sulfided state, but it is omitted during two periods (and the final three periods) to quantify its other effects on the product yields and compositions.

Note that the run plan presented above was the basic plan for the Run 260-03. There were other revisions with slightly different run lengths and initial feed rates that were based on current budget estimates and ideas for improved operability.

PDU DESCRIPTION AND MODIFICATIONS

HRI's Process Development Unit, unit 260, shown in drawing Number 260SF001, uses the ebullated-bed reactor system to convert coal and/or residual oil to high quality distillate fuels. The PDU is capable of operating at temperatures of up to 865°F and pressures up to 3,000 psig. Feed capacity is from 1/2 to 3 1/2 tons/day.

HRI's PDU is a totally integrated coal and oil hydrogenation process development unit. It includes coal and oil feed handling systems, slurry mixing and pumping, preheating, reaction, product separations, atmospheric and vacuum fractionation, naphtha stabilization, bottoms handling, product storage, and data acquisition/storage/reporting. The HRI PDU facilities have been used previously to develop and scale-up the H-Oil and H-Coal Processes and to produce jet fuel from shale oil for the Air Force.

For the CTSL™ PDU demonstration, the unit is configured as a two stage unit. Each stage is equipped with an ebullating pump and catalyst addition and withdrawal systems. A filtration section, to provide solids-liquid separation, has been added to the unit flow scheme.

The feed mixture, consisting of coal, recycled slurry oil and hydrogen, is brought to high pressure and preheated prior to being introduced to the reactor. Recycle gas (80-90% hydrogen), pressurized and preheated, is also introduced into the reactor. This mixture then enters the first ebullated catalyst bed. Catalyst systems are present to allow on-line catalyst replacement. Reactor effluent from the first-stage reactor flows directly to the second-stage reactor. Additional recycle gas is added to modify the inlet temperature to the second stage and maintain hydrogen partial pressure.

Second stage reactor effluent, which consists of various liquid and gaseous products, unconverted feed and unreacted hydrogen, enters into a separator.

The overhead effluent of this vessel consists primarily of unreacted hydrogen, gaseous reaction products, and lighter liquid products. Separator bottoms contain the heavier slurry product.

Separator overhead is mixed with water (to prevent ammonium chloride or ammonium sulfide plugging) and cooled in a heat exchanger before being introduced into a flashed vessel (O-5). This vessel separates the hydrogen and gaseous products from the lighter liquids. The overhead gases are scrubbed with No. 2 fuel oil, and the resulting hydrogen-rich gas is pressurized and recycled to the reactor. The liquid flash bottoms are depressurized and sent to vessel O-45 for further separation.

Separator bottoms are depressurized and undergo a flash separation in the reactor liquid flash vessel, O-13. The resultant slurry is sent to the filtration section. Here the solids containing stream is processed to maximize heavy oil recovery for recycle. The resultant high solids content filter cake is sent to storage.

The filtrate is sent to the Vacuum Tower, N-3, where vacuum gas oil is recovered. The vacuum bottoms stream is sent to the recycle oil tank, O-41. From O-41 the material is sent batchwise to the weigh cell equipped recycle oil feed drum, O-43. The recycle oil flow rate from O-43 to the slurry mix tank may be accurately measured and controlled by using the loss in weight of O-43 while allowing the level in O-41 to fluctuate as needed by vacuum still operations.

The vapors from O-13 are cooled and flashed in O-12 with the condensate entering the atmospheric still. Liquid from O-45 is also fed to the atmospheric still. Atmospheric still bottoms are fed to the vacuum tower to recover the heavy oil fraction for recycle. Atmospheric still overheads pass through a naphtha stabilizer which removes impurities such as hydrogen sulfide and light hydrocarbons. Liquid from the stabilizer column is collected as naphtha product.

All uncondensables from the unit are flared.

PDU FEED SECTION MODIFICATIONS

The PDU Clean Oil Tank (COT), and Slurry Mix Tank (SMT), were not sealed or properly vented. In addition, the PDU SMT vapor control device had a broken heat exchanger. The two tanks were sources of water, hydrocarbon vapors and dust inside the building and hydrocarbon vapors outside the building and posed a potential health and safety issue.

For the CTSL™ demonstration operation, the COT has been modified with a bolted top. The SMT vent system has been upgraded with clamped ventilation duct and strategically placed dampers to balance the ventilation flow.

These modifications were designed to:

- improve data correlation and material balance closure (less spills and less vapor losses)
- allow demonstration of a hot slurry mix tank system
- improve working conditions because of reduced vapors
- reduce HRI environmental risk to contaminate the ground water

DMDS FEEDING STATION

The CTSL™ program requires the fresh catalyst to be presulfided at the start of a PDU campaign and has demonstrated an improved product slate with continuous sulfur addition to the reactor during operation. It appears that sulfur can be added to the reactor in any of several different forms. To-date, HRI has successfully demonstrated sulfur addition using hydrogen sulfide, dimethyl disulfide (DMDS), and ditertiary nonyl polysulfide (DNPS). Others have shown that elemental sulfur can also be used.

As PDU run 260-003 is to be a demonstration run of CTSL™ technology, continuous sulfiding will be required as part of the daily operation. Of the four sulfiding agents, DMDS has been chosen for run 260-003 because of the disadvantages of the other three sulfiding agents. HRI has not demonstrated elemental sulfur. Continuous hydrogen sulfide addition, on a PDU scale, has more safety concerns than DMDS. Although probably the safest, TNPS produces a liquid by-product in the reactor that confuses the interpretation of the distillate yields.

A modular feed system designed for DMDS has been implemented on the PDU. The system minimizes transfer of material by taking injection pump suction directly from the shipping drum. Any environmental concerns due to spillage is minimized by the use of an overpack drum to contain the feed material.

HYDROGEN PURGE MODIFICATIONS

Purge gas, which is a slip stream of the recycle gas flow, is used to keep several level and differential pressure taps clear in the high pressure section of PDU 260. Prior to run 260-002, small (0.007" diameter) purge orifices were used to distribute the purge gas to the various users. A flowrate per orifice was assumed based on instrument shop calibrations. As these flows were not monitored, loss of purge flow went unnoticed until the primary instrument was affected. For the upcoming CTSL™ PDU demonstration run, five mass flow controllers were installed in critical areas to monitor and measure the purge gas flow.

WEIGHT TRANSMITTER MODIFICATIONS

In previous PDU-260 operations, seal oil, water injection and purge oil flows were monitored using flowmeters and level transmitters. Frequent breakdowns and unreliable readings, given by the flowmeters keep operators from obtaining accurate flow measurements. Therefore, proper pump settings could not be determined with great confidence and were often not adjusted for long periods of time. The accuracy of level transmitters was also not as high as desirable especially when rate calculations were made over short intervals. Using weight transmitters, the material discharged from the tanks to the process can be monitored accurately and with less mechanical problems. Three weight

transmitters, monitoring the water injection, the seal oil to the ebullating pump, and the purge oil to the ebullating line venturi pressure tops and to the catalyst withdrawal lines were installed.

FILTRATION SECTION

The objectives of the PDU-26O filtration system are to significantly reduce the solids concentration in the recycle oil sent to the slurry mix tank and to minimize the amount of recycle oil leaving the process with the solids stream.

The filtration system and operating procedures developed by British Coal⁽⁶⁾, for their Point of Ayr coal liquefaction facility in North Wales, have been chosen for use in the PDU.

This system provides for constant pressure filtration at elevated temperatures, in situ cake washing, and in situ screen cleaning. The resulting filter cake has been reported to contain 90-95% solids.

The filter to be used in this program is an Auto-Jet Model 130/100 vertical-leaf pressure filter from U.S. Filter. It has been modified for elevated-temperature-pressure (200 psig, 650°F) operation and is fitted with three leaves for a total filtration area of 75 ft². This filter was originally tested at the Wilsonville Advanced Liquefaction Facility for producing Solvent Refined Coal.

Temperatures, pressures, flow rates, pump capacities, and vessel sizes were determined based on the predicted PDU stream flows and the filter performance predicted by British Coal based on small scale filtration tests using slurry from bench unit operations. Their tests indicated the following which are incorporated into the design and procedures:

- 1) The filter feed slurry should be as hot as practicable.
- 2) Filtration rates increase fairly rapidly up to 4 bar pressure drop and increase more at 8 bar, but the additional pumping costs could make this pressure uneconomical.
- 3) Concentrating the slurry is not advisable because the viscosity increases slow the filtration.
- 4) Although the use of body aid increases the filtration rate slightly it is unlikely to be cost effective due to the increased cost for the body aid and its disposal.
- 5) 100 um woven wire screen is appropriate as it is the largest mesh that will be successfully bridged by the coal particles.
- 6) Washing with 1.0 cake volumes could recover up to 75% of the resid in the cake. Washing with larger quantities is unlikely to be cost effective due to the diminishing returns of resid recovery and the increased distillation capacity required.
- 7) Sluicing may be necessary to clear blinded screens.

Additionally, other small-scale filtration tests were performed at HRI using the same nominal 100 um twill screen material that was installed in the PDU vertical-leaf pressure filter. The tests utilized the 12-inch Bench Unit Filter to filter CTSL™ process slurries from the 260-03-02 shutdown.

Some of the slurry solids passed through the screen before the particles effectively bridged the holes. In one test with 5417 grams of 16.8%-solids slurry feed, 23.5% of the solids passed into the filtrate. In a second test with 5350 grams of the same feed, 17.4% of the solids passed into the filtrate. After this filtrate was returned for a second pass through the filter, only 0.8% of the original solids were lost to the filtrate, but the time required for two complete filter passes was an unacceptably long 351 minutes. However, a solids-free filtrate could be obtained in 126 minutes (based on first test) to 166 minutes (based on second test) if only enough feed was circulated through the filter to bridge the screen. The other alternative was for the feed to make one pass through the filter and to recycle the solids to the process. Based on actual PDU-flowrates and solids contents, the filtration times were projected to be 245 minutes for 25% recycle back to the filter and 214 minutes for returning solids to the process. However, even with the expected higher viscosities expected at PDU equilibrium operation, the higher vertical-leaf filter temperature (550°F instead of the 250°F in these tests) would lead to filtration durations of one-sixth to one-fourth of these times.

Despite the slightly shorter projected filtration time required for the case with the solids returned to the process, it was decided to pump the filter feed slurry through the filter until an initial cake was in place, assumed to correspond to a pressure drop of 60 psi. This was an easy procedure to implement, and it could be practiced as long as the filtration times did not exceed the allotted four hours.

Process Flow Overview

A typical filtration cycle consists of the following steps:

- 1) Filtering the feed material and collecting the filtrate.
- 2) Washing the filter cake.
- 3) Vacuum drying the filter cake.
- 4) Discharging the filter cake.
- 5) Sluicing the leaves.

As filtering the feed material is a batch process, the filtration time will be tailored to provide enough filtrate to maintain steady recycle oil flow to the slurry mix tank. Fluctuations in filtrate flow are handled by using intermediate storage tanks for feed material, filtrate, and vacuum tower feed. A simplified flow diagram of the filtration system is presented in drawing number 260SF001, and the individual steps of the filtration process are described below.

The O-13 bottoms stream is sent to a cycle holding tank, O-46, the purpose of which is to store the material while the filter is on-line. O-46 is fitted with a circulating pump, J-60. The O-13 bottoms from O-46 will be sent to the filter feed tank, O-47 as required.

When the filter is in operation, the filter is fed by the filter feed pump, J-61. This is a 100 gpm Discflow pump. The high flowrate is necessary to fill the filter, about 300 gallons dead volume, in a short period of time, in addition to providing circulation of the material in O-47.

J-61 is capable of operating at 125 psig discharge pressure. As the filtration will take place at 8 bar, 116 psig, this pump is adequate for the task. A high flowrate will be maintained throughout the filtration by using a pump around loop from the filter back to O-47 via the filter pressure control valve, PCU-XF1. The pumparound should minimize sedimentation in the filter.

The filtrate is sent to the filtrate holding tank, O-48, to be weighed and sampled. The filtrate is then sent to the N-3 feed tank, O-50 by the filtrate transfer pump, J-62. The purpose of the N-3 feed tank is to minimize disruptions of the feed to the vacuum tower, N-3, caused by the unsteady batch filtrations.

Atmospheric still, N-2, bottoms are accumulated until the filtrate is to be pumped to O-50. This procedure is necessary to reduce fluctuations in N-3 feed composition.

After a filtration run is completed, the filter is drained of feed material by the filter drain pump, J-66. At this time the feed material, about 300 gallons, is sent back to O-47. The filter case is now ready for washing.

Wash oil is sent to the filter from the wash oil tank, O-51, by the wash oil pump, J-65. This pump is a 50 gpm Durco capable of 125 psig discharge pressure. The purpose of the wash oil is to displace the heavy oil in the filter cake. Therefore, the volume of wash oil pumped through the cake should be equal or slightly greater than the filter cake volume, about 23 gallons. Once this volume has been passed through the filter cake, the wash oil flow to the filter is terminated. The filter is again drained of material by using J-66. However, the wash oil is directed to O-51, not to O-47, and will be used in subsequent filter cycles. Prior to entering the wash oil tank, the filter drainings are sent through a small guard filter.

The filter cake has been washed and is now ready for drying. Drying is accomplished by using a vacuum system. This vacuum system consists of a vacuum pump, J-67, a condenser, M-16, and a condensate receiver, O-49. Condensate is pumped back to O-51 by the condensate pump, J-63.

The vacuum is first applied to the filtrate nozzle of the filter. Once a vacuum has been established, the filter casing is opened to the vacuum system. As the filter is at about 550-575°F, the vacuum drying should be completed at a pressure of about 50 Torr. After the vacuum drying is completed, the filter is ready for filter cake removal.

Removal of the filter cake is accomplished by rotating the filter leaves and energizing the filter cake conveyor. The filter cake is removed through the filter cake block valve, V-XF1. This valve is a bidirectional Vanessa valve. Hot filter cake is sent to a filter cake cooler, M-15, and then to a product collection drum, D-8 for weighing and sampling.

If cleaning of the filter leaves is required, as determined by an increase in filtration time, then the sluicing system will come into play. This system is simply a sluice blowcase, O-52, which will send high pressure, 1,000 psig, wash oil to the filter internal sluice. The arms of the sluice system are fitted with special spray nozzles that will cause the liquid to fan out impinging on the external surface of the screens and thereby dislodging the material blinding the screens.

Used sluice liquid, about 37 gallons, is not drained or recovered. It remains in the filter for the next cycle.

The O-52 is filled with wash oil by the sluice blowcase fill pump, J-68.

If cleaning of the leaves is not required, then the filter is simply prepared for the next cycle.

OPERATIONS

PDU Run 260-03 included a total of 13 operating days, consisting of periods of continuous coal feed for 18 to 79 hours. The first coal operations were November 20-21, 1991 (Periods 1-2), after which there was a six-month delay during which major filter system improvements, corrections, and repairs were made.

In 1992 the PDU was operating on coal feed June 6-7 (Periods 3-4), June 18-20 (Periods 5-7), July 3-6 (Periods 8-11), and July 16-17 (Periods 12-13). Most of the shutdowns involved blockages in downstream equipment. The efforts to make an operable filtration system and the problems that caused the unit shutdowns are discussed separately below.

FILTRATION PROBLEMS AND REMEDIES

During the November operations the filter system was inoperable because the filter feed pump could not operate for an extended period of time and could not generate sufficient head pressure. A small amount of slurry was sent to the filter, but it apparently bypassed the filter leaves. A new drive motor and a new impeller were installed and the packing was replaced with a double mechanical seal with a gas purge. Interleaf gaskets were added to prevent the slurry from bypassing the filter leaves.

In Period 4 the filter had to be bypassed because of a leaking filter cake block valve. To prevent this from happening again, a pressure wash system was added that directs a series of high-pressure-liquid jets onto the valve seating area to clean off accumulated solids. After the Period 7 shutdown, leaking filter-leaf gaskets were replaced by new, higher temperature gaskets. Subsequently, approximately 30 separate filter operations were completed. The analyses of the slurry feed, filter cake, and filtrate and the effectiveness of the filtrations are discussed in the Results and Performance Evaluations section.

UNIT OPERATING HISTORY

Run 260-03 started November 20, 1991 when coal was first charged to the PDU. The feed and temperature schedule of the run plan were being followed, but there was some difficulty maintaining the specified feed rates because of coal feed disruptions and the low availability of heavy recycle solvent due to the inoperable filter. These factors contributed to a high coal concentration in the SMT near the end of Period 2 that caused an extended feed disruption and a high temperature leading to coking in the preheater. After this incident, the unit was cleaned and prepared for restart, but the run was put on hold until the problems with the filtration system were resolved.

The unit was restarted on June 6, 1992. After two days of operation, Periods 3 and 4, when the O-1 Separator level could not be controlled, the unit was shut down. Improper ebullation was suspected when catalyst was also found in the let-down valves.

The system was reassembled and restarted. During the restart, there were problems with second stage ebullation and a blocked recycle gas line, but these problems were alleviated and coal feed was started for Period 5 on June 18. In Period 7 catalyst again caused a shutdown of the unit as the let-down valves and separator plugged. It was noted that the catalyst from the second stage was reduced in size and contained a few large particles of solids.

An analysis indicated that a new improved spiral cup designed for effective gas separation may have been concentrational solids (unconverted coal and ash) in the reactor. The spiral H-Oil cup was replaced with a conventional design identical to the cup in Reactor #1.

Two additional attempts to operate in July with new catalyst in Reactor #2 and with a modified start-up procedure also ended in a similar manner with catalyst entering the let-down system. There were no carbonaceous lumps in the catalyst withdrawals and only minimal size reduction occurred.

Figures 4 and 5 show the history of the PDU operations in terms of reactor temperature and catalyst age. Reactor temperatures as high as 760°F 1st Stage and 810 2nd Stage had been attained before the shutdowns in Periods 7, 11, and 13, but they were not sustained long enough for steady product rates and compositions to be established. The catalyst in the 2nd Stage had to be replaced before the restarts in Periods 5, 8, and 12.

Catalyst attrition and subsequent downstream deposition was indicated by the molybdenum analyses of the restrictions that caused shutdowns. For example, the material in the O-1 letdown valve after the Period 11 shutdown contained 50.71% ash, containing enough molybdenum to account for 83% of that ash. Similarly, all of the 44.46% ash in the material from the 2nd stage ebullation block valve, after the 2nd Stage would not ebullate on June 15, was catalyst.

There was also excessive molybdenum present in the solid products. The molybdenum content of the THF-washed solids from five samples from Period 4 varied from 0.15 to 0.34 W%. This quantity of molybdenum would correspond to 18 lbs of catalyst during Period 3 and 4 coal operations. If this rate of catalyst attrition is extrapolated to the entire 12 days of operation, the catalyst loss becomes a very large portion of the original 240 lb inventory. Additional information regarding the recovered catalyst properties is presented in the Recovered Catalysts section.

The behavior of the catalyst was further investigated using HRI's 6-inch Cold Flow Model. These six 2-hour tests indicated that some of the smaller catalyst particles did carry over into the ebullation line when the disengaging height below the cup was half the specified distance. More and somewhat larger catalyst carried over when the gas velocity was increased, but the quantities of all carried-over size fractions were considerably less than the quantities of those fractions originally charged, indicating that the carryover could have been entirely due to segregation by particle size. To uncover problems with catalyst attrition longer term tests would be required.

RESULTS AND PERFORMANCE EVALUATION

FILTRATION

The filtration system was only solids rejection after the restart of the PDU in June 1992. Except for the problems of leaking filter-leaf gaskets and the mechanical failure in Period 10 (discussed in the Operations section), the filter adequately removed solids from the feed slurry. Filter feed ash analyses ranged from 1.10% in Period 3 to 4.52% in Period 13. The ash analysis for the Period 13 filtrate was 0.00%. This was the only ash analysis of filtrate during on-line filtrations when the slurry was not bypassing the filter leaves.

The feed and product solids contents from off-line testing with product slurry after the Period 11 shutdown are presented in *Table 4*. The filtrates contained only a small amount of solids (0.12 to 0.52%). Compared with the filtrations during the run, two of the cakes produced in these off-line tests had relatively low oil contents (72 and 84% solids). As noted on *Table 4*, in the July 12 filtration the cake was washed and vacuum-dried, but in the July 14 filtrations the cake was vacuum-dried only. The cakes were not washed in many of the filtrations because, with the unconsolidated sticky cakes that were formed, the wash was not very effective and might have pushed the cakes from the filter-leaf screen.

Table 5 shows the composition of the filter cakes analyzed during the run by quinoline filtration analyses of the filter cake. The cakes were fairly uniform, containing 46 to 59% solids (unconverted coal + ash). This solids content would be fairly typical for the batch pressure filtrations used in the bench operations, but it is much lower than the expected 90-95 % solids expected in the cake. Much of this deficiency could be due to the inability to effectively wash the unconsolidated, sticky filter cakes.

Typically, filtrations were conducted every four hours on all of the available O-13 bottoms. Filter balance data and filtration times for four filter cycles during the Period 13 operations are presented in *Table 6*. The average filtration time was 74 minutes. Because these slurries were relatively light (approximately 5% 850°F resid oil) and of low viscosity compared to the heavier (approximately 41% 850°F resid oil) slurries expected later in the run, it is likely that the filtration frequency would have to be increased to keep the filtration times in this acceptable range. The other steps in the filtration procedure that required substantial time were the vacuum drying of the cake (60 to 90 minutes) and the discharge of the filter cake (15 to 60 minutes). Most of the other filling and emptying steps only required 5 to 10 minutes because of the high volume pumps.

As indicated in *Table 6*, 700 to 1200 lbs of slurry feed passed through the filter, but an additional 2200 lbs was required to fill the filter volume. A similar quantity of slurry had to be drained before washing, drying, and discharging the cake.

The recoveries of filter products varied from very good to very poor, and the quantities of filter cake (10.3 to 22.8 W% of slurry feed) were not as consistent as they should have been. The most likely cause of these deviations is holdup within the filter.

YIELDS

Because there was not more than three continuous days of steady operations and the catalyst had not approached a reasonable equilibrium age most of the yield information is not representative of lined-out operations. The normalized yields were calculated four ways for Periods 10 and 13 (*Appendix A*) using four different sets of assumptions. The wide disparity in the resulting yields demonstrates the insignificance of most of the numbers. The basic deficiencies in the collected product data that led to this disparity are the extremely low 32% (Period 10) and 42% (Period 13) ash recoveries combined with excess total product recoveries. Also, the task of identifying exact vessel inventory weight and composition changes during the brief operating periods caused additional inaccuracies in the calculated yields.

The most reliable yields are for the C_1 - C_3 gases, which do not have the possibility for vessel inventory changes, and for unconverted coal, which can be calculated by ash balance. The collected C_1 - C_3 gas yields were 6.56 W% Dry Coal for Period 10 and 7.06 W% Dry Coal for Period 13. The coal conversions are presented in *Table 7* along with the pertinent operating conditions. These coal conversions did not correlate well with temperature or residence time, but the two highest coal conversions (87.5 and 88.2% in Periods 8 and 9) did correspond to the lowest coal rate. The coal conversions were also generally slightly lower than predicted by correlations based on bench unit performance. The lower coal conversions might have been partly due to the inferior recycle solvent quality that is discussed below and in the section on "Laboratory-Scale Studies" (page 22). Also, the microautoclave convertibility of different samples of the feed coal and the ultimate convertibility of product slurry solids is addressed in this section.

During the brief operating intervals, the goal of total resid recycle was accomplished. Because of vacuum bottoms holding tank inventory changes, in some periods less than 100% of the vacuum bottoms were recycled to the process and in other periods more than 100% of the vacuum bottoms were recycled, but on average all of the vacuum bottoms produced were able to be recycled. Thus, except for unit resid inventory increases and the greater-than-expected resid on the filter cake product, the objective of resid extinction was being implemented.

DISTILLATE PRODUCT QUALITY

Additional analyses of the distillation fractions were performed on the Period 10 and 13 liquid products. The analyses of these fractions for the Naphtha Stabilizer Bottoms (NSB), the Vacuum Still Overhead, and the Vacuum Still Bottoms are presented in *Table 8*. For one comparison with bench unit products, the H:C ratios of the 390-500°F fractions of the NSB products in Periods 10 and 13 were 1.74 and 1.75, a little higher than for the Bench Run CC-1 Period 6 and 10 Separator Overhead products with similar average boiling points and gravity (32.9 and 33.9 °API vs. 33.1 and 33.9 °API), which had 1.71 and 1.69 H:C ratios, respectively. Nine samples were analyzed at Consol by H-NMR using their procedure for characterizing protons of coal liquefaction products⁽⁷⁾. The results are presented in *Table 9*. The samples included three samples of the oils used to initiate operations during restarts. This material, located in Tank #4, was originally oil derived entirely from Wilsonville operations with Wyoming coal, but as Run 260-03 proceeded, heavy process solvent was returned to this tank, making its character increasingly like that of Run 260-03 products. The next five samples represent actual liquid products before distillation, either actual filter liquid or liquid from THF filtration of the filter cake. The last sample was a deposit from the filter cake removal line and was of interest because it was observed to be particularly waxy.

The analyses in *Table 9* indicate the change in paraffinicity of the Tank 4 startup oil after some of the Wilsonville oil was replaced with process oil. The sum of the alkyl beta and gamma protons increased from 44.2% for the Wilsonville oil to 53.8 and 53.3 % for the two Tank #4 samples. This change was also indicated by microautoclave solvent quality tests. The results of Consol and HRI solvent quality tests are listed below:

Sample	Coal Conversion, W% MAF Coal		
	Consol Tests	HRI Tests	
	W/Old Ben	W/III #6	W/Black Thunder
LO-6040 Wilsonville S/U/ Oil	69.1	51.3	48.9
LO-6041 Tank #4 Period 11	65.5		
LO-6042 Tank #4 End of Run	55.2	42.2	35.3

Although the conversion levels were different between the Consol and HRI tests due to different methods, all test results indicate that the solvent quality of the startup solvent was relatively poor at the beginning of the run and became worse after products from the process were added to it. This poor solvent quality could have been one reason for the lower than expected coal conversion.

The product liquids were also somewhat more paraffinic than the liquid products that had been generated in bench unit operations and in recent Wilsonville operations with Wyoming Coal. *Table 10* compares the paraffin content, as measured by the alkyl beta and gamma protons, of 260-03 products with Run 227-26 PFL and with Wilsonville Run 258, 260, and 262 V-138B products. Although these other operations were mostly at higher catalyst age than attained in Run 260-03, the generally non-overlapping ranges of the quantities of paraffinic protons indicate that the differences are greater than can be explained by additional hydrogenation at lower catalyst age. The hours of operation during restarts when there was only recycle solvent feed and the temperatures were less than 750°F would have been favorable for solvent hydrogenation. Also, during the first couple days on coal feed after each restart, the solvent: coal ratios were higher and the temperatures were lower than they would be later in the run. Even with these possibilities for increased hydrogenation, because of the magnitude of the differences in paraffin content, it is likely that the catalyst was especially active for hydrogenation.

It is possible that the unusually high paraffinicity could have caused phase separation problems that contributed to operating difficulties in the 2nd Stage and downstream valves, but there is no direct evidence for this. Waxy material was observed in the filter cakes and may have contributed to difficulties in getting a dry cake, but the process streams are usually more stable at the higher reactor and hot separator temperatures.

LABORATORY SCALE STUDIES

A program of 40 microautoclave tests was conducted to evaluate the reactivity of Black Thunder Mine coal feeds, the Criterion C-317 catalyst, and the start-up solvents used in the course of PDU Run 260-03, along with some reference runs with catalysts, coals and solvents used in other CTSL™ operations. Also, there were tests on filter-feed slurries that were produced in these PDU operations. Impact of high temperature exposure to an atmosphere of high water content on catalyst strength was also evaluated.

SUPPORTIVE MICROAUTOCLAVE TESTS

Coal Evaluation

The feed coal to the PDU Run 260-03 (designated as HRI-5991) was Black Thunder Mine coal which was ground and dried by Empire Coke Co. Various portions of this shipment were tested over a period of nine months to monitor any possible aging of the coal. The analyses for the HRI-5991 coal and for the HRI-5713 coal used in previous blend operations are presented in *Table 11*. These analyses are very similar except for the lower volatile matter in the HRI-5991 coal for the PDU.

Several samples were taken and tested between the period November 1991 and July 1992. A description of these samples are as follows:

Designation	Description
HRI-5991 1991	A coal sample (Bag 5) taken shortly after receipt of the coal in November, 1991 and stored in a closed metal can since then.
Run 260-03 Period 1 Feed	A feed coal sample taken during Period 1 of the run, in November, and stored in a closed metal can.
Run 260-03 Period 14 Feed	A feed coal sample taken during Period 14 after the final operation of the run in July.
HRI-5991 Bag 1,3,6, & 8	Samples taken in July, 1992 of the coal from the 1,000 lb. shipping modules in which they had been stored since November 1991.

The current program also tested the HRI-5887 shipment of Black Thunder Mine which had also been prepared by Empire Coke Co. for qualification of their operations.

The standard coal evaluation conditions were:

Temperature	800°F
Pressure (hot)	2000 psig H ₂
Time	30 minutes
Solvent/Coal	8g/2g
Catalyst/Coal	1/1 (in catalytic tests)

There were some tests at 825°F.

The following tabulation compares the microautoclave results for the HRI-5991 coal samples, in the standard coal evaluation tests using HRI-5198 solvent and presulfided Shell S-317 1/32" Ni/Mo catalyst, with those of the earlier shipment of Black Thunder Mine coal. The table gives the number of tests, the average coal conversion of those tests, and the statistical significance of the difference from the average for the pooled data of the tests of the earlier shipments.

<u>SHIPMENTS</u>	<u>THERMAL EVALUATION</u>			<u>CATALYTIC EVALUATION</u>		
	No. of Tests	Average Coal Conversion	Significance, %	No. of Tests	Average Coal Conversion	Significance, %
All HRI-5991 Samples	11	70.2	99.3	6	85.9	87.5
HRI-5991 1991 Sample	1	66.8	98.8	1	87.4	23.5
Run 260-03 Period 1	1	70.8	92.6	1	85.7	79.4
Run 260-03 Period 14	5	74.6	89.6	1	80.4	99.9
HRI-5991 1992 From Storage	4	70.0	99.6	3*	87.4	35.9
HRI-5887	2	77.0	39.8	2	91.5	98.7
Pooled HRI-5613, 5630, 5713	5	78.6	---	8	87.9	---

* Discarding result for Bag 3 in Run XX-026 (73.7% conversion)

These results indicate that the HRI-5991 shipment was less reactive than the average of the earlier shipments, by 2.0% in the catalytic tests (87.5% statistical confidence level) and 8.4% in the thermal tests (99.3% statistical confidence level).

The HRI-5887 shipment from Empire Coke Co. was more reactive than the HRI-5991 shipment, also prepared by them, and gave the highest catalytic conversion results, 3.6% higher than obtained with the earlier shipments (98.7% confidence level), although the thermal conversions with the HRI-5887 shipment were slightly lower than obtained with the earlier shipments. Expressing the HRI-5887 results relative to those of the HRI-5991 results, indicates 5.6% higher catalytic test conversion (99.1 confidence level for the difference), and 5.1% higher thermal test conversion (88.6% confidence level of the difference).

The Run 260-03 Period 14 coal sample gave the lowest catalytic conversion result of these tests, but the thermal conversion results were in the general range of the other samples of the HRI-5991 shipment. Microautoclave tests using the Run 260-03 Period 14 coal with other solvents and catalysts gave conversions in the general range obtained with the other HRI-5991 samples, see below.

COAL EVALUATION WITH VARIOUS SOLVENTS AND CATALYSTS

There was a series and catalyst evaluation tests (with Illinois and Black Thunder Mine coal). Four solvents were used. The origin of these solvents are described in the following table:

Designation	Description
HRI-6002	Wilsonville Solvent Boiling range: 450-985°F
HRI L-769	Start-up solvent for Run 260-03 Topped HRI-6002 (650°F+) Boiling range: 540-985°F)
HRI L-769 7/92	Material from the PDU Solvent Tank (Tank #4) sampled in July/92 consisting of the original L-769 and process solvent generated from Run 260-03.
HRI-5198	Solvent used in the microautoclave coal evaluation tests, produced during Wilsonville operations with Illinois coal.

The catalyst tested were the following:

Designation	Description
HRI-5903 C-317	The Criterion C-317 $\frac{1}{16}$ " extrudate catalyst used in Run 260-03. This catalyst was not presulfided for the Microautoclave tests.
HRI-5394 S-317	The Shell S-317 $\frac{1}{32}$ " extrudate catalyst used in various CTSL™ Bench Unit operations. This catalyst was not presulfided for the Microautoclave tests.

HRI-5394P The Shell S-317 $\frac{1}{32}$ " extrudate catalyst used in various CTSL™ Bench Unit operations. The "P" designation indicates that the catalyst had been presulfided in a fixed bed before the microautoclave tests.

HRI-6043 AO-60 Experimental $\frac{1}{16}$ " NiMo Catalyst received through Southern Clean Fuels.

The following table summarizes the results of tests with the HRI-5991 shipment of Black Thunder Mine coal and various solvents and catalysts.

Catalyst HRI No.	Solvent	Number of Tests	Coal Conversion [W%]	Residual Selectivity [W% coal conv.]
HRI-5394P S-317	HRI-5198	6	85.9	24.7
HRI-5394 S-317	HRI-6002	2	88.6	27.2
HRI-5903 C-317	HRI-5198	1	88.3	30.0
HRI-5903 C-317	HRI-6002	2	88.0	29.6
HRI-5903 C-317	HRI L-769	1	90.8	22.2
HRI-6043P AO-60	HRI-6002	1	83.0	31.6
HRI-5394P S-317P	HRI-5198	6*	87.9	22.0
HRI-5394P S-317P	HRI-5198	2**	91.5	24.2

* Tests with earlier shipment of Black Thunder Mine Coal

** Tests of HRI-5887 shipment of Black Thunder Mine Coal

These results indicate the relative performance of the catalysts in terms of lower residual yield was in the order:

S-317P > S-317 > C-317 > AO-60

However, the greatest difference in residual oil yield, 7.2% lower for the S-317P catalyst than for the AO-60 catalyst, has a relatively low statistical confidence level of 72.6%.

Similarly, the relative performance of the solvents in terms of lower residual oil yield was in the order:

L-769 > HRI-6002 ~ HRI-5198

with a statistical confidence level of 82.2% for the 7.8% lower residual oil yield with the L-769 solvent.

When judged by coal conversion, the order of performance of the solvents and catalysts was the same but the levels of confidence were very low.

SOLVENT EVALUATION

In *Table 12*, the results of the current microautoclave solvent evaluation tests are compared with the results of the other solvents which have been used as start-up solvents for CTSTM Bench Unit operations. The conditions for these tests are 30 minutes, 750°F with a solvent/coal ratio of 2/1 in 2000 psig nitrogen. The tests determine the conversion of the test coals which are HRI-5174 Illinois No. 6 coal, and HRI-5613 Black Thunder Mine coal.

With Illinois coal, the HRI-5198 solvent (the solvent for microautoclave coal conversion evaluations) gave a solvent evaluation results in the higher part of the range of results for the earlier solvent tests, and both the HRI-5969 (Wilsonville solvent V-124 used in the November startup of the PDU Run) and the HRI-6002 solvent (from which the L-769 start-up oil for Run 260-03 was distilled) gave a range result. The initial L-769 start-up oil had a result slightly below the lowest value obtained previously, while the L-769 solvent as developed during the course of operations through July, 1992 has an exceptionally low solvent quality result.

With the Black Thunder Mine coal, only the initial L-769 material and the HRI-6002 solvent had results in the range of values obtained earlier and the results were higher than those of only one of the previous tests. The HRI-5198 results was slightly lower than those values, while, again, the L-769 solvent in July, 1992 had an exceptionally low result.

The essential conclusion is that L-769 materials used during Run 260-03 had poor solvent quality performance, which deteriorated even further as the run continued.

REACTIVITY OF FILTER FEED SLURRIES

Table 13 summarizes the results of catalytic microautoclave tests using the filter feed slurries from Period 10A and Period 13A of Run 260-03. The test conditions were those used in the standard coal evaluation tests and the liquid/catalyst and coal solids/catalyst ratios corresponded closely to the ratios that are used in the standard coal evaluation tests.

The solids content of the slurries were 23.6 W% (Period 10 sample) and 16.7 W% (Period 13 sample) and they were of a composition corresponding to

80-82% conversion of the maf coal that had been fed to the PDU operation. TGA analysis of the liquid components indicated residuum contents of 7.2 W% (Period 10A) and 3.8 W% (Period 13A). The atomic hydrogen to carbon ratio of the liquids were about 1.6/1.

In both the microautoclave tests about 57% of the moisture-ash-free (maf) coal fed in the microautoclave feed was reacted, which results in solids composition corresponding to about 92% conversion of the maf coal originally fed to the PDU operation. The residual oil content of liquid products for both tests was higher than that in the liquid feed, by an amount that corresponded to about 20% of amount of coal converted in the test. This amount of residual oil formation is slightly below the amounts formed in the various catalytic coal evaluation tests.

CATALYST STRENGTH EVALUATION

A series of eight microautoclave tests were performed to determine the effect upon catalyst strength of exposure to high temperatures and an atmosphere of high water content. Four catalysts, including Criterion C-317, Shell S-317, Davison GR-14 and AO-60, were tested at 800°F and 2,000 psig for 64 hours in an atmosphere which contained 25-30 V% water vapor. The test was a static test, without reactor agitation, to avoid mechanical breakage of the catalyst during the extended test. In addition, the C-317 and S-317 catalysts were tested in 30 minute tests with four parts of oil to catalyst, both with calcined catalyst and with catalysts containing about 9.0 W% water. Crush strength and attrition losses were determined on the charged and treated catalysts.

The high temperature treatment lowered the crush strength, and caused attrition losses, with a greater change where there was water in the reactor, either presence as free water or water adsorbed upon the charged catalyst. The following table compares the crush strength and attrition losses of the variously treated catalysts with the values for the fresh catalysts;

Water in Reactor W% Catalyst	Crush Ratio		Attrition Ratio	
	C-317	S-317	C-317	S-317
0.0 (calcined) (A)	0.79	0.83	1.88	1.62
9.0 (adsorbed) (A)	0.71	0.82	2.77	1.84
13.3 (free water)(B)	0.73	0.73	2.74	2.25

As summarized in the following *table*, the water treatment in the Statics 64-hour tests had the greatest effect upon the Davison GR-14 catalyst and possibly the least effect, although considerable, upon the S-317 catalyst.

<u>Catalyst</u>	<u>Crush Ratio</u>	<u>Attrition Ratio</u>
GR-14	0.59	4.15
AO-60	0.62	2.58
C-317	0.73	2.74
S-317	0.73	2.25

(A) Static 64-hour test, 0 oil.

(B) Agitated 30-min. test, 4/1 oil/catalyst.

CATALYST

FRESH CATALYST

Criterion C-317 catalyst (HRI-5903), a $\frac{1}{16}$ " nickel-molybdenum catalyst, was used in PDU Run 260-03. It had been expected that it would have a pore structure similar to the Shell S-317 catalyst that had been used in the bench program, but as indicated in *Table 14*, the pore size distribution is different. The greatest difference between the two catalysts is in the size of the minipores, where the HRI-5903 catalyst modal pore diameter (the point of inflection of the volume versus pore size plot) was only 46 Angstroms while that of the Shell S-317 catalyst was 95 Angstroms. This difference is also shown in the attached figure of pore volume versus pore size for the two catalysts.

The total pore volumes of the two catalysts (Quantachrome Instrument) were virtually the same. An earlier measurement of the Shell S-317 catalyst with the American Instrument Company indicated a somewhat higher pore volume for that catalyst, although the pore size distribution was similar to that obtained with the Quantachrome Instrument (*see Figure 6*).

RECOVERED CATALYST

Catalysts removed from the reactors after each shutdown in 1992 showed varying amounts of attrition. On June 11, after Period 4, the catalyst was fairly intact with only 0.4 and 1.7 W% -20 mesh material (predominantly catalyst) in two different second stage samples. However, after Period 7 there was more fine catalyst present, especially in Reactor 2. The screen analyses for the catalysts removed from Reactors 1 and 2 are:

	Reactor 1		Reactor 2	
	<u>Norm. W%</u>	<u>Observation</u>	<u>Norm. W%</u>	<u>Observation</u>
Lumps	0.0		0.9	
+20 Mesh	91.8	not badly worn	71.1	not badly worn
20-30 Mesh	1.7	mostly catalyst	3.4	all catalyst
30-100 Mesh	6.4	some catalyst	16.6	all catalyst
-100 Mesh	0.1	catalyst indistinguishable	7.6	catalyst indistinguishable

The screen analyses and the length distributions for the Period 11 and 13 catalyst are included in *Tables 16 and 17*. The weight percentages of the first and second stage -20 mesh material were 0.2 and 10.3 after Period 11 and 5.8 and 1.6 after Period 13. Except after Period 13, the second stage contained more catalyst fines than the first stage despite appreciably lower catalyst ages for the second stage, which had a fresh catalyst charge after each of these shutdowns.

The catalyst length distributions correspond to the relative amounts of fines noted above. The second stage catalyst after Period 11 had a factor of 3 increase in the proportion of particles shorter than 2.5 mm. After Period 13, there was just slightly more -2.5 mm catalyst in the first stage catalyst than in the fresh catalyst, and there was even less -2.5 mm catalyst in the second stage than in the fresh catalyst. The drum attrition test losses for both Period 13 catalysts were about twice that of the fresh catalyst. Although there could be some sampling variability, the general pattern is that there was somewhat excessive break-up of catalyst, especially in the second stage, which could have caused the downstream blockages and ebullating problems that caused the shutdowns described in the "Operations" section (page 15).

The catalysts removed from the second stage after Period 4 and from the first and second stages after Periods 11 and 13 were also analyzed for elemental composition. These results are shown in *Tables 15, 16, and 17*. The molybdenum contents of the two Period 4 second stage +20 mesh catalyst samples corresponded to 78.1 and 82.5 W% actual catalyst content. The amount of impurities present was also indicated by the 25.3 W% increase in bulk density from 0.611 g/cc for the fresh catalyst to an average of 0.818 g/cc for the recovered catalyst and by the average 23.9 W% loss on ignition. However, with an average carbon content of 10.6 W%, there was only enough analyzed organics to explain a 13.6 W% loss on ignition. The sulfur contents were only 58.9 and 60.8 W% of the amounts corresponding to the formation MoS_2 and NiS , while catalysts recovered after bench unit operations had sulfur contents corresponding to 80-100 % metal sulfide formation.

The catalysts recovered from the two stages after Period 11 contained moderate amounts of carbon, 12.2 and 12.4 W%; whereas the catalysts recovered from after Period 13 contained slightly lower amounts of carbon, 10.1 and 10.5 W%. The first stage catalyst molybdenum content, 10.06 W%, indicates almost pure catalyst, and the second stage catalyst molybdenum content, 8.28 W%, indicates 82 W% actual catalyst content.

TABLE 1
PRINCIPAL OPERATING VARIABLES - PDU RUN 260-03

Run Length	- 26 days of coal operations
Coal	- Black Thunder Mine Wyoming Coal 200 lbs/hr (Dry) 55 lbs/hr/cubic foot catalyst (stage)
Catalyst	- Criterion C-317 Catalyst 1/16" Extrudates - presulfided Equilibrium Make-up 3 lbs/ton coal Half Rate Alternate Days through Day 16 DMDS addition to maintain sulfided state
Solvent Recycle	- 1.2 lbs/lb dry coal Filtered Vacuum Still bottoms topped for bottoms extinction.
Temperatures	- First Stage 750-775°F Second Stage 800-825°F
Pressures	- 2900 psig reactor pressure 2000 psi hydrogen partial pressure
Recycle Filtration	- 550-575°F Cake washed with light oil

TABLE 2
RUN PLAN - PDU RUN 260-3
Revision 11/20/91

Day	Temperature, °F				Coal lb/Hr	Vsb Recyc.		DMDS lb/hr	Cat. Add. Lbs.		
	<u>1st Stage</u>	<u>2nd Stage</u>	<u>0-1</u>	<u>Vac Still (Equiv.)</u>		<u>lb/Hr</u>	<u>lb/hr</u>		<u>1st Stage</u>	<u>2nd Stage</u>	
0	700	750	625	600	0	240	6.0	3.6	3.6		
1	715	765	640	620	80	240	6.0	0.0	0.0		
2	730	780	655	640	120	240	6.0	1.8	1.8		
3	745	795	670	660	160	240	6.0	0.0	0.0		
4	760	810	685	680	200	240	6.0	1.8	1.8		
5	760	810	685	700	215	240	6.0	0.0	0.0		
6	760	810	685	(1)	215	240	6.0	1.8	1.8		
7	765	815	690	(1)	215	240	6.0	0.0	0.0		
8	765	815	690	(1)	215	240	6.0	1.8	1.8		Work-up
9	765	815	690	(1)	215	240	NO	0.0	0.0		
10	770	820	695	(1)	215	240	NO	1.8	1.8		DMDS Analysis
11	770	820	695	(1)	215	240	6.0	0.0	0.0		
12	770	820	695	(1)	215	240	6.0	1.8	1.8		
13	775	825	700	(1)	215	240	6.0	0.0	0.0		
14	775	825	700	(1)	215	240	6.0	1.8	1.8		
15	775	825	700	(1)	215	240	6.0	0.0	0.0		
16	775	825	700	(1)	215	240	6.0	1.8	1.8		Work-up
17	775	825	700	(1)	215	240	6.0	3.6	3.6		
18	775	825	700	(1)	215	240	6.0	3.6	3.6		
19	775	825	700	(1)	215	240	6.0	3.6	3.6		
20	775	825	700	(1)	215	240	6.0	3.6	3.6		Work-up
21	775	825	700	(1)	215	240	6.0	3.6	3.6		
22	775	85	700	(1)	215	240	6.0	3.6	3.6		Work-up
23	775	825	700	(1)	215	240	6.0	3.6	3.6		
24	775	825	700	(1)	215	240	NO	3.6	3.6		
25	775	825	700	(1)	215	240	NO	3.6	3.6		
26	775	825	700	(1)	215	240	NO	3.6	3.6		Detailed Work-up

(1) As required to prevent accumulation of VSB (Filtered Recycle).

(2) Coal Rate Assumes 7 W% moisture. Adjust according to actual coal analysis.

TABLE 3
PROJECTED YIELDS
PDU EXTINCTION MODE OPERATIONS

Product Fraction	<u>Yield, W% of Dry Coal</u>
C ₁ -C ₃ Hydrocarbons	8.3
C ₄ -390°F Naphtha	16.0
390-700°F Distillate	38.1
700-975°F Distillate	0.6*
975°F+ Residuum	1.1*
Unconverted Coal	11.3
Ash	6.7
Water	20.7
Carbon Oxides	3.3
Ammonia	0.9
Hydrogen Sulfide	0.3
Hydrogen Consumption	-7.0
TOTAL	100.0
Coal Conversion	87.9
C ₄ -700°F Distillate	54.1
Residual Oil in Recycle Solvent, W%	30.4

* Retention on Washed Filter Cake

TABLE 4
SOLIDS CONTENT OF PDU FILTER STREAMS
FROM OFF-LINE TESTING*

DATE	7/12	7/13	7/14	7/14
TIME	<u>1900</u>	<u>2300</u>	<u>0600</u>	<u>1840</u>
FILTER FEED				
Quinoline Insols, W%	---	---	20.48	20.97
Ash, W%	---	---	6.65	6.72
FILTRATE				
Quinoline Insols, W%	0.27	0.25	0.52	0.12
Ash, W%	0.03	0.01	0.11	0.00
FILTER CAKE				
Quinoline Insols, W%	<u>84.22</u>	39.40	---	<u>71.77</u>
Ash, W%	27.95	13.38	---	22.96
CAKE TREATMENT				
Washed	Yes	Yes	No	No
Vacuum Dried	Yes	Yes	Yes	Yes

* These results are from off-line testing using feed materials collected prior to Period 11 (see page 18 under filtration).

TABLE 5

FILTER CAKE COMPOSITIONS*

RUN 260-03

Date	7/10	7/12	7/13	7/13	7/13	7/13	7/14	7/14	7/14	7/14	7/17	7/17
Period	6	8	9	9	9	9	10	10	10	13	13	13
Time			05:20	15:10	22:00	08:40	11:40	No Time	01:20	16:00	10:25	
975°F Oil, W% Cake	47.45	44.22	49.94	51.51	43.57	44.76	46.34	44.90	49.41	42.04	42.48	
975°F, W% Cake												
Oil	8.00	3.40	3.38	5.15	7.45	8.25	7.43	6.91	8.30	2.93	3.02	
Unconverted Coal	28.31	29.73	26.66	26.38	28.47	28.83	28.51	31.09	28.13	38.85	38.21	
Ash	16.24	22.65	20.02	16.96	20.51	18.16	17.70	17.10	14.16	16.18	16.29	

* As determined by quinoline filtrations and TGA resid determination.

Results obtained during continuous PDU operation. See page 18 under Filtration.

TABLE 6
PERIOD 13 FILTER BALANCES

Period	13	14	14	15
Date	7/17	7/18	7/18	7/19
Completion Time	16:00	01:20	09:20	08:15
Filtration Duration, Min.	81	40	100	74
Filter Pressure Drop, psi	54	55	53	53
Vacuum Drying Duration, Min.	--	90	--	60
Flows Into Filter, Lbs				
Slurry to Fill Filter	2315	2268	1958	1994
Slurry During Filtration	748	737	1220	1183
Sluice Liquid (A)	224	189	266	197
TOTAL IN	3287	3194	3444	3374
Flows out of Filter, Lbs				
Filtrate	703	700	1208	1195
Filter Drainings	1988	2049	1950	1986
Filter Cake	127	76	278	154
TOTAL OUT	2818	2825	3436	3335
Overall Recovery, W% of Total Feed	85.7	88.4	99.8	98.8
Net Recovery W% of Net Slurry Feed (B)	63.9	67.8	99.5	97.2
Filter Cake, W% of Filter Slurry Feed	17.0	10.3	22.8	13.0
Cake Wash Balance (C)				
Flows from 0-51 Into Filter, Lbs				
To Fill Filter		2118	2141	
To Wash Cake		146	528	
TOTAL IN		2264	2669	
Flows Out, Lbs				
Additional Filtrate		146	410	
Return to 0-51		2035	2194	
TOTAL OUT		2181	2604	
Recovery		96.3	97.6	

(A) From previous filtration

(B) (Cake + Filtrate)/(Slurry During Filtration + Slurry to Fill - Drainings)

(C) Filter cakes were washed and dried during the 1200 and 0920 filtration cycles. Cake wash balance was not included in the above Overall Recoveries and Net Recoveries.

TABLE 7
COAL CONVERSION
RUN 260-03

Period	Temperature, °F		Sp Velocity/Stage lb/hr/ft ³ Cat	Recycle/Coal Ratio	Conversion, W% MAF Coal
	1st Stage	2nd Stage			
					80.6
2B	731	783	41	1.61	
6B	756	807	48	2.35	82.0
8B	710	761	20	5.05	87.5
9A1	718	771	26	3.24	88.2
9B1	726	776	36	2.80	86.8
10A1	744	792	51	1.65	85.4, 85.1, 82.5, 84.0
					80.6
10B	748	795	53	0.94	
11A	753	807	61	0.79	83.3, 83.8
					82.4, 82.7
13B1	748	820	48	1.93	78.1

TABLE 8
PDU RUN 260-03 PRODUCT INSPECTIONS

Analysis	Period 10						Analysis	Period 13					
	Distribution (W%)	Carbon (W%)	Hydrogen (W%)	Nitrogen (Wppm)	Sulfur (Wppm)	API		Distribution (W%)	Carbon (W%)	Hydrogen (W%)	Nitrogen (Wppm)	Sulfur (Wppm)	API
Naphtha Stabilizer Bottoms							Naphtha Stabilizer Bottoms						
IBP-390°F	52.2	85.60	14.09	144.0	204.2	50.8	IBP-390°F	22.2	86.80	14.08	141.0	136.9	50.3
390-500°F	24.7	86.66	12.70	383.0	355.3	33.9	390-500°F	17.4	86.80	12.73	343.0	191.7	33.1
500-650°F	20.4	87.41	12.36	396.0	140.0	26.6	500-630°F	50.7	87.66	12.28	324.0	64.7	25.7
650°F	2.7	88.31	11.93	474.0	130.0	---	630°F	9.7	87.41	11.67	374.0	154.0	20.3
Whole Sample	100	86.14	13.30	276.0	314.7	40.7	Whole Sample	100	86.93	12.61	322.0	304.6	31.5
Vacuum Still Overheads							Vacuum Still Overheads						
IBP-650°F	50.38	87.62	12.21	314.5	90.5	24.5	IBP-702°F	99.34	87.58	12.25	214.7	172.0	24.1
650-821°F	48.64	87.43	11.69	340.2	170.2	19.5	702°F	0.66	---	---	---	---	---
821°F	0.98	---	---	---	---	---	Whole Sample	100	87.77	12.14	231.6	183.0	24.4
Whole Sample	100	88.03	12.00	344.0	97.0	22.1							
Vacuum Still Bottoms							Vacuum Still Bottoms						
IBP-859°F	27.3	88.61	11.60	1770.00	130.0	18.1	IBP-650°F	15.93	87.94	11.84	824	67.9	
859°F	72.7	74.35	6.59	5700.00	4100.0	-14.4	650-850°F	66.7	88.61	11.41	1821.0	68.4	
Whole Sample	100	80.52	8.19	5000.0	2730.0	-6.1	850-963°F	7.61	88.75	10.50	5100.0	88.8	
							963°F	9.76	53.27	3.27	---	7520.0	
							Whole Sample	100	86.35	11.05	1800.0	500.0	14.0

Note: Period 10B Sample contains solids (Filter operation was bypassed)

By TGA Method, W%	9.88
Ash	44.5
975°F (incl. IOM)	45.62
975°F	

TABLE 9

PROTON DISTRIBUTION AND PHENOLIC-OH CONCENTRATION*											
Sample	Period	HPI NO. LO-	Proton Distribution (%)						Phenolic-OH		
			Cond. Arom	Uncond. Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Conc. meg/g	cm
L-769 Wilsonville Solvent	S/U	6040	6.7	5.8	13.5	9.1	20.7	27.1	17.1	0.35	3315
Tank #4	S/U	6041	5.4	4.7	9.8	7.3	19.1	33.2	20.6	0.18	3316
Tank #4	13S/D	6042	4.9	3.9	10.3	7.7	20.0	34.3	19.0	0.10	3322
Filtrate	2A	6045	3.1	4.2	8.7	7.1	20.7	35.0	21.2	<0.10	3330
Filtrate	13B1	6046	4.3	2.6	7.9	5.6	18.6	39.4	21.5	<0.10	3325
THF Solubles in Filter Cake	10A	6047	6.0	2.9	9.9	6.3	20.8	36.0	18.1	0.10	3309
THF Solubles in Filter Cake	12A	6048	5.6	2.8	7.0	5.6	18.1	38.0	22.8	0.11	3311
THF Solubles in Filter Cake	13B	6049	5.6	3.0	7.7	6.3	18.8	36.9	21.8	0.12	3306
Deposit in Filter Cake Product Line	13S/D	6097*	6.3	2.6	9.6	7.3	19.9	35.9	18.4	0.13	3306

- * Date obtained 9/14/92
- * Date obtained 10/25/92

(1) Winschel, et al, Coal Liquefaction in Process Streams Characterization and Evaluation, Consol, Report No. DOE/PC89883-66, DOE Contract #DE-AC22-89PC89883, Nov. 1992 and succeeding reports.

TABLE 10

**COMPARISON OF PARAFFIN CONTENT OF RUN 260-03 LIQUIDS
WITH OTHER WYOMING-COAL-DERIVED LIQUIDS**

	HRI		Wilsonville		
	Run 260-3 Liquid	Run 227-26 PFL	Run 258 V-131B	Run 260 V-1311B	Run 262 B-131B
No. of Points	5	23	13	6	7
Alkyl Beta, %					
Range-High	35.0	29.4	21.8	29.8	33.1
-Low	39.4	33.4	27.5	37.6	36.0
Average	37.1	31.6	25.6	33.4	34.7
Gamma, %					
Range-High	18.1	14.2	9.7	12.6	11.5
-Low	22.8	18.0	14.3	15.6	19.3
Average	21.1	16.3	12.2	14.0	15.6

From Consol Data: Winschel, et al, Coal Liquefaction in Process Streams Characterization and Evaluation, Consol, Report No. DOE/PC89883-66, DOE Contract #DE-AC22-89PC89883, Nov. 1992 and succeeding reports.

Alkyl Beta and Gamma Protons are classified as paraffins.

TABLE 11

**BLACK THUNDER MINE (WYOMING) COAL ANALYSES
FOR RUN 260-03 (HRI-5991)
(With HRI-5713 (Runs 227-69 and 227-70) Analyses show for Comparison)**

FEED DESIGNATION, HRI NUMBER	5991	5713
PROXIMATE ANALYSIS (TGA), W%		
Moisture	6.34	6.56
Volatile Matter (MAF Basis)	46.38	54.65
Fixed Carbon (MAF Basis)	53.62	45.35
ULTIMATE ANALYSIS (W% DRY BASIS)		
Carbon	68.65	67.55
Hydrogen	4.56	4.23
Sulfur	0.50	0.51
Nitrogen	0.87	0.92
Chlorine	0.02	---
Ash	(7.36)	(7.62)
Sulfur in Ash	(4.15)	(4.71)
Ash (SO ₃ -Free)	6.60	6.72
Oxygen (By Difference)	18.82	20.07
SULFUR FORMS (W% DRY BASIS)		
Sulfate	0.01	0.01
Pyritic	0.14	0.07
Organic (By Difference)	0.32	0.48
HEATING VALUE, BTU/LB (DRY)	11933	11653
Btu/Lb MAF	12776	12492
MINERAL ANALYSIS OF ASH, (W%, IGNITED)		
Silica, SiO ₂	35.33	36.16
Alumina, Al ₂ O ₃	18.72	17.54
Titania, TiO ₂	1.22	1.27
Ferric Oxide, Fe ₂ O ₃	5.48	5.01
Lime, CaO	21.15	19.69
Magnesia, MgO	4.46	3.99
Potassium Oxide, K ₂ O	0.55	0.43
Sodium Oxide, NaO	0.55	0.39
Sulfur Trioxide, SO ₃	10.37	12.93
Phosphorous Pentoxide, P ₂ O ₅	1.10	0.89
Strontium Oxide, SrO	0.30	0.95
Barium Oxide, BaO	0.65	0.64
Manganese Oxide, Mn ₃ O ₄	0.12	0.11
Undetermined	0.00	0.00

TABLE 12
MICROAUTOCLAVE EVALUATION OF SOLVENTS

Coal Conversions in Tests at
750°F for 30 Minutes
Solvent/Coal Ratio: 2/1
2000 psig Nitrogen Atmosphere

TEST COAL	ILLINOIS NO. 6	BLACK THUNDER
	HRI-5174	HRI-5613
SOLVENT		
L-769 1991 ⁽¹⁾	51.3	48.9
L-769 1992 ⁽²⁾	42.2	35.3
HRI-6002 ⁽³⁾	59.8	47.7
HRI-5198 ⁽⁴⁾	66.3	44.8
HRI-5910	70.2	53.8
HRI-5648	70.1	61.5
L-742	67.4	65.9
HRI-5911	65.8	51.7
HRI-5757	61.9	58.8
L-721	60.8	63.7
	61.6	
HRI-5658	59.3	57.0
HRI-4907	58.0	65.4
HRI-5443	69.4	54.8
	57.8	54.7
HRI-5969	53.4	53.0
227-25 Shut-Down	55.3	47.2

- (1) Topped HRI-6002 for Run 260-03 Start-up in Nov. 1991
- (2) Sample of oil in July, 1992, after replenishing original inventory of L-769 by returning oil from PDU operations.
- (3) Coal derived distillate from Wilsonville (V-123), received Dec. 4/92.
- (4) Test Solvent for coal evaluation tests. Hydrotreated solvent from Wilsonville operations on Illinois Coal.
Received November, 1985.

TABLE 13

MICROAUTOCLAVE TESTS ON FILTER FEED SLURRY FROM PDU RUN 260-03 OPERATIONS

Tests at 825°F, 2000 psig H₂, 30 minutes
5 gm slurry per gm of HRI-5903 Criterion C-317 Catalyst

MICROAUTOCLAVE RUN	<u>XX11</u>	<u>XX12</u>
Feed Slurry Inspection		
Period No.	10A	13A
Composition, W%		
Ash	7.20	4.78
Coal	16.39	11.88
Liquid	76.40	83.33
Liquid Component Analysis, W%		
Carbon	88.18	88.28
Hydrogen	11.63	11.80
Nitrogen	0.24	0.17
Sulfur	0.02	0.03
TGA Analysis		
"THF"	0	0
Residuum	7.24	3.84
Microautoclave Product		
W% of Feed		
Ash	7.42	4.64
Coal	7.22	4.95
Liquid*	83.62	87.11
Total	98.26	96.27
Liquid Component Analysis, W% *		
Hydrogen	88.26	88.46
Carbon	10.98	11.26
Nitrogen	0.24	0.20
Sulfur	0.03	0.03
Total	99.51	99.95
TGA Analysis		
"THF"	4.94	4.26
Residuum	9.10	5.32
Conversion (Ash balanced)		
Coal fed to Microautoclave	57.2	57.1
Conversion Level, W% of Coal to PDU Operation		
Microautoclave Feed	81.9	80.2
Microautoclave Product	92.3	91.5

* Rotoevaporated liquid washed from autoclave with THF.

TABLE 14

**FRESH CATALYST PROPERTIES - PDU RUN 260-03 (HRI 5903)
Comparison with Shell S-317 Catalyst Used in Bench Unit (HRI 5394)**

HRI No.	5903	5394
Source	Criterion	Shell
Nominal Extrudate Diameter	1/16"	1/32"
CHEMICAL ANALYSIS (W%, DRY BASIS)		
Molybdenum, HRI Analyses	10.11	11.4
Vendor Specification		12.0
Nickel, HRI Analyses	2.38	2.2
Vendor Specification		2.5
Calcium	0.04	
Iron	0.00	
Sodium	0.00	
PHYSICAL PROPERTIES		
Bulk Density, Compacted, Lb/Ft ³	38.1	36.7
Loose Pack, Lb/Ft ³	35.8	
Particle Density, gm/cc*	0.938	0.966 (0.941)
Surface Area (Calc.), M ² /gm*	302	204 (267)
M ² /cc particle*	283	194 (251)
BET, M ² /gm	314	
Pore Volume, cc/gm*	0.645	0.652 (0.697)
cc/cc particle*	0.605	0.630 (0.656)
Average Crush Strength, Lb/mm	2.73	1.94
Drum Attrition Test Loss, W%	2.71	
Weight Loss @ 105°C, W%	0	
Weight Loss @ 1200°C, @%	3.46	2.20 (850°F)
Particle Diameter, Average, mm	1.65	0.98
Particle Length, Average, mm	3.8	4.5
PORE SIZE DISTRIBUTION, CC/GM*		
Diameter > 30°A	0.64	0.65 (0.70)
Diameter > 100°A	0.30	0.39 (0.40)
Diameter > 250°A	0.27	0.19 (0.15)
Diameter > 500°A	0.24	0.16 (0.14)
Diameter > 1500°A	0.18	0.11 (0.11)
Diameter > 4000°A	0.08	0.02 (0.03)
Modal Diameter, Minipores, °A	46	95 (95)
Modal Diameter, Macropores, °A	4200	2800 (2500)
PENETRATION TEST		
Avg. Penetration, % of Diameter	48.0	34.9
Particles less than 10% Penetration, %	30	17.5

* Values based on Quantachrome Instrument. Bracketed Values based on American Instrument Company Instrument.

TABLE 15**RECOVERED SECOND STAGE CATALYST ANALYSES****PDU RUN 260-03, June 11, 1992 After Period 4**

SAMPLE NUMBER	1	2
Catalyst Age, Lb Coal/Lb Catalyst	83	83
Screen Analysis of Oil-Free Catalyst		
Lumps, W%	0.0	0.0
+20 mesh, W%	99.60	98.27
20-100 mesh, W%	0.38	1.57
-100 mesh, W%	0.02	0.06
ANALYSES OF OIL-FREE		
+20 MESH CATALYST, W%		
Carbon	10.73	10.51
Hydrogen	0.91	0.90
H/C Ratio	1.02	1.03
Nitrogen	0.25	0.22
Sulfur	3.92	3.62
Molybdenum	8.35	7.90
Nickel	1.62	1.62
Loss on Ignition, W%	23.8	24.0
Bulk Density, Gm/cc	0.816	0.819
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS		
Molybdenum, W%	5.52	7.98
Nickel, W%	3.12	1.76

TABLE 16

RECOVERED CATALYST ANALYSES

PDU RUN 260-03, July 7, 1992 After Period 11

Stage	<u>1</u>	<u>2</u>	<u>Fresh</u>
Catalyst Age, Lbs Coal/Lb Catalyst	175	52	0
Screen Analysis of Oil-Free Catalyst			
Lumps, W%	0.0	0.0	
+20 mesh, W%	99.8	89.7	
20-30 Mesh, W%	0.06	2.5	
30-100 mesh, W%	0.11	7.4	
-100 mesh, W%	0.01	0.4	
Analysis of Oil-Free			
+20 mesh Catalyst, W%			
Carbon	12.21	12.42	
Hydrogen	1.16	0.96	
H/C Ratio	1.14	0.93	
Nitrogen	0.26	0.32	
Calcium	0.13	0.18	
Length Distribution			
< 0.5 mm, W%	0.0	0.3	0.0
0.5-1.0 mm, W%	0.3	4.4	0.8
1.0-1.5 mm, W%	3.1	7.2	2.3
1.5-2.5 mm, W%	8.0	17.4	6.9
2.5-6.3 mm, W%	88.6	63.4	83.7
> 6.3 mm, W%	0.0	7.2	6.2
Analysis of 30-100 Mesh Oil-Free Solids			
Molybdenum, W%	7.09		

Notes:

- First Stage Catalyst - Dull charcoal luster, with less than 1% tan (young). Tips of extrudates were slightly rounded.
- Second stage Catalyst - Slightly shiny charcoal luster, with 3-5% tan (young). Tips of extrudates were not rounded. There were a few 3-8 mm diameter lumps.

TABLE 17

RECOVERED CATALYST ANALYSES

PDU RUN 260-03, July 18, 1992 After Period 13

Stage	<u>1</u>	<u>2</u>	<u>Fresh</u>
Catalyst Age, Lbs Coal/Lb Catalyst	248	52	0
Oil In Original Sample, W%	31.1	27.3	
Screen Analysis of Oil-Free Catalyst			
Lumps, W%	0.0	0.0	
+20 mesh, W%	93.8	98.4	
20-30 Mesh, W%	1.4	0.3	
30-100 mesh, W%	3.6	0.8	
-100 mesh, W%	0.8	0.5	
Analysis of Oil-Free			
+20 Mesh Catalyst, W%			
Carbon	10.05	10.49	
Hydrogen	0.97	0.93	
H/C Ratio	1.16	1.06	
Nitrogen	0.25	0.17	
Calcium	0.05	0.02	
Molybdenum	10.06	8.28	10.1
Drum Attrition Test Loss, W%	5.3	5.9	2.7
Length Distribution			
< 0.5 mm, W%	0.0	0.0	0.0
0.5-1.0 mm, W%	1.9	0.6	0.8
1.0-1.5 mm, W%	3.1	1.0	2.3
1.5-2.5 mm, W%	8.1	0.0	6.9
2.5-6.3 mm, W%	83.9	91.7	83.7
> 6.3 mm, W%	3.0	6.7	6.2
Analysis of 30-100 Mesh Oil-Free Solids			
Molybdenum, W%	0.62	5.50	
Ash, W%	87.2	77.0	
Analysis of -100 Mesh Oil-Free Solids			
Molybdenum, W%	0.74	2.22	
Ash, W%	82.4	75.1	

FIGURE 1

EQUILIBRATION WITH CATALYST REPLACEMENT

Proj. PDU Oper. - 3.0 Lbs Cat/Ton Coal

FIGURE 2

PROCESS DEVELOPMENT UNIT NO. 260
SIMPLIFIED PROCESS FLOWSHEET, RUN 3

TITLE: PROCESS DEVELOPMENT UNIT RUN 260-003	HYDROCARBON RESEARCH, INC.			DATE
	JOB NO. 820-403			ECH 6/5/92
	DRAWING NUMBER 260SF001			CHKD ISSUE 4

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FIGURE 4

Catalyst Age vs. Period Reactor 1

FIGURE 5

CATALYST PORE SIZE DISTRIBUTION

HRI 5394 Shell S-317 and HRI 5903 Criterion Catalysts

APPENDIX A

PRODUCT YIELDS NORMALIZATION RUN 260-03, PERIODS 10 AND 13

Tables A-1 and A-2 summarize the normalized yields for Run 260-03 Period 10 and Period 13 which have been calculated using four methods. The table includes some collected yield parameters for comparison with the results of the various normalization techniques.

Normalization Methods

The normalization results summarized in the second column of the tables, the "net" method, of the tables were those presented to DOE in our August 26th meeting. Here, the weight of normalized NET products is equal to the weight of the feed quantities (coal, seal oil, DMDS, and coal moisture) plus calculated hydrogen consumption after appropriate ash balance, carbon, nitrogen, and sulfur balances. In this calculation, the normalized vacuum bottoms yield was taken to be the same as the collected vacuum bottoms yield (for no essential material balance justification, but rather to avoid reducing calculated residual oil yields), the filter cake yield was obtained by ash balance, and the other carbon containing streams were adjusted for carbon balance closure by a common "carbon normalization factor" given in the table, which in this case was only 0.545 times the collected quantities of those streams.

The third column of the tables summarizes the "gross" normalization, that is the total of the net products plus the recycled vacuum bottoms and recycled vacuum overhead is equal to the weight of the coal, seal oil, DMDS, coal moisture plus the recycled vacuum bottoms and recycled vacuum overhead.

The fourth column of the tables is a "net" normalization, similar to that of the second column, excepting the vacuum bottoms yield was adjusted in common with the other products.

The fifth column of the tables is a "gross" normalization, similar to that of the third column, excepting the vacuum bottoms yield was adjusted in common with the other products. This method of normalization is similar to that used in normalizing the results of the CTSL Bench Unit operations.

Discussion

As indicated in the tables, the collected yields from both period were characterized by very low ash recoveries (32 and 42 W%), high (over 100%) total weight recovery, associated with high carbon recovery, again over 100%. The deviations from closure are exacerbated when filter cake yields are increased to

obtain an ash balance, with increases in the filter cake weight corresponding to 28 and 30 W% of the coal fed, and a consequent increase in the carbon recovery to over 130 W% of the carbon in the net feed. Normalization, with carbon closure (in order to obtain reasonable water yields which were essentially calculated by an oxygen-by-difference balance) then requires very large downward adjustments of the products other than the filter cake. For Period 10 this adjustment, the "carbon normalization factor" given in the tables, was as low as 0.545 for the net normalization without adjustment of the vacuum bottoms yield. For the "gross" normalization, and adjustment of the vacuum bottoms yield, this factor increased to 0.845.

Consequently, normalized gas yields were always lower than the collected gas yields, with the gross normalization (including vacuum bottoms adjustment) corresponding most closely to the collected quantity. This normalization method resulted in the lowest residual yields (actually, with virtually no net residual oil yield in the Period 13 calculation). The normalized yield of C₄-975°F distillate was the highest by this gross normalization technique, more markedly for the Period 10 calculations than for the Period 13 calculations where there was essentially the same distillate obtained by the four calculations techniques.

TABLE A-1
PDU RUN 260-03 PERIOD 10
CTSL WYOMING COAL
VARIOUS NORMALIZATION METHODS

Period Number	<u>10T</u>				
Period Start Date	07/05/92				
PROCESS CONDITIONS					
REACTOR #1 TEMPERATURE °F	746				
REACTOR #2 TEMPERATURE °F	794				
Calc. Hydrogen Inlet Partial Pressure, psig	2929				
Catalyst Sp. Vel., Lb/Hr/Ft ³ (Each Stage)	52				
Hydrogen Purity at Reactor #1 Inlet, MOL%	87.3				
Calc. Hydrogen Exit Partial Pressure, psig	2050				
Unit Back Pressure, psig	2890				
Reactor #1 Cat age, Lb Dry Coal/lb Cat.	175				
Reactor #2 Cat. Age, Lb Dry Coal/Lb Cat.	52				
Material Balance Recovery, W% of Total Feeds	106.6				
Excess Recovery, W% of Dry Coal	11.8				
Normalization Method	Collected	Net	Gross	Net	Gross
Vacuum Bottoms Yield		Unadjusted		Normal	Normal
Carbon Normalization Factor		0.545	0.754	0.591	0.838
STREAM YIELDS, W% OF DRY COAL					
C ₁ -C ₇ Gases (DMDS adjusted)	8.87	4.31	6.40	4.77	7.22
Naphtha Still Bottoms	33.08	18.04	24.97	19.54	27.73
Vacuum Still Overhead (net)	25.17	13.73	4.55	14.87	11.66
Vacuum Still Bottoms (net)	17.56	17.56	17.56	10.37	-7.31
Filter Cake	3.93	34.27	34.27	38.47	48.80
Water (less Injection Water)	35.00	25.83	25.75	25.76	25.54
Carbon Recovery	107.76	100.00	100.00	100.00	100.00
Ash Recovery	31.82	100.00	100.00	100.00	100.00
NORMALIZED YIELDS, W% OF DRY COAL					
H ₂ S		0.26	0.26	0.27	0.28
NH ₃		0.75	-7.5	0.77	0.82
H ₂ O		19.22	19.03	19.03	18.82
CO+CO ₂		0.11	0.14	0.11	0.16
C ₁ -C ₃ (Ex CH ₄ from DMDS)	6.56	3.07	4.68	3.42	5.32
C ₄ -390°F		10.50	14.53	11.37	16.14
390°F-500°F		5.45	6.67	5.90	7.80
500°F-650°F		11.07	13.13	11.98	12.87
650°F-850°F		17.56	13.23	17.35	14.01
850°F-975°F		8.72	8.63	8.15	6.69
975°F* (Solids-Free)		6.93	6.93	5.33	1.39
Unconverted Coal		16.33	16.33	16.33	16.34
Ash (SO ₃ -Free)	2.10	6.60	6.60	6.60	6.60
TOTAL (100+H ₂ Cons)		106.30	106.77	106.61	107.24
PROCESS PERFORMANCE					
975°F + Conversion, W% MAF		75.1	76.3	76.8	81.0
Coal Conversion, W% MAF		82.5	82.5	82.5	82.5
Total C ₄ -975°F, W% MAF Coal		57.1	55.7	58.6	61.6
Hydrogen Consumption, W% Fresh Feed		6.30	6.77	6.61	7.24

TABLE A-2
PDU RUN 260-03 PERIOD 13
CTSL WYOMING COAL
VARIOUS NORMALIZATION METHODS

Period Number	13T				
Period Start Date	07/17/92				
PROCESS CONDITIONS					
REACTOR #1 TEMPERATURE °F	745				
REACTOR #2 TEMPERATURE °F	807				
Calc. Hydrogen Inlet Partial Pressure, psig	2755				
Catalyst Sp. Vel., Lb/Hr/Ft ² (Each Stage)	48				
Hydrogen Purity at Reactor #1 Inlet, MOL%	93.7				
Calc. Hydrogen Exit Partial Pressure, psig	2365				
Unit Back Pressure, psig	2880				
Reactor #1 Cat age, Lb Dry Coal/lb Cat.	248				
Reactor #2 Cat. Age, Lb Dry Coal/Lb Cat.	52				
Material Balance Recovery, W% of Total Feeds	102.3				
Excess Recovery, W% of Dry Coal	4.9				
Normalization Method	Collected	Net	Gross	Net	Gross
Vacuum Bottoms Yield		Unadjusted		Normal	Normal
Carbon Normalization Factor		0.694	0.742	0.675	0.867
STREAM YIELDS, W% OF DRY COAL					
C ₁ -C ₄ Gases (DMDS adjusted)	10.79	7.10	7.68	6.86	9.19
Naphtha Still Bottoms	83.74	58.09	52.14	56.60	72.63
Vacuum Still Overhead (net)	6.86	4.76	-0.63	46.3	3.01
Vacuum Still Bottoms (net)	-6.99	-6.99	-6.99	-4.72	-24.86
Filter Cake	20.17	47.62	47.62	47.62	48.80
Water (less Injection Water)	20.11	25.66	25.63	25.61	26.01
Carbon Recovery	111.38	100.00	100.00	100.00	100.00
Ash Recovery	42.42	100.00	100.00	100.00	100.00
NORMALIZED YIELDS, W% OF DRY COAL					
H ₂ S		0.26	0.26	0.26	0.26
NH ₃		0.79	0.79	0.78	0.82
H ₂ O		18.89	18.93	18.84	19.24
CO+CO ₂		0.21	0.23	0.20	0.26
C ₁ -C ₄ (Ex CH ₄ from DMDS)	7.06	4.51	4.91	4.35	5.95
C ₄ -390°F		14.90	15.94	14.49	18.64
390°F-500°F		10.81	11.46	10.49	13.65
500°F-650°F		20.26	18.32	19.39	26.08
650°F-850°F		7.64	7.58	8.97	-2.89
850°F-975°F		-0.16	-0.16	0.03	-1.69
975°F* (Solids-Free)		1.66	1.66	1.88	-0.08
Unconverted Coal		20.46	20.46	20.46	20.46
Ash (SO ₃ -Free)	2.80	6.60	6.60	6.60	6.60
TOTAL (100+H ₂ Cons)		106.56	106.97	106.76	107.31
PROCESS PERFORMANCE					
975°F + Conversion, W% MAF		86.3	76.3	76.1	78.2
Coal Conversion, W% MAF		78.1	78.1	78.1	78.1
Total C ₄ -975°F, W% MAF Coal		57.2	56.9	57.2	57.6
Hydrogen Consumption, W% Fresh Feed		6.56	6.97	6.76	7.31

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