1 of 3

CATALYTIC TWO-STAGE LIQUEFACTION (CTSL) PROCESS BENCH STUDIES
WITH BITUMINOUS COAL

FINAL TOPICAL REPORT

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ABSTRACT

Reported herein are the details and results of Laboratory and Bench-Scale experiments using bituminous coal concluded 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 the application of coal cleaning methods and solids separation methods to the Catalytic Two-Stage Liquefaction (CTSL) Process. Additionally a predispersed catalyst was evaluated in a thermal/catalytic configuration, and an alternative nickel molybdenum catalyst was evaluated for the CTSL process.

Three coals were evaluated in this program: 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 tests involving the Illinois coal are reported herein, and the tests involving the Wyoming and New Mexico coals are described in Topical Report No. 1.

On the laboratory scale, microautoclave tests evaluating coal, start-up oils, catalysts, thermal treatment, CO₂ addition and sulfur compound effects are reported in Topical Report No. 3. Other microautoclave tests, such as tests on rejuvenated catalyst, coker liquids, and cleaned coals, are described in the Bench Run sections to which they refer. The microautoclave tests conducted for modelling the CTSL process are described in the CTSL 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 - Summary of Entire Program

In this report, Topical No. 2, the bench-scale runs that used bituminous Illinois No. 6 coal are discussed. There are five 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.

Task 3 is addressed in this report, Topical No. 2. 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 bituminous coal, most of the subtasks under the Continuous Bench-Scale Operations and PDU Scale-Up tasks were addressed as follows:

Task 3.1 - Reactor Configurations

devoted to studies with sub-bituminous coal (see Topical No. 1)

Task 3.2 - Feedstock Effects

Run CC-6 - evaluated coal that had been cleaned by a selective solvent oil-agglomeration process (heptane and petroleum derived asphalt).

Run CC-8 - evaluated coal cleaned by OTISCA Industries, using a process that removes impurities from a water slurry of micronized coal.

Task 3.3 - Catalyst Studies

Run CC-14 - compared the activities of predispersed iron oxide hydroxide, dispersed molybdenum, and no dispersed catalyst with supported catalyst only in the final stage.

Run CC-16 - Evaluated Akzo AO-60 NiMo catalyst.

Task 3.4 - Solids Separation

Run CC-9 - evaluated delayed coking of the atmospheric still bottoms as a method of solids separation.

PROGRAM OBJECTIVES AND SCOPE OF WORK

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.

The scope of work covered by this report on the Catalytic Two-Stage Liquefaction of bituminous coal consists of continuous bench-scale testing to obtain process yield and product quality data as well as data on other processing steps such as coal pretreatment and solids separation.

EXECUTIVE SUMMARY

INTRODUCTION

In a recently completed program (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; however, the process data was considered inadequate to provide a complete assessment of the technical and economic viability of two stage liquefaction. 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.

The CTSL process shown in *Figure 1* 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 2,000 cc ebullated-beds with vapor/liquid separation, continuous atmospheric distillation, filtration and a 1,000 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 minimal 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

Figure 1

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, with a feed corresponding to the chemical hydrogen consumption plus the amount of hydrogen to be recycled in plant-scale operations. Application of data to plant-scale design using impure hydrogen is by adjusting system pressure to obtain experimental partial pressure.

EBULLATED-BED BENCH UNIT 227

FIGURE 2

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 at lower capital and production costs.

In support of this objective, bench studies were conducted on cleaned Illinois No. 6 coals, new catalysts and with different process and reactor configurations.

Coals cleaned by selective solvent oil agglomeration were shown to be more reactive than uncleaned coals producing higher distillate yields and higher resid and coal conversion. An OTISCA cleaned coal in a water slurry was also tested. This micronized coal did not convert as well as the oil-agglomerated cleaned coal; however, better hydrogenation and quality was indicated.

From a process integration standpoint and based on CTSL economic studies the oil-agglomeration cleaned coal will reduce the cost of coal derived liquids whereas the drying of the OTISCA coal adds to process and operating costs. Economics are presented in Topical No. 3 of this contract.

Additional Bench-Scale tests with Illinois No. 6 coal addressed a solid separation technique and dispersed and supported catalysts.

Delayed coking was found to be an acceptable process for solid separation. There was, however, a penalty in the production of coke from the resid present in the heavy oil feed stream. Pre-dispersed iron and molybdenum catalyst were also evaluated using a pretreatment reactor plus two reaction stages. Favorable distillate yields were obtained. The present technique of dispersing iron in the total coal being fed would result in a prohibitive cost increase. Other more cost effective addition techniques are required.

During the bituminous portion of this program, a total of five bench runs encompassing over 62 operating days were completed. Supporting work has included laboratory studies and technical assessments. The major conclusions from the bench unit operations with the bituminous coal are highlighted below and discussed in detail in the body of this report.

- ◆ The tests with Illinois No. 6 coal cleaned by oil agglomeration had improved liquefaction performance, almost as good as had previously been established in tests with other cleaned Illinois No. 6 coals. Improved coal conversion, distillate yield, and product quality were achieved.
- ◆ The Illinois No. 6 coal cleaned by Otisca Industries also performed favorably and, in fact, produced products with the highest quality among all the runs with Illinois No. 6 coal. The limitations of using this cleaned coal were the necessity to remove the water from the coal slurry and the

high liquid recycle rates required to keep the coal slurry viscosity from becoming excessive. Partly because of the lower coal concentration, the coal conversion was not as high as had been achieved with the oil-agglomeration cleaned coal.

- ◆ A workable system for removing water from coal-water slurries was developed. Procedures using stripping nitrogen with maximum temperatures of 275°F were effective. Higher temperatures resulted in higher slurry viscosities and lower coal conversions.
- ◆ Delayed coking was shown to be applicable as the final solids-rejection and recycle-oil-formation step in CTSL operations. Additional distillate was produced in the coking tests with bench unit atmospheric bottoms, but additional solids were also formed from the resid, which could have been converted to more-valuable distillate if it had been recycled to the CTSL process.
- ◆ Pre-dispersed iron and dispersed molybdenum catalysts had definite catalytic effects in an otherwise thermal first stage reactor. A cost analysis would be required to determine if this potentially less expensive processing scheme has advantages over the CTSL process, which can have somewhat improved yields of higher quality products.
- ◆ The Akzo AO-60 catalyst was very nearly as active as the best previously tested catalysts and would be an acceptable catalyst in future CTSL operations.

RECOMMENDATIONS

Based on this series of Bench-Scale studies on Illinois No. 6 coal, further effort is required to reduce costs and/or improve yield and quality. Additional studies with oil agglomeration cleaned coals using coal derived liquids, other coking methods and with various coal preparation and pretreatment methods are recommended.

Specific areas for further studies are:

- Catalysis

Dispersed, soluble and supported catalysts have been used in coal liquefaction since the discovery of the technology. Research and Development activities are continuing in this area and new promising catalysts are becoming available. Present work with sub-bituminous and bituminous coals with soluble molybdenum and iron catalysts has shown promise and further testing is warranted.

- **Alternate Illinois Coals**

Under DOE's Two-Stage Coal Liquefaction Programs, many coals have been evaluated; however, the majority of testing has been on Illinois No. 6 Burning Star Mine #2 coal.

Coals of national interest that need to be evaluated utilizing the CTSL Technology are large reserves of high sulfur, high H/C ratio Illinois bituminous coals such as from the Monterey and Illinois No. 2 Seam will have low value under the new Clean Air Act of 1990. Assessment of these alternate Illinois coals will also lead to improved understanding of the effect of feedstock properties on process performance.

Coals containing less than 82% carbon, over 5% hydrogen, more than 75% reactive minerals and over 35% volatile matter on a moisture-ash free basis are preferred.

- **On-Line Hydrotreating**

On-Line Hydrotreating has been shown to be an economic method of upgrading coal derived naphtha through the utilization of available hydrogen pressures. In previous experiments on low rank coals, nitrogen levels were reduced from 1300 ppm to less than 10 ppm, and sulfur from 230 to less than 15 ppm.

This work needs to be continued on both a laboratory and bench-scale and with high sulfur bituminous coals. A study is recommended, particularly with a high sulfur Illinois or similar coal.

- **Promoters Hydrogen Sources and Pretreatments**

The effects of various concentrations of light and heavy distillates, off gases (CO, CH₄, CO₂, H₂S and NH₃), additives (SO₂) and pretreatments (thermal or CO₂, SO₂) have been studied to a very limited extent in continuous back-mixed systems. Knowledge of these effects with different coals and catalysts would be invaluable in direct liquefaction. H₂S addition has been found to improve conversion by as much as 50% on sub-bituminous coals, CO₂ improves coal conversion but also shifts to more gas and water production. Pretreatment with dispersed FeOOH and molybdenum salts also appears to enhance operability and yields.

- **Coal Slurry Feed Concentration**

Increasing the concentration of coal in feed slurries has a direct effect on capital cost since this influences preheat reactor and recycle system size. Coal-water slurries at concentrations of 70% are commercially pumpable

thus with coal derived oils at elevated temperature this concentration may be achievable.

- Other Process Improvements
 - Introduction of soluble homogeneous catalysts in combination with dispersed and/or supported catalysts.
 - The use of surfactants to increase diffusion and reaction rates for higher conversions at lower severity.
 - A two-stage experiment with in-line hydrotreating and bottoms coking with recycle of coker liquids; incorporating some of process concepts tested at the Bortrop Pilot Plant in Germany.
 - Tailored recycle streams - 1) Remove phenols and oxygenates from recycle oils, 2) extract nitrogen compounds, 3) introduce a light distillate that flashes at reactor conditions thus improving kinetics of coal and heavy oils.

BENCH UNIT STUDIES

Table 1 shows some of the conditions for all of the bench runs in which Illinois No. 6 bituminous coal was used. The objectives and basic conditions being tested are identified for each run. The results and conclusions are described below. These runs, with bituminous coal included CC-6, CC-8, CC-9, CC-14, and CC-16.

RUN 227-63 (CC-6) - OIL AGGLOMERATION CLEANED COAL

Run 227-63(CC-6) completed, as scheduled, 13 days of operation with Burning Star Mine Illinois No. 6 coal, both with material that had been cleaned by oil agglomeration to reduce the ash content to 4.6 W%, and run-of-mine uncleaned coal with 15.2 W% ash. The run conditions were selected to correspond to those of earlier Bench Unit CTSL operations with mine-cleaned coal containing 10.5 W% ash, with heavy-media cleaned coal with 5.3 W% ash, and with electrostatically cleaned coal with 4.9 W% ash.

Coal conversions with the agglomerated coal were high, about 1% higher than obtained with mine-washed coal, but about 1.5% lower than obtained with the two other cleaned coals. The run-of-mine coal gave coal conversions about 2% lower than were obtained with the agglomerated coal. This pattern is consistent with the expectation that the cleaning methods remove some of the less reactive portions of the organic coal along with the ash. However, it would appear that the agglomeration cleaning method does not reject as large a proportion of such constituents as by the other cleaning methods.

The coal conversion with the oil-agglomeration cleaned coal was higher than obtained earlier with mine-cleaned coal, but lower than those with the other low ash content cleaned coals. The conversion with the run-of-mine coal was the lowest obtained with the various coals tested. The total distillate oil yield in this run with the oil-agglomeration cleaned coal was higher than obtained in earlier comparable operations, because of relatively low residual oil yields, possibly associated with the change in catalyst preparation in using TNPS (tertiary nonyl polysulfide) as the presulfiding agent rather than DMDS (di-methyl di-sulfide).

RUN 227-66 (CC-8) - OTISCA PROCESS CLEANED ILLINOIS COAL

Run 227-66(CC-8) completed, as scheduled, 14 days of CTSL operation with Burning Star Mine Illinois No. 6 coal, both with material that had been cleaned by Otisca Industries by their proprietary process to reduce the ash content to 3.5 W% and uncleaned coal with 10.6 W% ash, which had been micronized and incorporated in a water slurry in preparation for the Otisca cleaning operation. The run conditions were selected to correspond to those of earlier Bench Unit CTSL operations with mine-cleaned coal containing 10.5 W% ash, with

heavy-media cleaned coal with 5.3 W% ash, with electrostatically cleaned coal with 4.9 W% ash and oil-agglomeration cleaned coal containing 4.6 W% ash.

The Otisca processed coals are produced in a water slurry containing 30-35 W% coal. A major part of the experimental effort was in developing a method of removing the water from this slurry while preparing a feed slurry using recycled solvent for feed to the CTSL unit. The solvent/coal slurries with the Otisca process coal proved to be of higher viscosity than those made with the other cleaned and uncleaned coals, so that to obtain a pumpable feed slurry the proportion of solvent to coal for the Run CC-8 operations was considerably higher than had been necessary in the earlier operations.

The coal conversions in Run CC-8 with the Otisca processed coal, after drying the coal/water slurry to a moisture content equivalent to about 1 W% of the dry coal content, were 2.5-4.0% lower than obtained with the other cleaned coals that have been tested, in part because of the high proportion of solvent recycle and in part because of apparently low reactivity of the coal after the severe slurry drying. Some operations with lower severity drying of the coal/water slurry, to an equivalent moisture content of 28 W%, had coal conversions that were higher by 2.5%. The general product distribution for the Otisca processed coal was similar to that which had been obtained with the other cleaned Illinois coals. The catalytic activity for hydrogenation and denitrogenation reactions in Run CC-8 was higher than had been obtained in earlier operations.

The OTISCA processed coal will probably entail increased operating costs because of the additional costs of the slurry drying that is needed and the relatively high proportion of recycle solvent that is needed to maintain feed slurry pumpability.

RUN 227-66E (CC-9) - PREPARATION OF PRODUCT SLURRY FOR DELAYED COKING TESTS

The primary objective of this run was to produce about 20 kg of atmospheric bottoms to evaluate an alternative solids-separation technique, namely delayed coking. This operation, as practiced in the petroleum industry, involves partial conversion of a heavy liquid into lighter liquid by rejecting carbon with the formation of solids and simultaneous separation of solids from liquids by vaporization. For it to be used effectively as a solids separation technique in coal liquefaction, it would have to be modified to give more emphasis to liquid recovery (less coke formation) relative to liquid quality.

Illinois No. 6 bituminous coal (of two different ash contents) was liquefied at a space velocity of 67 lb/hr/ft³ of catalyst in an eight-day extension of Run 227-66(CC-8). Atmospheric bottoms were collected at two conditions: first with the first and second reactor temperatures at 750 and 800°F, and then with the reactor temperatures at 775 and 810°F.

The coking tests were conducted at Foster Wheeler Development Corporation in a 4-inch diameter minicoker. They found that coal liquefaction bottoms could be processed by delayed coking; however, the coking temperature had to be significantly lower and the steam-to-feed ratio significantly higher than practiced commercially in the petroleum industry. About 85 W% of the liquid present in the coking feed was recovered. The liquid product had a low residuum content as most of the resid present in the feed was either converted to a lighter product or to coke.

The liquid product from delayed coking showed good coal liquefaction quality in microautoclave tests and would be suitable as recycle solvent. Using delayed coking as a solids separation operation would lead to overall higher residuum conversion if the residuum conversion in the liquefaction reactors is maintained. The major disadvantage of delayed coking is the conversion of resid, which could be converted to distillate in a CTSL extinction operation, to solids.

RUN 227-72 (CC-14) - EVALUATION OF A PRE-DISPERSED IRON CATALYST IN TWO-STAGE LIQUEFACTION

The objective of this run was to investigate the performance of predispersed iron oxide hydroxide catalyst in a thermal/catalytic reactor configuration, comparing it with the performance of dispersed molybdenum catalyst and with no catalyst in the first (thermal) reaction stage.

The initial work with Illinois #6 coal and this highly dispersed FeOOH catalyst was performed at PETC over several years by A. V. Cugini et al(1). Tests were conducted in 40-ml microreactors and then scaled to 1-liter bench-scale continuous units. The highly dispersed FeOOH catalyst showed very good activity at low concentrations (2,500 ppm) when compared with other dispersed iron and molybdenum catalysts.

The catalyst comparisons in Run 227-72(CC-14) were conducted with a pretreater at 527°F, the first liquefaction stage (without supported catalyst) at 825°F, and the second liquefaction stage (with Shell S-317 supported catalyst) at 775°F. The space velocity was 44 lb/hr/ft³ catalyst.

The results from Run 227-72(CC-14) indicated some catalytic effect for the FeOOH and Ammonium Tetrathiomolybdate dispersed catalysts; however, there were essentially no differences in the coal conversions, which ranged from 94 to 95 W% (maf). Distillate yields, which decreased from 75 W% of maf coal at the beginning of the run to 66 W% at the end of the run, were relatively high, but still less than the 77 W% that had been sustained in the process demonstration run 227-47(I-27).

After considering the deactivation of the supported catalyst, the 975°F+ conversions were slightly higher in the operations with the dispersed iron catalyst

and in the operations with the dispersed molybdenum catalyst, compared to the operations with no dispersed catalyst. The nitrogen removal declined at a slow, steady rate from 88% in Period 8 to 83% in Period 20, except that it was lower than this trend, 79%, when no dispersed catalyst was used in Period 17. In general, the product quality of the distillation fractions from the first liquefaction stage (with only dispersed catalyst) was the highest in operations with the molybdenum catalyst and lowest in operations without any dispersed catalyst, but the differences were small.

RUN 227-76 (CC-16) - EVALUATION OF AKZO AO-60 NICKEL-MOLY CATALYST

Run 227-76(CC-16) completed, as scheduled, 13 days of operation with Illinois No. 6 coal, testing the activity of Akzo AO-60 1/16" nickel molybdate extrudate catalyst in the CTSL process. The conditions for the run duplicated the conditions of three previous catalyst evaluation runs, which had tested 1/32" Amocat 1C extrudates, 1/20" UOP RCM4 spheres, and 1/32" Shell S-317 extrudates. These three catalysts had performed similarly and very well in Runs 227-35, -36, and -37 (I-16, -17, and -18).

The resid conversions and distillate yields for the AO-60 and the other catalyst were very similar. In Condition 1 (750°F first stage, 800°F second stage, and 46 lb/hr/ft³ catalyst/stage), resid conversion decreased from 88.4 to 82.9 W% of maf coal, and the C₄-975°F distillate yield decreased from 73.7 to 68.6 W% between Periods 4 and 9. In the higher severity Condition 2 (775°F first stage, 810°F second stage, and increased feed coal concentration), the resid conversion averaged 90.0 W%, and the distillate yield averaged 72.7 W%. The AO-60 catalyst did selectively produce slightly more naphtha and less vacuum gas oil and residuum than the other three catalysts.

In general, the product quality in Run 227-76(CC-16) with AO-60 catalyst was not quite as high as had been attained with the other three catalysts. The H/C ratio of the three heaviest oil fractions averaged 0.04 lower, and the nitrogen content of the two gas oil fractions averaged 0.03 W% higher for the AO-60 catalyst. However, the nitrogen content of the resid was only 0.68 W% in operations with the AO-60 catalyst compared to an average of 0.81 W% with the other three catalysts.

Overall, the AO-60 catalyst performed very well in the CTSL process. The slightly lower product-quality-improvement activity was somewhat offset by its slightly higher selectivity for lighter product formation. There was no apparent excessive physical degradation of the catalyst in this 13-day operation. Based on the information from this run, the AO-60 catalyst would be an appropriate catalyst for future CTSL operations.

The process performance of Akzo AO-60 1/16" NiMo extrudates was found very similar to that of Shell S-317 1/32" NiMo catalyst; however, they have different hydrodynamic behavior. Larger diameter 1/16" catalysts are favored for the rigors of PDU-Scale operation whereas due to equipment (pump) limitations the 1/32" catalysts perform with more safety at the Bench-Scale. An extensive Bench-Scale data base exists with S-317 extending from 1986, thus this catalyst will probably continue to be utilized at the Bench-Scale.

TABLE 1**Bench-Scale Runs**

Run No.	Days	Objective	Conditions	Remarks
227-63 CC-6	12	Test oil-agglomeration cleaned coal	750-800°F, 750/810°F 42 lb maf coal/hr/ft ³ catalyst	Increased conversion by 1.5% and distillate yield by 6%
227-65, 66 CC-8	17	Test "OTISCA" micronized cleaned after removing water from coal slurry	750/800°F, 775/810°F ~44 lb maf coal/hr/ft ³ catalyst higher ~2.0 oil/solids in feed	Improved conversion not as good as CC-6
227-66E CC-9	6	Produce slurry product to evaluate delayed coking as a solids-separation method	750/800°F, 775/810°F 67 lb coal/hr/ft ³ catalyst higher 2 to 2.6 oil/solids in feed	Delayed Coker conversion is 40% of resid to oil
227-72 CC-14	19	Evaluate PETC predispersed iron oxide hydroxide catalyst	Thermal/catalytic 800 or 825/775°F with 527°F pretreater 44 lb coal/hr/ft ³ catalyst Dispersed iron, molybdenum, or no catalyst	Yields @ mild temperatures equal to CTSL
227-76 CC-16	13	Evaluate Akzo AO-60 catalyst	750/800°F, 775/810°F 46 lb coal/hr/ft ³ catalyst 1.5 and 1.1 oil/solids in feed	Performance equal to that of Shell 317

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SECTION I

RUN 227-63 (CC-6) - OIL AGGLOMERATION CLEANED COAL

Run 227-63 (CC-6) completed, as schedule, 13 days of operation with Burning Star Mine Illinois No. 6 coal, both with material that had been cleaned by oil agglomeration to reduce the ash content to 4.6 W% and run-of-mine uncleaned coal with 15.2 W% ash. The run conditions were selected to correspond to those of earlier Bench Unit CTSL operations with mine-cleaned coal containing 10.5 W% ash, with heavy-media cleaned coal with 5.3 W% ash, and with electrostatically cleaned coal with 4.9 W% ash (see page 2 and reference 5, DOE-80002-T-2, September, 1988).

The coal conversion with the oil-agglomeration cleaned coal was higher than obtained earlier with mine-cleaned coal, but lower than those with the other low-ash-content cleaned coals. The conversion with the run-of-mine coal was the lowest obtained with the various coals tested. The total distillate oil yield in this run with the oil-agglomeration cleaned coal was higher than obtained in earlier comparable operations, because of relatively low residual oil yields, possibly associated with the change in catalyst preparation in using TNPS (tertiary nonyl polysulfide) as the presulfiding agent rather than DMDS (di-methyl di-sulfide).

SUMMARY

Coal conversions with the agglomerated coal were high, about 1% higher than obtained with mine-washed coal, but about 1.5% lower than obtained with the two other cleaned coals. The run-of-mine coal gave coal conversions about 2% lower than were obtained with the agglomerated coal. This pattern is consistent with the expectation that the cleaning methods remove some of the less reactive portions of the organic coal along with the ash. However, it would appear that the agglomeration cleaning method does not reject as large a proportion of such constituents as by the other cleaning methods.

The C₄-975°F distillate yield with the agglomerated coal was about 76 W% of maf coal. This yield was about 4 W% higher than had been obtained with the other cleaned coals, and 6 W% higher than with mine-washed coal. The largest part of the difference was in lower residual oil yield and lower residual oil concentrations in Run 227-63(CC-6) product liquids, which were about two-thirds as high as in both reference runs at a common catalyst age. The run-of-mine coal operation of Run 227-63(CC-6) had residual oil yields (concentrations) more nearly those observed in the earlier operations, although not quite as high. The improved catalyst performance was possibly associated with the change in pre-sulfiding procedure, the substitution of TNPS for DMDS.

SCOPE OF WORK

The oil agglomerated Burning Star Mine Illinois No. 6 coal used in this run was obtained from the Homer City, PA, facility of the Bechtel Group. The agglomerated material was reported to contain 1.93% agglomerating asphalt. An assay provided by Bechtel indicated 5.52% ash, while the samples of feed material to Run 227-63(CC-6) averaged 4.62 W% ash content (asphalt-free basis). The sample provided by Bechtel of the run-of-mine material from which the agglomerated coal had been prepared contained 15.2 W% ash.

The catalyst for both stages was Shell S-317 1/32" nickel molybdate on alumina extrudates, a commercially available catalyst, which had been presulfided using TNPS. Shell S-317 catalyst, presulfided using DMDS, had been used in earlier CTSL tests with mine-washed, and low ash cleaned Illinois Coal in Runs I-18, I-19, and I-27.

The operating conditions for the three conditions used during the run are summarized in *Table 1*.

The following table summarizes the conditions used in this run:

<u>Cond.</u>	<u>Days of Operation</u>	<u>Coal Feed</u>	<u>Temp. °F</u>		<u>PFL Recycle Lb/Lb Coal</u>
			<u>First</u>	<u>Second</u>	
1	1-4	Agglomerate	750	800	1.78
2	6-9	Agglomerate	750	810	1.30
3	10-13	Run-of-Mine	750	810	1.15

The coal feed rate for all of these operations was about 42 Lbs maf coal/hour/ft³ catalyst (stage).

Condition 1 corresponds to those of reference operations in the first part of Run 227-37(I-18) and in Run 227-39(I-19) with mine washed (10.5 W% ash), heavy media cleaned (5.3 W% ash), and electrostatically cleaned (4.9 W% ash) Burning Star Mine coal. The other two Conditions correspond to those of the final operations of Run 227-37(CC-18) and of the demonstration operation for this coal, using heavy media cleaned coal, of Run 227-47(I-27). The catalyst for the current run was fresh Shell S-317, presulfided using TNPS as the sulfiding agent. In the reference operations, this catalyst was used after presulfiding with DMDS as the presulfiding agent⁽⁵⁾.

Samples of the slurry circulating in the first stage were taken at the end of the Condition 2 and Condition 3 operations for use in evaluating the performance of the individual stages.

PROGRAM RESULTS AND ANALYSES

RUN 227-63 (CC-6)

This section discusses the conversions, product yields, process performance and product quality for Run 227-63(CC-6). *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.

Figures 1 to 5 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.

COAL CONVERSION

Figure 1 summarizes the coal conversions during Run 227-63(CC-6). For the Condition 1 operation, with the cleaned coal, coal conversions were 93.8-94.5 W% of maf coal. In the Condition 2 operation, with 10°F higher second stage temperature and solvent recycle/coal ratio lowered to 1.3 lbs/lb coal from 1.8 lbs/lb, coal conversions increased to 95.3-95.4 W% of maf coal. In the Condition 3 operation, with feed changed to Run-of-Mine coal, the coal conversions were 93.0-93.7 W% of maf coal.

The coal conversions during the Condition 1 and Condition 2 operations with the agglomeration-cleaned coal are very close to those that are projected using a correlation of coal conversions during CTSL operations with mine-washed Burning Star Mine coal, which contained 10.5 W% ash. The correlation assumed first order (with respect to the weight fraction of the reacting species) kinetics with three coal species, two of differing reactivities and an unreactive third species. The key correlating parameters were as follows:

Coal Distribution	
High Reactivity	0.905
Low Reactivity	0.060
Unreactive	0.035
Reaction Rates at 750°F	
Lbs/Hr/Ft ³	
High Reactivity	1790
Low Reactivity	11.95
Activation Energy, Kcal/Mole	
Both Reactive Components	53.8

Applying these parameters to the operating conditions of Run 227-63(CC-6) gave the following results:

Condition	Coal	—— Conversions ——	
		Projected	Experimental
1	Cleaned	94.5	94.1-94.5
2	Cleaned	95.3	95.3-95.4
3	Run-of-Mine	95.2	93.0-93.7

This comparison indicates that the earlier correlation for mine-washed coal applies closely to the oil-agglomeration cleaned coal results, particularly with respect to the proportion of inert coal. However, the projection for the Run-of-Mine Coal deviates from the experimental values by more than the probable error of the conversions.

Apparently, the higher conversion with the cleaned coal is because some low reactivity or unreactive species have been selectively removed along with ash in the cleaning operation. This single data point cannot resolve the various alternatives. However, if the run-of-mine coal was assumed to contain 5.0% unreactive macerals, rather the 3.0%, then the projected conversion would be 93.7% for the Condition 3 operation.

This analysis also indicates the cleaning by mine-washing results in some selective removal of low reactivity species, but the incremental cleaning by oil-agglomeration has no further removal of such species.

Table 3 summarizes petrographic analyses of the two coal feed 5 to Run 227-63(CC-6) and their reflectance analyses along with reflectance analyses of the solids products from the three Conditions of the run. These analyses are virtually identical for the two coal feeds. However, they present an interesting pattern in that the low reflectance materials, corresponding to vitrinite, were very highly converted (98.0-99.6%). The intermediate reflectance materials, corresponding to liptinite and semi-inertinite, were appreciably converted, 74-92.5% with the cleaned coal, and 56-68.5% with the run-of-mine coal. The highest reflectance materials, corresponding in quantity to inertinite, were converted to a degree, 61.6-63.4% and 52.0% for the two coals.

The pattern of the change in conversion of the various reflectance cohorts between Periods 4 and 9 of the run, where the conversion severity was increased by raising the second stage temperature 10°F and lowering ratio of PFL recycle, indicates that cohorts up to 2.5% reflectance are possibly completely convertible, while the highest reflectance cohort (inertinite) is partially converted but contains a component, about 2.0% of the cleaned coal and 2.6% of the run-of-mine coal, which is unreactive. This proportion of unreactive coal is slightly lower than the

values, 3-5%, indicated by correlation of the coal conversion data from CTSL operations on Illinois No. 6 coal. These reflectance analyses indicate that the coal cleaning selectively removed some inert coal, and a portion of the low reactivity components.

PRODUCT DISTRIBUTION

Figure 2 compares, for the three Conditions of Run 227-63(CC-6), the cumulative yields, on a moisture-ash free basis, of the C_4^+ distillate and residuum. *Figure 3* compares the yields of each of the major distillate product fractions. *Figure 4* is a similar comparison of the other major products for the run.

The C_4 -975°F yield for the Condition 2 operation, with the washed coal, was the highest of the run, 76.2 W% of maf coal, 1.3 W% higher than for the Condition 1 operation, and 8.4 W% higher than for the Condition 3 operation, with the run-of-mine coal. This difference in Condition 1 and Condition 2 results corresponded to the increased coal conversion for the Condition 2 operation because of the lower solvent recycle rate and higher second stage temperature of that Condition. The largest part of the difference in Condition 2 and Condition 3 results corresponded mostly to lower coal conversion (1.6 W%) and higher residual oil yield (3.6 W%) of the operation with the run-of-mine coal, but the difference in residual oil yields was probably not due to a difference in coal feed, but rather due to the higher catalyst age of the final Condition 3 operations (see below).

In the Condition 2 operation there was a slightly higher proportion of C_4 -390°F naphtha product, and lower proportion of 650-975°F product than in the Condition 1 operation by 3-5 W% of maf coal, possibly because of the slightly higher severity of the Condition 2 operation. In Condition 3 operation, there was a slightly lower yield of each of three major distillate product fractions, approximately in the same proportion so that the distribution was virtually the same as in the Condition 2 operation.

Normalized C_1 - C_3 gas yields ranged from 7.6 to 8.9 W% of maf coal for the three Conditions of the run. The average gas yield of the run was about 0.5 W% higher than projected from the correlation of the gas yields of earlier operations with mine-washed Illinois coal. However, the differences in gas yields for the three conditions of the run did not correspond to the projected impact from the correlation. The increased severity of the Condition 2 operation compared to that of Condition 1 was expected to cause an increase in this yield of about 1 W%, whereas experimentally the yields were the same. The change from cleaned coal to run-of-mine coal between Condition 2 and Condition 3 was expected to result in virtually the same gas yield on an maf basis, while the experimentally this gas yield increased by 1.3 W%. The gas yield for Condition 2 corresponded most closely to the expected yield. Actually, this scatter from the correlation, a mean square deviation of 0.8 W%, is not appreciably different from the standard error of the correlation, about 0.7 W% yield for the correlation which had R-squared

value (variance removal) of 0.909. Consequently, there is no strong evidence of differences in gas yields for the run-of-mine, mine-washed, and oil-agglomeration cleaned coals.

975°F residual oil yields increased progressively through the run from Condition 1, to Condition 2, to Condition 3, from a level of 2 W% of maf coal up to 7 W%. This pattern corresponds to the normal deactivation pattern for previous CTSL operations. *Figure 5* is plot of the concentration of residual oil against time of coal operations for the run. The change in this concentration during the three modes of operation of the run follow a common trend, increasing by 1.5 W% per day of coal operations. This rate of increase is greater than in earlier run (I-18) with mine-washed Illinois coal and the shell S-317 catalyst, 1.2 W% per day. However, this difference in the trends of the two runs reflects lower residual oil concentrations (nominally, higher catalyst activity) for the first operations of Run 227-63(CC-6), and approximately equal concentrations at the end of the run.

Water yields were in the same range, 11-13 W% of maf coal, with the oil-agglomeration cleaned coal and the run-of-mine coal.

Hydrogen consumptions, calculated by comparison of the hydrogen contents of the feed and products, with the two coal feeds were virtually the same at about 7.5 W% of maf 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 227-63(CC-6) 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 heavier liquid product fractions are graphically summarizes in *Figure 6*.

The hydrogen contents of the heavier liquid product fractions declined progressively throughout Run 227-63(CC-6), by 0.4-0.5 W% in the IBP-650°F and 650-850°F fractions in the PFL product (recycle solvent), and by 1.0-1.1 W% in the 850-975°F and residual oil fractions.

These hydrogen contents correspond very closely, within 0.1 W%, to those of the same product fractions from Run I-27 (over the same interval of the two runs), which was with the Shell S-317 catalyst and Illinois Coal that had been cleaned

to 5.8 W% ash content by float-sink gravity separation. However, the downward trend in hydrogen contents was greater in Run 227-63(CC-6) than in Run I-18, with the Shell S-317 catalyst and mine-washed Illinois coal containing 10.6 W% ash. The hydrogen contents, which were virtually the same for the first operations of the two runs, declined slower in Run I-18, so that by the thirteenth day of the two runs the decline was about 1/2 to 2/3 as great.

The hydrogen contents of the lower boiling products from Run 227-63(CC-6) for the final operation of Condition 3, with the run-of-mine coal, were 0.2-0.3 W% lower than for the initial operations of Condition 1 with the cleaned coal. However, the hydrogen contents for the Condition 2 operations were still lower by 0.1-0.3 W%. The hydrogen contents of these products were about 0.2 W% higher, on the average, than for the products of the same boiling range from Run I-18, which processed the mine-washed coal.

Nitrogen Contents

The nitrogen contents of the heavier liquid product fractions are graphically summarized in *Figure 7*.

The nitrogen contents of the heavier liquid product fractions increased progressively through Run 227-63(CC-6), by factors of 1.2 to 1.9 (more markedly for the heaviest products) between the fourth and twelfth days. For the most part, these nitrogen contents are higher than in the same product fractions for Run I-18 (with mine-washed coal) and Run I-27 (with heavy-media cleaned coal), although the proportional changes with increasing catalyst age were of the same order. The average of these nitrogen contents for Run 227-63(CC-6) were higher by 0.05-0.15 W% than during the other two runs.

Similarly, in Run 227-63(CC-6) the nitrogen contents of the lower boiling separator overhead and atmospheric overhead products increased progressively through the run, by factors of 3-4.

Sulfur Contents

Sulfur contents of the liquid products in run 227-63(CC-6) were generally low, generally less than 0.04 W%. *Table 6* summarizes the distribution of sulfur in the liquid and solid products for the run. The sulfur retained in the liquid products was only 0.4 to 1.7% of the organic sulfur in the feed coal. The sulfur in the solids products corresponded to about 50% conversion of the original pyritic sulfur to hydrogen sulfide.

These trends of the product analyses indicate that 1) the removal of mineral matter by washing does not appreciably decrease the rate of catalyst deactivation and 2) the catalytic effect of the mineral matter in the run-of-mine coal is very small.

COMPARISON WITH PERFORMANCE OF OTHER CLEANED COAL

Table 7 compares the results of Run 227-63(CC-6), processing oil agglomeration cleaned coal, with those of earlier runs that processed Illinois No. 6 coal that had been cleaned by float-sinking heavy media separation.

Coal conversions with the oil-agglomeration cleaned coal was 1-1.5% lower than with the heavy media cleaned coal.

The C₄-975°F distillate yield in the operation with oil-agglomerated coal in Run 227-63(CC-6) was intermediate, plus and minus 3 W% of maf coal, between those of two runs with Heavy-media cleaned coals. The difference from the higher yields of Run I-27 was principally because of the bottoms "extinction" effort of that run, in which the oil in the filter cake product was extracted and recycled (which was not done in Run CC-6). The lower C₄-975°F yields of Run I-19 (which did not involve oil recovery from the filter cake) reflected a relatively high residual oil yield in that run, in part due to the apparently poorer residual secondary oil kinetic performance which required higher residual oil concentrations in the product PFL, see above, and in part because of high oil (PFL) retention on filter cake in that run which increased the amount of PFL liquid withdrawn as product and reduced the amount of residual oil available for recycle. The following tabulation summarizes the oil retention of the product filter cake for the three runs;

Filter Cake in Run CC-6 contained 50.4 W% oil (cleaned)
37.6 W% oil (ROM)

Filter Cake in Run I-19 contained 62.5 W% oil

Filter Cake in Run I-27 contained 50.5 W% oil (Period 8)
53.6 W% oil (Period 16)
69.5 W% oil (Period 25)

It is not certain that the high oil retention of Run I-19 is solely associated with the type of coal cleaning, since in Run I-27 there was a wide range of such oil retention. The trend in retained oil during Run I-27 was associated with some increase in degree of coal conversion (increasing from about 95.5% to 97%), composition of the oil being filtered (increasing from 30 W% residual oil to 50% residual oil), and increased filtration temperatures (250°F to 375°F). The filtration conditions of Runs I-19 and CC-6 corresponded to those of Run I-27 where there was the lowest proportion of oil retention on the filter cake.

The proportion of C₄-390°F product in Run 227-63(CC-6) was slightly higher than in the runs using the heavy media cleaned coals at 20-22 W% of dry coal compared to 17-18 W%, but the heavy gas oil (650-975°F) yield was comparable to that of Run I-19, which was a comparable operation without the "extinction" feature of Run I-27.

In general, the differences in performance with the oil-agglomeration cleaned and heavy media cleaned coals were relatively small, and the choice between them would be based principally upon the relative cost of the two methods of coal cleaning.

FIRST STAGE SLURRY ANALYSES AND INTERPRETATION

Samples of the first stage slurry were obtained during the Condition 2 and 3 operations of Run 227-63(CC-6). 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 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.

Table 9 interprets these 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* 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.

Note that 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 runs from the previous CTSL program, where it was assumed the first stage vapor flows equaled the second stage vapor flows.

COAL CONVERSION

The coal conversion after the first stage for Condition 2 operation with cleaned coal operations was 89.2 W% of maf coal, and it was 90.8 W% for the Condition 3 operation with the run-of-mine coal. The Condition 2 first stage conversion level is about 1.5 W% lower than that projected using the model parameters summarized above in the section concerning overall coal conversions. The Condition 3 first stage conversion was 0.5 W% higher than projected using the correlation.

RESIDUAL OIL FORMATION

The pattern of residual oil formation/conversion was similar to that observed in earlier runs with the Illinois coal. There was a net formation of residual oil in the first stage corresponding to 15-20% of the dry coal fed, and a net consumption of residual oil in the second stage of 10-15% of dry coal fed, leaving a net production of residual oil.

The pattern of residual oil formation/conversion was similar to that observed in earlier runs with the Illinois coal. There was a net formation of residual oil in the first stage corresponding to 15-20% of the dry coal fed and a net consumption of residual oil in the second stage of 10-15% of dry coal fed, leaving a net production of residual oil of about 5 W% of dry coal fed. The earlier results have been correlated as indicating a primary formation of residual oil of 60.5 W% of the coal reacted, with its secondary reaction to lower boiling products at rates that are a function of temperature and catalyst age (deactivation particularly in the second stage). The principal reason for the relative formation/conversion values in the first and second stages is that there is a high proportion of primary formation in the first stage associated with the large proportion of coal reacted in that stage.

The formation of residual oil in the first stage during Run 227-63(CC-6) was relatively low compared to the values observed in Runs I-12 and I-13, with mine washed coal, where the range of formation was 20-30% of dry coal fed at comparable conditions. This difference is reflected in the apparent first order reaction rate constants of the secondary reaction of the residuum, which are summarized in *Table 11* for the current operations and for the earlier operations with mine-washed coal and heavy media washed coals. The apparent rate constant for the Run 227-63(CC-6) operation with oil-agglomeration cleaned coal was the highest of all the values calculated. Statistical analysis of these data indicate the following impacts of the variables indicated in *Table 11*:

- A) These residual oil reaction rate constant for the oil-agglomeration cleaned coal and the heavy-media cleaned coal were significantly higher than for the mine-washed coal (99.7% and 99.3% statistical confidence levels) by factors of 1.7 and 1.4, respectively. However, the difference in the rate constants for the two types of cleaned coals was not statistically significant (79.5% confidence level);
- B) The performance of run-of-mine coal was not appreciably different from that of mine-washed coal. The difference in the rate constants by a factor of 1.25 has a confidence level of 74.9%;
- C) The two catalysts involved gave virtually the same performance in these terms, with a ratio of 1.05 in averaged rate constants having a statistical confidence level of 40.9%;

- D) There is fair correlation of the reaction rate constants against reactor temperature, with an indicated increase by a factor of about 1.15 in rate constants at 775°F compared to 750°F (an activation energy of 10,000 cal/gram mole), having a statistical confidence level of 91.9%.

HYDROGEN CONTENT

The hydrogen contents of the oil fractions of the liquids in the first and second stages show a mixed pattern. For the lowest boiling components (up to 850°F boiling point) the hydrogen contents in the second stage were higher than in the first stage, by 0.1-0.3 W%, while for the residual oil component the second stage hydrogen contents were lower by 0.1-0.3 W%. In general, there was more hydrogen content increase (or less decrease) between the two stages during the Period 12 operation with run-of-mine coal.

In terms of relative stage performance these results indicate slightly better second stage hydrogenation performance than obtained with earlier runs with Illinois coals. The following tabulation compares average changes in hydrogen content (second stage less first stage values) for various runs:

Run	CC-6	I-12	I-13	I-18	I-19	I-27
Coal	Oil Aggl. R-O-M	Mine Washed	Mine Washed	Mine Washed	Heavy Media	Heavy Media
Catalyst						
Stage 1	S-317	Amoc IC	Amoc IC	S-317	S-317	S-317
Stage 2	S-317	Amoc IA	Amoc IC	S-317	S-317	S-317
H ₂ Diff. %						
650-850°F	+0.18	-0.21	0.00	-0.24	-0.03	+0.07
850-975°F	0.00	-0.12	-0.10	-0.14	-0.21	+0.04
975°F+	-0.12	-0.24	-0.024	-0.29	-0.07	+0.17

While the Run CC-6 results correspond to less dehydrogenation in the second stage compared to the various results with mine-washed coal, the scatter of the individual data points (a standard error of about 0.19 W%) indicates very low statistical significance to such a difference.

However, these changes in hydrogen content between stages for all of the operations with Illinois Coal are more moderate than was observed in Runs CC-1, CC-2 and CC-6 with Black Thunder Mine sub-bituminous coal. The following tabulation compares the averages of the changes in hydrogen content (second stage content less first stage content) for all of the available data for the two types of coals (11 data points for the Black Thunder Coal, and 22 data points for the Illinois coal):

Fraction	Black Thunder	Illinois
650-850°F	- 0.23	- 0.10
850-975°F	- 0.45	- 0.12
975°F+	- 0.76	- 0.21

Statistically, the difference between the two coals, with an average of 0.45 W% greater second stage dehydrogenation with the Black Thunder coal, has a confidence level of over 99.9%. A possible reason for the greater impact with the Black Thunder Coal is that a higher proportion of the coal is reacted in the second stage (20-25% of the maf coal compared to 3-10% for the Illinois Coal). The higher conversion would result in increased hydrogen donor consumption, and also the generation of relatively low hydrogen content components.

NITROGEN CONTENTS

In Run 227-63(CC-6), nitrogen contents in the product fractions in the second stage liquid were lower than those in the first stage liquids, by factors of 0.5-0.9. The proportion of denitrogenation was generally lower for the Period 12 operation with the run-of-mine coal, and also for the higher boiling product fractions.

This pattern of denitrogenation corresponds to that of Runs I-19 and I-27, with heavy-media cleaned Illinois coal, over the same span of catalyst ages. The operations with mine-washed Illinois coal in Runs I-12, I-13, and I-18 did not exhibit a clear cut pattern of second stage denitrogenation. In Runs CC-1 and CC-2, with Black Thunder Mine coal, there was second stage denitrogenation comparable to that of Run 227-63(CC-6) over the same span of catalyst ages, but which deteriorated at higher catalyst ages.

DETAILS OF OPERATIONS

This report summarizes the operations of Run 227-63(CC-6) in the CTSL bench unit, using Burning Star Mine Illinois No. 6. Coal cleaned by an oil-agglomeration technique at the Homer City, Pa. facility of the Bechtel Group was fed during Conditions 1 and 2, and the Run-of-Mine Coal from which the cleaned coal had been prepared was fed during Condition 3. 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 mine-washed coal, and heavy media cleaned Illinois No. 6 Coal.

Run 227-63(CC-6) completed 291 hours of operation with the cleaned and Run-Of-Mine coal.

The principal operating problem during the run was a 74-minute power interruption to the R&D center in the fifth day (102 hours) of the run. The emergency power generation system was used to maintain flows through the unit during the power interruption. Reactor temperatures were lowered by 25°F, and start-up oil was pumped to the unit while stabilizing the unit after the interruption before resumption of normal operations with coal feed and recycled solvent using the second set of operating conditions that were to be used. However, subsequent to the power outage there were appreciable increases in pressure drops, first up to 50 psi over the second stage in the seventh day, but moderating to normal level of 7 psi in the 11th day. Later, in the eighth day first stage pressure drop increased to 100 psi, and continued to be high until the end of the run when it had reached 180 psi. Nevertheless, operations were smooth during this interval.

OPERATIONS

Preoperational Procedures - Operations were started using HRI 5648 vacuum distillate 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 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*. 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. However, this first sample was not obtained at the end of the Condition 1 operations, because of the interruption of operations caused by the power-failure.

Condition 1 (Periods 1 through 4) - This operation was with the oil-agglomeration cleaned coal, having an ash content of 4.62 W%. The

operating conditions were the same as had been used in Run 227-39(I-19), which evaluated mine-washed Illinois coal (10.55% ash), and coals that had been cleaned by float-sink heavy media separation (5.33% ash) and by electrostatic treatment (4.93% ash).

Condition 2 (Periods 6 through 10A) - This operation continued the use of the cleaned coal, with the oil recycle lowered to 1.3 lbs/lb coal from the earlier rate of 1.8 lbs/lb coal and with the second stage temperature increased from 800°F to 810°F. The lower solvent recycle rate had been used in Runs 227-37(I-18), which tested mine-washed Illinois Coal, and 227-47(I-27), which tested heavy-media float sink cleaned Illinois Coal in the demonstration operation where the high boiling liquid products were virtually eliminated from the net product distribution by adjusting the recycle solvent composition.

Condition 3 (Periods 10B-13A) - The feed coal for this operation was the Run-of-Mine Illinois coal, containing 15.21 W% ash, that had been used to prepare the oil-agglomeration cleaned coal. The operating conditions were the same as during the Condition 2 operation, except the dry coal feed rate was adjusted to result in the same moisture-ash-free coal feed rate.

During the inspection after the run, the entire catalyst bed in the first stage was found against the outlet screen at the top of the reactor. The catalyst was removed from the first stage reactor only after heating it to 400°F and applying a pressure of 1500 psig. Possibly, this displacement of the catalyst was a consequence of the power-outage upset in the fifth day of the run. However, excessive pressure drop across the first stage reactor, a possible indicator of a development of fixed bed of catalyst, was not apparent until the eighth day of the run, at which time no associated operating problems were reported.

The catalyst in the second stage reactor was found in the normal settled position, settled to a position corresponding to a loss of about 7% of the catalyst charged. The catalyst flowed freely from the second stage reactor.

The internal recycle lines and pumps, and the downstream equipment were found in good condition, free of significant accumulations of solids.

COAL FEED

The oil-agglomeration cleaned coal and the Run-of-Mine coal were received from the Homer city, Pa. facility operated by the Bechtel Group immediately prior to the start of Run 227-63(CC-6). *Table 12* summarizes the analyses of the two coal feedstocks, and *Table 3* summarizes their petrographic and reflectance analyses and the reflectance analyses of the solids product from

Run 227-63(CC-6). The coal was prepared using a spherical agglomeration procedure that consists of a two-step process, high shear treatment with heptane then a low shear with asphalt to form large agglomerates for separation⁽⁷⁾.

The agglomeration cleaned coal contained about 30% moisture as received and was dried in a nitrogen swept tray oven at 200°F to an average moisture content of 6.8 W%, requiring 8-10 hours. The dried coal was stored in drums under nitrogen blanket until fed to the bench unit. The Run-of-Mine coal was crushed to -1/2 inch, ground to pass a 70 mesh screen in a micropulverizer, and then similarly dried to an average water content of 2.5 W%.

The oil-agglomeration cleaning reduced the ash content to 4.62 W% from 15.2 W%. On a moisture-ash-free basis the hydrogen to carbon ratio, the nitrogen content, and the nominal oxygen content (by difference) were minimally different for the two feed materials. There was about one-fourth less sulfur in the oil-agglomeration cleaned coal, which contained about one-third as much pyritic sulfur, roughly in the proportion of the ash contents, and apparently a possibly slightly higher proportion of organic sulfur (on an maf basis), by a factor of 1.15. The petrographic maceral analyses, as well as the reflectance analyses, for the two coal feeds were virtually identical, indicating that low-reactivity inertinite components had not been selectively removed during the cleaning. However, the reflectance analyses of the product solids indicate that liptinite/semi-inertinite/inertinite components remaining in the cleaned coal were the more reactive portion of these components.

Microautoclave evaluation of the two coal feeds, indicated appreciably higher conversion for the Run-of-Mine coal in the test in which no catalyst was used. However, when S-317 catalyst was used in the microautoclave tests, considerably higher conversions, which were virtually the same for the two coal feeds, were obtained. Apparently, there was some catalytic impact of the higher ash/pyrite content of the Run-of-Mine coal, but the contribution of this factor was relatively minor in the presence of liquefaction catalyst.

START-UP/MAKEUP OIL

The start-up oil for Run 227-63(CC-6) was a heavy distillate, HRI 5648 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. A small amount of this oil was also used as a makeup oil. *Table 13* summarizes the analyses of the HRI 5648 oil.

The solvent quality evaluations of this oil were relatively high, 70.1% conversion in the test using Illinois No. 6 Coal, compared to a range of 53.4% to 70.2% for other solvent used as start-up oils, and 61.5% conversion in the test using Black Thunder Mine sub-bituminous coal, where the range has been 51.7 to 65.9% for the other solvents.

The HRI 5648 oil has a hydrogen content of 10.01 W%, approximately the same as the recycled oils of the same boiling range that were produced in the first operations of Run 227-63(CC-6). The nitrogen content of HRI 5648 oil, 0.46 W%, was almost twice that of the equivalent fraction of the recycled solvent.

FRESH CATALYST

The catalyst used in both stages for Run 227-63(CC-6) was Shell S-317, 1/32" extrudate, nickel-molybdate on alumina. The designation was HRI No. 5394, the same lot that had been used in previous CTSL operations with Illinois Coal, Ohio Coal and Black Thunder Mine Coal. The inspections on the fresh catalyst are presented in *Table 14*.

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). TNPS was used as the sulfiding agent, in place of DMDS (Dimethyl Disulfide) which had been used in preparing catalyst for earlier CTSL operations with Illinois coal 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 227-63(CC-6) are given in *Table 15*.

The catalyst recovery from the first stage reactor was 79% based on the relative volumes of charged and recovered +20 mesh oil-free catalysts, and 84% 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 5% of the amount of molybdenum in the catalyst charged.

The carbon accumulation on the recovered catalyst from the second stage reactor, 15.1 W%, was somewhat higher than on first stage catalysts after earlier operations with Illinois Coal and S-317 catalyst, 9.5-14.7 W%. Metals contaminants accumulation was low, a total of 1.37 W%, with sodium as the largest component. The sulfur content of the recovered catalyst was 87% of the amount corresponding to formation of MoS₂ and NiS.

The catalyst recovery from the first stage reactor was 80% based on the relative volumes of charged and recovered +20 mesh oil-free catalysts, and 73% 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 11% of the amount of molybdenum in the catalyst charged.

The carbon accumulation on the recovered catalyst from the second stage reactor, 22.2 W%, was somewhat higher than on the second stage catalysts after earlier operations with Illinois Coal and S-317 catalyst, 13.8-19.6 W%. Metals contaminants accumulation was low, a total of 1.55 W%, with titanium as the largest component. The sulfur content of the recovered catalyst was 103% of the amount corresponding to formation of MoS_2 and NiS .

TABLE 1

RUN 227-63(CC-6) OPERATING CONDITIONS

Catalyst - Shell S-317 (HRI 5394) in Both Stages
 Coal Feed - Burning Star Mine Illinois No. 6 Coal
 Oil-agglomeration cleaned, and Run-of-Mine

CONDITION	1	2	3
PERIOD (DAYS)	1A-4B	6A-10A	10B-13A
COAL FEED	Cleaned	Cleaned	R-O-M
W% Ash	4.62	4.62	15.27
NOMINAL CONDITIONS			
Unit Pressure, Psig	2500	2500	2500
Coal, Lb(dry)/hr/ft ³ (catalyst)			
First Stage	44	44	48
Second Stage	44	44	48
Coal, Lb(maf)/hr/ft ³ (catalyst)			
First Stage	42	42	42
Second Stage	42	42	42
Solvent Recycle, Lb/Lb Coal			
Filtered Liquid	1.8	1.3	1.1
Makeup Oil (HRI 5648)	0	0.03	0.03
Topped Separator Bottoms	0	0	0
Oil/Solids in Feed	1.7	1.2	1.0
Atmos. Still, Temp., °F (Vapor)	500	500	500
Reboiler	600	625	625
H ₂ S, W% of Dry Coal	0	0	0
Reactor Temperatures, °F			
First Stage	750	750	750
Second Stage	800	810	810

RUN 227-63 OPERATING SUMMARY

TABLE 2
Part 1 of 2

BENCH-SCALE TWO STAGE COAL LIQUEFACTION

COAL: ILLINOIS NO. 6--Periods 1-9: Oil Agglomeration Cleaned Illinois No. 6 (NRI 5716)

--Periods 10-12: Run of Mine Illinois No. 6 (NRI 5715)

CATALYST: Both Stages: SHELL S-317 NiMo 1/32" Extrudates (NRI 5394)

Period Number	1	2	3	4	5	6	7	8
Date (Start of Period)	12/15/89	12/16/89	12/17/89	12/18/89	12/19/89	12/20/89	12/21/89	12/22/89
Hours of Run (End of Period)	24.	48.	72.	96.	117.	141.	165.	189.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	18.	47.	77.	106.	127.	153.	179.	206.
Coal Type	----- Cleaned -----							

TEMPERATURES, F

First Stage Reaction	725.	750.	750.	751.	731.	749.	750.	750.
Second Stage Reaction	778.	801.	802.	800.	782.	808.	812.	810.
Slurry Mix Tank	192.	189.	191.	191.	195.	197.	212.	255.

PRESSURES, PSIG

Unit Back Pressure	2530.	2528.	2529.	2529.	2534.	2535.	2533.	2520.
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SPACE VELOCITIES

Dry Coal Sp. Vel. - Stg. 1, Lb/Hr/Ft ³ Catalyst	29.7	46.3	47.7	46.5	40.2	41.9	41.9	43.5
Dry Coal Sp. Vel. - Two-Stage, Lb/Hr/Ft ³ Catal.	14.4	23.2	23.8	23.2	20.1	21.0	21.0	21.8

RECYCLES, W% OF DRY COAL

Pressure Filter Liquid	197.3	169.4	169.4	169.4	148.5	119.5	113.0	120.4
PFL to Buffer - Stage 1	5.5	3.9	4.9	4.0	6.2	5.2	4.8	5.0
PFL to Buffer - Stage 2	6.1	4.5	4.4	4.3	6.0	5.0	5.2	5.9
Separator Bottoms	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Make-up Oil (NRI 5648 + Oil on Coal)				-1.8				-4.5
TOTAL MATERIAL RECOVERY (GROSS)	98.94	100.74	98.95	99.35	110.07	97.79	98.58	98.42

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C1-C3 in Gases	7.57	7.31
C4-C7 in Gases	3.96	4.01
IBP-390 deg-f in Liquids	15.86	19.14
390-500 deg-f in Liquids	11.09	12.19
500-650 deg-f in Liquids	22.40	24.98
650-850 deg-f in Liquids	14.36	11.42
850-975 deg-f in Liquids	3.83	1.19
Toluene Soluble 975F+ Oil	1.91	1.48
Toluene Insoluble 975F+ Oil	0.03	0.20
Unconverted Coal	5.28	4.45
Ash	4.62	4.62
Water	12.04	12.07
CO	0.04	0.05
CO2	0.04	0.04
NH3	1.67	1.57
H2S	2.52	2.51
Total (100 + H2 Reacted)	107.23	107.21

PROCESS PERFORMANCE

C4-975 deg-f Distillates, W% of MAF Coal	75.0	76.5
975F+ Conversion, W% MAF	92.4	93.6
Coal Conversion, W% MAF	93.8	94.1
HDS, W%	81.6	81.4

BENCH-SCALE TWO STAGE COAL LIQUEFACTION

COAL: ILLINOIS NO. 6--Periods 1-9: Oil Agglomeration Cleaned Illinois No. 6 (HRI 5716)

--Periods 10-12: Run of Mine Illinois No. 6 (HRI 5715)

CATALYST: Both Stages: SHELL S-317 NiMo 1/32" Extrudates (HRI 5394)

Period Number	9	10	11	12	13
Date (Start of Period)	12/23/89	12/24/89	12/25/89	12/26/89	12/27/89
Hours of Run (End of Period)	213.	237.	261.	285.	291.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	233.	261.	289.	319.	327.
Coal Type	Cleaned	-----	Run-Of-Mine	-----	-----

TEMPERATURES, F

First Stage Reaction	753.	751.	750.	749.	748.
Second Stage Reaction	811.	810.	811.	812.	799.
Slurry Mix Tank	299.	314.	300.	283.	282.

PRESSURES, PSIG

Unit Back Pressure	2521.	2525.	2526.	2524.	2526.
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SPACE VELOCITIES

Dry Coal Sp. Vel. - Stg. 1, Lb/Hr/Ft ³ Catalyst	43.8	44.4	45.6	48.0	51.2
Dry Coal Sp. Vel. - Two-Stage, Lb/Hr/Ft ³ Catal.	21.6	22.2	22.8	24.0	25.6

RECYCLES, W% OF DRY COAL

Pressure Filter Liquid	120.4	111.6	102.1	103.8	106.5
PFL to Buffer - Stage 1	5.3	5.6	5.4	5.2	4.1
PFL to Buffer - Stage 2	5.3	6.3	5.4	5.3	4.0
Separator Bottoms	0.0	0.0	0.0	0.0	0.0
Make-up Oil (HRI 5648 + Oil on Coal)	-4.0			-4.6	

TOTAL MATERIAL RECOVERY (GROSS)

	96.97	100.58	98.27	100.51	96.65
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ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C1-C3 in Gases	7.28		7.57
C4-C7 in Gases	3.94		3.28
IBP-390 deg-f in Liquids	18.36		14.35
390-500 deg-f in Liquids	10.93		9.09
500-650 deg-f in Liquids	22.14		20.06
650-850 deg-f in Liquids	14.65		10.59
850-975 deg-f in Liquids	2.67		0.98
Toluene Soluble 975F+ Oil	4.32		5.22
Toluene Insoluble 975F+ Oil	0.56		0.77
Unconverted Coal	4.43		5.34
Ash (SO ₃ -free)	4.62		15.21
Water	8.96		9.59
CO	0.05		0.07
CO ₂	0.04		0.04
NH ₃	1.56		1.35
H ₂ S	2.51		2.74
Total (100 + H ₂ Reacted)	106.99		106.25

PROCESS PERFORMANCE

C4-975 deg-f Distillates, W% of MAF Coal	76.2		68.8
975F+ Conversion, W% MAF	90.2		86.6
Coal Conversion, W% MAF	95.4	93.0	93.7
HDS, W%	81.3		67.9
H ₂ N, W%	83.8		83.8

TABLE 3
PETROGRAPHIC AND REFLECTANCE ANALYSES - RUN 227-63(CC-6)

Coal Feeds and Product Solids					
Coal Feed	---- Coal Feeds ----		---- Product Solids ----		
	HRI 5715 Run-of-Mine	HRI 5716 Cleaned	Period 4 --- Cleaned ---	Period 9	Period 12 Run-of-Mine
Petrographic Macerals					
V% Ash-Free					
Vitrinite	88.7	88.7			
Liptinite	2.0	2.5			
Semi-Inertinite	4.2	3.2			
Inertinite	5.1	5.6			
Reflectance Analysis, V%					
0.00-0.49% Reflectance	27.0	36.5	9.0	3.5	8.5
0.50-0.99% Reflectance	59.0	45.5	4.5	5.0	3.0
1.00-1.99% Reflectance	6.5	8.5	31.0	31.0	32.5
2.00-2.49% Reflectance	2.0	4.0	19.0	14.5	14.0
2.50-5.00% Reflectance	5.5	5.5	36.5	46.0	42.0
Percent of Original Coal					
Total			5.5	4.6	6.3
0.00-0.49% Reflectance			0.50	0.16	0.53
0.50-0.99% Reflectance			0.25	0.23	0.19
1.00-1.99% Reflectance			1.70	1.43	2.05
2.00-2.49% Reflectance			1.04	0.64	0.88
2.50-5.00% Reflectance			2.01	2.11	2.64
Conversion, %					
Total			94.5	95.4	93.7
0.00-0.49% Reflectance			98.6	99.6	98.0
0.50-0.99% Reflectance			99.4	99.5	99.7
1.00-1.99% Reflectance			80.0	92.5	68.5
2.00-2.49% Reflectance			74.0	84.0	56.0
2.50-5.00% Reflectance			63.4	61.6	52.0

TABLE 4

PRODUCT FRACTION ANALYSES - RUN 227-63(CC-6)

Condition	1	2	3
Period Number	4	9	12
Catalyst Age, Lbs Coal/Lb Catalyst	106	233	319
TOTAL LIQUID (Recycle Solvent)			
Gravity, deg-API	8.0	3.5	1.2
Elemental Analyses, Wt			
Carbon, Wt	89.74	89.75	90.42
Hydrogen, Wt	10.08	9.40	8.94
Sulfur, Wt	0.019	0.045	0.06
Nitrogen, Wt	0.23	0.37	0.60
Total	100.07	99.57	100.02
650 F-, Wt	9.4	8.8	8.6
650-850 deg-F, Wt	52.6	47.8	45.2
850-975 deg-F, Wt	20.6	16.4	14.2
975 deg-F+, Wt	16.6	26.7	31.0
Loss, Wt	0.9	0.4	1.1
LGO (IBP-650 F)			
Gravity, deg-API	17.7	16.2	14.2
Carbon, Wt	89.03	89.63	89.38
Hydrogen, Wt	11.57	11.39	11.08
Sulfur, Wt	0.001	0.004	0.016
Nitrogen, Wt	0.11	0.10	0.13
VGO (650-850 F)			
Gravity, deg-API	11.6	9.7	8.3
Carbon, Wt	89.40	89.39	90.28
Hydrogen, Wt	10.59	10.29	10.15
Sulfur, Wt	0.005	0.003	0.025
Nitrogen, Wt	0.21	0.23	0.35
HVGO (850-975 F)			
Gravity, deg-API	2.7	0.7	-2.0
Carbon, Wt	90.25	90.46	90.72
Hydrogen, Wt	9.63	9.20	8.68
Sulfur, Wt	0.007	0.029	0.038
Nitrogen, Wt	0.29	0.32	0.56
RESIDUUM (975 F+)			
Gravity, deg-API	-5.9	-8.0	-11.2
Carbon, Wt	89.95	90.12	89.96
Hydrogen, Wt	7.95	7.29	6.88
Sulfur, Wt	0.12	0.18	0.34
Nitrogen, Wt	0.68	0.92	1.18
Cyclohexane Insolubles, Wt	19.96	31.89	45.90
Toluene Insolubles, Wt	0.87	8.68	12.38
SOLIDS (THF INSOLUBLE)			
Ash, Wt	46.00	48.66	74.96
Elemental Analyses			
Carbon, Wt	43.67	41.11	18.15
Hydrogen, Wt	2.05	1.77	1.03
Sulfur, Wt	5.92	6.48	6.32
Nitrogen, Wt	0.66	0.59	0.31
Total	98.30	98.61	100.77
Sulfur/Ash	0.129	0.133	0.084

TABLE 5

PRODUCT STREAM ANALYSES - RUN 227-63(CC-6)

Operations With Illinois No. 6 Coal - Shell S-317 Catalyst

Period Number	4	9	12
Coal Feed	-- Cleaned ---		ROM
Catalyst Age, Lbs Coal/Lb Catalyst	106	233	319
SEPARATOR OVERHEAD			
Volume Average Boiling Point, F	389	401	407
Gravity, deg-API	38.2	35.8	35.8
Watson Characterization Factor	11.15	11.06	11.00
Carbon, W%	87.13	87.93	87.68
Hydrogen, W%	13.19	12.87	13.00
Sulfur, W%	0.00	0.04	0.09
Nitrogen, W% (Kjeldahl)	0.03	0.04	0.09
Total	100.35	100.98	100.79
H/C Ratio	1.80	1.74	1.77
ATMOSPHERIC OVERHEAD			
Volume Average Boiling Point, F	515	529	525
Gravity, deg-API	25.6	23.6	22.0
Watson Characterization Factor	10.94	10.86	10.74
Carbon, W%	87.90	88.01	88.34
Hydrogen, W%	12.26	11.69	11.94
Sulfur, W%	0.01	0.01	0.02
Nitrogen, W% (Kjeldahl)	0.04	0.07	0.15
Total	100.21	100.15	100.45
H/C Ratio	1.66	1.58	1.61
PRESSURE FILTER LIQUID PRODUCT (SOLVENT)			
Gravity, deg-API	8.0	3.5	1.2
Compostion			
IBP-650 F, W%	9.37	8.78	8.54
650-850 F, W%	52.56	47.81	45.21
850-975 F, W%	20.61	16.38	14.17
975 F+ Residuum, W%	16.57	36.67	30.96
Loss, W%	0.89	0.38	1.12
Carbon, W%	89.74	89.75	90.42
Hydrogen, W%	9.77	9.40	8.94
Sulfur, W%	0.02	0.05	0.12
Nitrogen, W% (Perkin-Elmer)	0.23	0.37	0.60
Total	99.76	99.57	100.08
H/C Ratio	1.30	1.25	1.18
SOLIDS (THF INSOLUBLE)			
Ash, W%	46.00	48.66	74.96
Elemental Analyses, Ash-free Basis			
Carbon, W%	80.87	80.07	72.48
Hydrogen, w%	3.80	3.43	4.11
Sulfur, W%	10.96	12.62	25.24
Nitrogen, W%	1.22	1.15	1.24
Total	96.85	97.28	103.07
Sulfur/Ash	0.129	0.133	0.084

Nitrogen, W% (Perkin-Elmer) - Perkin-Elmer 240B Elemental Analyzer
 Nitrogen, W% (Kjeldahl) - Wet Chemical determination

TABLE 6

DISTRIBUTION OF SULFUR IN PRODUCTS

Run CC-6(227-63) Operations with Oil Agglomerated
And Run-Of-Mine Illinois No. 6 Coal

Period	4	9	12
Coal Feed			
Type	Agglomerated	Agglomerated	Run-Of-Mine
Analysis			
Ash, W%	4.62	4.62	15.21
Sulfur, W%	2.90	2.90	3.80
Pyritic, W%	0.59	0.59	1.84
Sulfate, W%	0.19	0.19	0.12
Organic, .W%	2.12	2.12	1.84
Sulfur in Products			
W% of Coal Feed			
In Liquids	0.007	0.028	0.031
In Solids	0.596	0.589	1.189
Organic*	0.129	0.098	0.116
Mineral*	0.466	0.491	1.073
Organic Sulfur			
Distribution, W%			
In Liquids	0.4	1.3	1.7
In Unconverted Coal*	6.1	4.6	6.3
Converted	93.5	94.1	92.0
Mineral Sulfur			
Distribution			
In Product Solids*	59.7	62.9	54.7
Converted	40.3	37.1	45.3
Converted Mineral Sulfur			
W% of Pyritic Sulfur	53	49	48

* Organic sulfur in unconverted coal in product solids assumed to be the same as that in the feed coal (maf basis).

Run63sulfdist.tab

TABLE 7

CTSL PERFORMANCE OF OIL AGGLOMERATION CLEANED AND HEAVY MEDIA CLEANED ILLINOIS NO. 6 COAL
BENCH-SCALE TWO STAGE COAL LIQUEFACTION

Run CC-6: Bechtel Oil Agglomerated Cleaned Coal, 4.62 W% Ash, Periods 1-9,
Run-of-Mine Coal, 15.21 W% Ash, Periods 10-12
Run 1-19: Bituminous Coal Research Heavy Media Cleaned Coal, 5.33 W% Ash
Run 1-27: Bituminous Coal Research Heavy Media Cleaned Coal, 5.77 W% Ash
Demonstration Run with Solvent Fractionation for Bottoms Extinction

Run	----- CC-6 -----			1-19	1-27
Coal Treatment Condition	Oil Agglomeration ROM Cleaned			Heavy Media Cleaned	
Period Number	4	9	12	10	8
Hours of Run (End of Period)	96.	213.	285.	240.	192.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	106.	233.	319.	290	209
Temperatures, F					
First Stage Reaction	751.	753.	749.	751	753
Second Stage Reaction	800.	811.	812.	800	807
Unit Back Pressure, psig	2529.	2521.	2524.	2463	2488
Space Velocity Stage					
Lb Dry Coal / Hr / Ft ³ Catalyst	44	41	46	44	43
RECYCLES, W% OF DRY COAL					
Pressure Filter Liquid (PFL)	177.7	131.0	114.3	194.0	149.0
Topped Separator Bottoms	0.0	0.0	0.0	0.0	0.0
Make-up Oil	2.0	4.2	4.6	0.0	0.0
Oil/Solids In Feed Slurry	1.69	1.23	1.08		1.17
Material Recovery, W%	99.35	96.97	100.51	100.08	973.7
Normalized Yields, W% of dry Coal					
C1-C3 in Gases	7.57	7.28	7.57	5.78	6.76
C4-390 deg-f in Liquids	19.82	22.30	17.63	17.13	17.75
500-650 deg-f in Liquids	33.49	33.07	29.15	33.07	41.21
650-975 deg-f in Liquids	18.19	17.32	11.57	18.44	15.91
975 F+ Oil	1.94	4.88	5.99	8.16	2.94
Unconverted Coal	5.28	4.43	5.34	3.75	3.63
Ash	4.62	4.62	15.21	5.33	5.77
Water	12.04	8.96	9.59	11.27	9.37
CO	0.04	0.05	0.07	0.24	0.04
CO ₂	0.04	0.04	0.04	0.08	0.00
NH ₃	1.67	1.56	1.35	1.49	1.62
H ₂ S	2.52	2.51	2.74	2.34	2.51
Total (100 + H ₂ Reacted)	107.23	106.99	106.25	107.07	107.19
Process Performance					
W% of MAF Coal					
C4-975 deg-f Distillates	75.0	76.2	68.8	72.5	79.6
975F+ Conversion	92.4	90.2	86.6	87.4	93.5
Coal Conversion	94.5	95.4	93.7	96.0	96.2
Hydrodesulfurization, W%	81.6	81.3	67.9		
Hydrodenitrogenation, W%	90.1	83.8	83.8	82.9	88.3

TABLE 8

COMPARISON OF FIRST AND SECOND STAGE PRODUCT FRACTION ANALYSES
RUN 227-63

	-----First Stage-----			-----Second Stage-----		
Condition	1	2	3	1	2	3
Period Number	4	9	12	4	9	12
Catalyst Age, Lbs Coal/Lb Catalyst	106	233	319	106	233	319
TOTAL LIQUID						
Gravity, deg-API		1.7	-2.1	8.0	3.5	1.2
Elemental Analyses, WZ						
Carbon, WZ		89.31	88.65	89.74	89.75	90.42
Hydrogen, WZ		9.18	8.55	10.08	9.40	8.94
Sulfur, WZ		0.12	0.22	0.019	0.045	0.06
Nitrogen, WZ		0.55	0.74	0.23	0.37	0.60
Total		99.06	98.16	100.07	99.57	100.02
650 F-, WZ		8.7	7.3	9.4	8.8	8.6
650-850 deg-F, WZ		41.8	37.2	52.6	47.8	45.2
850-975 deg-F, WZ		18.1	16.6	20.6	16.4	14.2
975 deg-F+, WZ		30.5	37.9	16.6	26.7	31.0
Loss, WZ		0.9	1.0	0.9	0.4	1.1
LGO (IBP-650 F)						
Gravity, deg-API		17.2	14.5	17.7	16.2	14.2
Carbon, WZ		88.22	87.93	89.03	89.63	89.38
Hydrogen, WZ		11.31	10.77	11.57	11.39	11.08
Sulfur, WZ		0.017	0.06	0.001	0.004	0.016
Nitrogen, WZ		0.20	0.31	0.11	0.10	0.13
VGO (650-850 F)						
Gravity, deg-API		9.8	8.1	11.6	9.7	8.3
Carbon, WZ		89.05	89.11	89.40	89.39	90.28
Hydrogen, WZ		10.21	9.87	10.59	10.29	10.15
Sulfur, WZ		0.012	0.05	0.005	0.003	0.025
Nitrogen, WZ		0.30	0.42	0.21	0.23	0.35
HVGO (850-975 F)						
Gravity, deg-API		1.3	-2.6	2.7	0.7	-2.0
Carbon, WZ		89.90	89.44	90.25	90.46	90.72
Hydrogen, WZ		9.20	8.68	9.63	9.20	8.68
Sulfur, WZ		0.045	0.11	0.007	0.029	0.038
Nitrogen, WZ		0.44	0.60	0.29	0.32	0.56
RESIDUUM (975 F+)						
Gravity, deg-API		-7.1	-10.8	-5.9	-8.0	-11.2
Carbon, WZ		88.56	87.81	89.95	90.12	89.96
Hydrogen, WZ		7.54	6.98	7.95	7.29	6.88
Sulfur, WZ		0.62	0.49	0.12	0.18	0.34
Nitrogen, WZ		1.05	1.29	0.68	0.92	1.18
Cyclohexane Insolubles, WZ				19.96	31.89	45.90
Toluene Insolubles, WZ				0.87	8.68	12.38
Ash, WZ						
SOLIDS (THE INSOLUBLE)						
Ash, WZ		28.49	66.14	46.00	48.66	74.96
Elemental Analyses						
Carbon, WZ		56.03	28.70	43.67	41.11	18.15
Hydrogen, WZ		3.54	1.84	2.05	1.77	1.03
Sulfur, WZ		4.14	4.96	5.92	6.48	6.32
Nitrogen, WZ		1.29	0.62	0.66	0.59	0.31
Total		93.49	102.26	98.30	98.61	100.77
Sulfur/Ash						
Sulfur In Ash, WZ						
SAMPLE FILTRATION						
Filter Cake, Percent of Sample		27.57	45.00	10.03	12.18	20.65
THE Insolubles, WZ of Filter Cake		35.93	39.54	49.06	49.03	61.97

Run63stan.tab (corrected 10/1/90)

TABLE 9

FIRST AND SECOND STAGE FLOWS
RUN 227-63 (CC-6)

Flows - Percent of Dry Coal Feed

Period	9	12
Coal Feed Treatment	Cleaned	Run of Mine
Coal Rate, Lbs/Hr/Ft ³	41.1	45.6
Recycle PFL, W% of Dry Coal Feed	131.0	114.3
Recycle TSB, W% of Dry Coal Feed	0.0	0.0
Makeup Oil, W% of Dry Coal Feed	4.0	4.6
Catalyst Age, Lb/Lb	233	319
First Stage Temperature, F	753	749
Second Stage Temperature, F	811	812
FIRST STAGE FEED		
650 F-	11.49	10.53
650-850 F	61.26	50.61
850-975 F	31.87	16.91
975 F+	35.06	35.53
Quinoline IOM	95.33	84.79
Ash	4.62	15.21
Total	229.68	213.58
SECOND STAGE BUFFER		
650 F-	0.48	0.51
650-850 F	2.53	2.40
850-975 F	0.87	0.75
975 F+	1.35	1.64
Quinoline IOM	0.00	0.00
Ash	0.00	0.00
Total	5.30	5.30
FIRST STAGE PRODUCT		
650 F-	15.94	12.11
650-850 F	69.42	54.16
850-975 F	30.02	24.10
975 F+	50.66	55.22
Quinoline IOM	10.35	7.79
Ash	4.62	15.21
Vapor (estimated)	48.67	44.69
Total	229.68	213.58
SECOND STAGE PRODUCT		
650 F-	32.15	29.95
650-850 F	74.96	61.25
850-975 F	25.40	19.06
975 F+	41.36	41.65
Quinoline IOM	4.437	5.34
Ash	4.62	15.21
Vapor	52.06	46.42
Total	234.98	218.88

TABLE 10

FIRST AND SECOND STAGE YIELDS

Flows - Percent of Dry Coal Feed

Period	9	12
Coal Feed Treatment	Cleaned	Run of Mine
Coal Rate, Lbs/Hr/Ft ³	41.1	45.6
Recycle PFL, W% of Dry Coal Feed	131.0	114.3
Recycle TSB, W% of Dry Coal Feed	0.0	0.0
Makeup Oil, W% of Dry Coal Feed	4.0	4.6
Catalyst Age, Lb/Lb	233	319
First Stage Temperature, F	753	749
Second Stage Temperature, F	811	812
FIRST STAGE FORMATION		
W% of Dry Coal Feed		
Vapors	48.67	44.99
650 F-	4.45	1.58
650-850 F	8.16	3.55
850-975 F	8.15	7.18
975 F+ Oil	15.59	19.69
Quinoline IOM	-85.03	-77.00
Ash	0.00	0.00
Total 975 F-	69.44	57.30
Total 975 F+ Residuum	15.59	19.70
Coal Converted (W% of maf Coal)	89.15	90.82
SECOND STAGE FORMATION		
W% of Dry Coal Feed		
Vapors	3.39	1.43
650 F-	15.72	17.32
650-850 F	3.01	4.69
850-975 F	-5.49	-5.79
975 F+ Oil	-7.59	-15.22
Quinoline IOM	-5.92	-2.44
Ash	0.00	0.00
Total 975 F-	16.63	17.66
Total 975 F+ Residuum	-10.40	-15.22
Coal Converted (W% of maf Coal)	6.20	2.88
TWO STAGE FORMATION		
W% of Dry Coal Feed		
Vapors	52.06	46.42
650 F-	20.17	18.91
650-850 F	11.17	8.24
850-975 F	2.67	1.40
975 F+ Oil	4.87	4.48
Quinoline IOM	-90.95	-79.25
Ash	0.00	0.00
Total 975 F-	74.24	70.08
Total 975 F+ Residuum	4.87	4.48
Coal Converted (W% of maf Coal)	95.35	93.70

TABLE 11**APPARENT REACTION RATE CONSTANTS FOR SECONDARY REACTION
OF RESIDUUM****First Stage - CTSL Bench Unit Operations with Illinois No. 6 Coal****Primary formation - 60.5% of Converted Coal**

Run	Coal Treatment	Catalyst	Temp.	Reaction Rate Constants
CC-6	Oil-Agglom. Run-of-Mine	Shell S-317	750	23.7
		Shell S-317	750	16.9
I-12	Mine-Washed	Amocat 1C	750	15.2, 13.1, 12.2, 16.3, 15.3, 12.5
I-13	Mine-Washed	Amocat 1C	725	10.9
			750	10.3, 11.5, 19.7
			775	16.7, 14.0, 18.1, 18.8
I-18	Mine-Washed	Shell S-317	750	13.6, 17.2
			775	13.3, 13.4
I-19	Hvy. Med. Washed	Shell S-317	750	21.1
I-27	Hvy. Med. Washed	Shell S-317	749	16.8
			757	21.6

TABLE 12

FEED COAL ANALYSES FOR RUN 227-63(CC-6)

Run 227-63 Feed: Illinois No. 6 Burning Star Mine

FEED DESIGNATION, HRI No.	5715 (Run of Mine)	5716** (Agglomerated)
227-63 Periods	10-12	1-9
Moisture, W%	2.33	6.81
ULTIMATE ANALYSIS (W%, Dry Basis)		
Carbon	65.12	74.75
Hydrogen	4.57	5.23
Sulfur	3.80	2.90
Nitrogen	1.33	1.53
Chlorine	--	--
Ash	15.21	4.62
Oxygen (By Difference)	9.97	10.97
SULFUR FORMS (W%, Dry Basis)		
Sulfate	0.12	0.19
Pyrite	1.84	0.59
Organic	1.74	2.23
MINERAL ANALYSIS OF ASH (W%, Ignited)		
Silica, SiO ₂	49.50	38.40
Alumina, Al ₂ O ₃	19.62	18.00
Titania, TiO ₂	0.90	0.99
Ferric Oxide, Fe ₂ O ₃	20.52	28.02
Lime, CaO	4.08	4.96
Magnesia, MgO	1.04	1.10
Potassium Oxide, K ₂ O	1.76	1.70
Sodium Oxide, NaO	0.85	1.30
Sulfur Trioxide, SO ₃	1.09	4.11
Phosphorous Pentoxide, P ₂ O ₅	0.31	0.31
Undetermined	0.33	1.11
MICROAUTOCLAVE RESULTS*		
Thermal Coal Conversion	88.2	76.3
Catalytic Coal Conversion	93.4	93.7

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

** Includes 1.93% asphalt (for pelletizing) 1.05 Sp. Gr.,
 3.76 W% sulfur, 17596 Btu/lb HHV, estimated 8.88 W% hydrogen.
 Cited coal analyses adjusted to oil-free basis.

TABLE 13

INSPECTION OF STARTUP AND MAKEUP OIL
FOR RUN 227-63 (CC-6)

Designation	HRI 5648
Gravity, API	6.4
Distillation, F	
IBP	696
5 V%	769
10 V%	789
20 V%	807
30 V%	820
40 V%	831
50 V%	841
60 V%	875
70 V%	892
80 V%	909
90 V%	950
E.P.	975
V% @ 650 F	76
V% @ 850 F	96
V% @ 975 F	94
IBP-650 F, W%	0.0
650-850 F, W%	52.5
850-975 F, W%	41.1
975 F+, W%	5.9
Loss, W%	0.5
Carbon, W%	89.27
Hydrogen, W%	10.01
Sulfur, W%	0.01
Nitrogen, W%	0.46
Solvent Quality Test*	
Illinois Coal	70.1
Black Thunder Coal	61.5

* Coal conversion, 750 F, 30 Minutes,
2000 psig N₂, 2/1 solvent/coal

TABLE 14
FRESH CATALYST PROPERTIES - RUN 227-63(CC-6)

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 [°] 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 15
RECOVERED CATALYSTS ANALYSES
RUN 227-63 (CC-6)

STAGE	First	Second
CATALYST AGE, LB COAL/LB	327	329
CATALYST RECOVERY, Vol. %	79.0	79.5
Bulk Density, Gm/cc	0.859	0.952
ANALYSES OF OIL-FREE		
+20 MESH CATALYST, W%		
Carbon	15.14	22.25
Hydrogen	0.69	1.17
H/C Ratio	0.55	0.63
Nitrogen	0.18	0.35
Sulfur	5.91	5.44
Molybdenum	8.73	6.80
Cobalt		
Nickel	1.75	1.37
Titanium	0.20	0.64
Iron	0.18	0.38
Calcium	0.06	0.09
Sodium	0.93	0.44
Total Metal Contaminants	1.37	1.55
Loss on Ignition, W%	21.62	24.83
Particle Density, Gm/cc particle*	1.290 1.445	1.534
Pore Volume (D>30°A), cc/gm	0.389 0.389	0.289
cc/cc particle	0.50 0.56	0.443
Surface Area (calc.), M ² /gm	159	122
M ² /cc particle	205	187
Modal Pore Diameter, Angstrom		
Macro-pores	940	1960
Mini-pores	62	90
ANALYSES OF IGNITED CATALYST		
Particle Density, gm/cc particle*	1.145	1.155
Pore Volume (D>30°A, cc/gm	0.664	0.616
cc/cc particle	0.760	0.711
Surface Area (Calc.), M ² /gm	213	266
M ² /cc particle	244	307
Modal Pore Diameter, Angstrom		
Macro-pores	2250	2500
Mini-pores	99	90
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS		
Weight, Grams	40.5	119.0
Molybdenum, W%	7.13	5.37
Nickel, W%	1.47	1.11
* In mercury at 10 psia.		

FIGURE 1

COAL CONVERSION

Run 227-63(CC-6)

FIGURE 2

LIQUID YIELDS - RUN 227-63(CC-6)

FIGURE 3

DISTILLATE YIELDS – RUN 227-63(CC-6)

FIGURE 4

YIELDS — RUN 227-63(CC-6)

FIGURE 5

RESIDUAL OIL CONCENTRATION IN PRODUCT SLURRY

Run 227-63(CC-6)

FIGURE 6

HYDROGEN CONTENTS OF PRODUCT FRACTIONS

Run 227-63(CC-6)

FIGURE 7

NITROGEN CONTENTS OF PRODUCT FRACTIONS

Run 227-63(CC-6)

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SECTION II

RUN 227-66 (CC-8) - OTISCA PROCESS CLEANED ILLINOIS COALS

Run 227-66 (CC-8) completed, as scheduled, 14 days of CTSL operation with Burning Star Mine Illinois No. 6 coal, both with material that had been cleaned by OTISCA Industries by their proprietary process to reduce the ash content to 3.5 W% and uncleaned coal with 10.6 W% ash, which had been micronized and incorporated in a water slurry in preparation for the OTISCA cleaning operation. The run conditions were selected to correspond to those of earlier Bench Unit CTSL operations with mine-cleaned coal containing 10.5 W% ash, with heavy-media cleaned coal with 5.3 W% ash, with electrostatically cleaned coal with 4.9 W% ash and oil-agglomeration cleaned coal containing 4.6 W% ash.

The OTISCA processed coals are produced in a water slurry containing 30-35 W% coal. A major part of the experimental effort was in developing a method of removing the water from this slurry while preparing a feed slurry using recycled solvent for feed to the CTSL unit. The solvent/coal slurries with the OTISCA process coal proved to be of higher viscosity than those made with the other cleaned and uncleaned coals, so that to obtain a pumpable feed slurry the proportion of solvent to coal for the Run CC-8 operations was considerably higher than had been necessary in the earlier operations.

The coal conversions in Run CC-8 with the OTISCA processed coal, after drying the coal/water slurry to a moisture content equivalent to about 1 W% of the dry coal content, were 2.5-4.0% lower than obtained with the other cleaned coals that have been tested, in part because of the high proportion of solvent recycle and in part because of apparently low reactivity of the coal after the severe slurry drying. Some operations with lower severity drying of the coal/water slurry, to an equivalent moisture content of 28 W%, had coal conversions that were higher by 2.5%. The general product distribution for the OTISCA processed coal was similar to that which had been obtained with the other cleaned Illinois coals. The catalytic activity for hydrogenation and denitrogenation reactions in Run CC-8 was higher than had been obtained in earlier operations.

SUMMARY

The final coal/water slurry drying was carried out on eight hour batches at 275°F using a nitrogen sparge approximately equal to the amount of water removed. Preliminary tests at higher temperatures had developed very plastic, unpumpable mixtures, and lower temperatures resulted in incomplete water removal. The lowest solvent recycle/coal ratio that resulted in pumpable feed slurry was 1.67 lbs/lb.

The first attempted operation with the OTISCA processed coal, Run 227-65, was with only partial removal of water to 28 W% of the dry coal content, but had to be abandoned because of a plug in the internal recycle line of the first stage. There had been unusually high loss of first stage catalyst, which had become considerably weaker, possibly because of the high water content of the high pressure system corresponding to 500 psi partial pressure of water. Subsequently, in Run CC-8 (227-66) with 1-2% water in the slurry feed, there were no significant operating problems except with feed slurry preparation when the recycle solvent to coal ratio was lowered to about 1.2 lbs/lb.

The coal conversion for the OTISCA processed coal in Run CC-8 (227-66) was 92% of maf coal, in the usual mode of operation with filtered product slurry as the solvent recycle. In Run 227-65, the coal conversion had been over 94%. In Run CC-8, the conversion was over 95% when some unfiltered product slurry was included as a portion of the solvent recycle, resulting in solids recycle amounting to about 8% of the solvent recycle. With the micronized water slurry of the run-of-mine coal, used by OTISCA in preparing the cleaned coal, the coal conversion was 2.5% lower than had been obtained with the cleaned coal.

The highest yield of C₄-975°F distillate, 73.8 W% of maf coal, in Run CC-8 was in the operation with solids recycle, reflecting the higher coal conversion of that operation. The residual oil yields were about the same as had been obtained with oil-agglomeration cleaned coal, and 1-3 W% lower than expected from earlier operations with cleaned and mine-washed coal, possibly reflecting improved catalyst performance with the change in presulfiding agent to TNPS from DMDS in the latter two runs. There were no other substantial differences in the liquid product distribution for the OTISCA processed coal products from those obtained with the other cleaned coals. Because of the lower coal conversions obtained with OTISCA processed coal it would probably give about 2 W% lower distillate yields than can be obtained with the coals obtained by other cleaning processes, although some process modification by incorporating solids recycle could reduce this deficiency.

The hydrogenation and denitrogenation performance during Run CC-8 was superior to that of all of the other tests with cleaned and uncleaned Illinois coal. The hydrogen contents of the liquid products were 0.8 W% higher, and the nitrogen contents about two-thirds as great as in the other tests. Catalyst pretreatment conditions were the same as in the operation with oil-agglomeration cleaned coal, but the apparent sulfiding of the catalyst during Run CC-8 was higher than in the earlier run. The recovered catalyst after Run CC-8 had low carbon content and low metals accumulation.

The OTISCA processed coal will probably entail increased operating costs because of the additional costs of the slurry drying that is needed and the relatively high proportion of recycle solvent that is needed to maintain feed slurry pumpability.

SCOPE OF WORK

The OTISCA-process cleaned Burning Star Mine Illinois No. 6 coal used in this run was obtained from the Syracuse, N.Y. facility of OTISCA Industries, Ltd. The cleaned coal contained 3.46 W% ash (dry basis) and was delivered as produced in a slurry of the micronized coal (5 microns median diameter) containing 60-65 W% water. A sample of the feed coal/water slurry to their operation, with the coal containing 10.46 W% ash, was also tested. The catalyst for both stages was Shell S-317 1/32" nickel molybdate on alumina extrudates, a commercially available catalyst, which had been presulfided using TNPS. Shell S-317 catalyst had been used in earlier CTSL tests with mine-washed, and low ash cleaned Illinois Coal, presulfided using TNPS in Run CC-6 (227-63), and presulfided using DMDS in Runs I-18, I-19, and I-27.

The operating conditions for the three conditions used during Run 227-66 (CC-8) are summarized in *Table 1*, as well as those for Run 227-65 which was aborted after 62 hours when there was high pressure drop across the first stage, and loss of internal recycle flow.

The following table summarizes the conditions used in Run 227-66 (CC-8):

Cond.	Days of Operation	Coal Feed	Temp. °F		Recy., Lb/Lb Coal	
			First	Second	PFL	TSB
1	1-5	Cleaned	750	800	2.0	0.0
2	6-9	Cleaned	750	810	0.4	2.2
3	10-15	Run-of-Mine	750	810	1.8	0.0

The coal feed rate for all of these operations was about 42 Lbs maf coal/hour/ft³ catalyst (stage).

Condition 1 corresponds to those of reference operations in the first part of Run 227-37 (I-18) and in Run 227-39 (I-19) with mine washed (10.5 W% ash), heavy media cleaned (5.3 W% ash), and electrostatically cleaned (4.9 W% ash) Burning Star Mine coal. Condition 2 used TSB (Unfiltered reactor product slurry from which middle distillate oils had been removed by atmospheric distillation) allowing solids recycle to improve the coal conversions attendant to the dilution caused by the higher solvent recycle ratio required to obtain a pumpable feed slurry. Condition 3 compared the performance of the run-of-mine coal with that of the cleaned coal in Condition 1. In the fifteenth day of operations preparation of pumpable feed slurry was attempted with lower proportions of solvent recycle, which was successful with 1.67 lbs PFL/lb coals but unsuccessful with a solvent ratio of 1.17 lbs/lb. After completion of the scheduled operations of Run CC-8,

the run was continued using the OTISCA prepared feeds as Run CC-9 to prepare slurry products for coking evaluation tests. These operations continued to a total of 552 hours of operation with coal feed.

PROGRAM RESULTS AND ANALYSES

RUNS 227-65 AND 227-66 (CC-8)

This section discusses the conversions, product yields, process performance and product quality for Runs 227-65 and 227-66 (CC-8). *Tables 2 and 3* are operating summaries for the two runs giving the principal operating conditions for each Period (day), and normalized product distributions for periods which were considered to represent equilibrated results.

Figures 1 to 5 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.

COAL CONVERSION

Figure 1 summarizes the coal conversions during Runs 227-65 and 227-66 (CC-8). In Run 227-65, the coal conversion reached a value of 94.5% in the third day of operations, with lowest recycle oil/coal ratio of that run, 2.2/1. For the first condition in Run-CC-8 (227-66), coal conversion averaged 92.0% of maf coal, which was 2.5% lower than the conversion in Run 227-65 with the same operating conditions and proportion of recycle solvent. Possibly, the more strenuous drying effort in Run 227-66 contributed to this lower conversion level, either by a detrimental impact upon the conversion characteristics of the coal or by a favorable impact upon coal conversion of the higher water vapor pressure in the reactor environment during Run 227-65. This high, over 30% of dry coal, water content of the reactor feed slurry increased the partial pressure of water in reactor vapors by a factor of about four to about 500 psi.

In the second condition of Run CC-8 (227-66), with about 80% of the recycle solvent being solids-containing Topped Separator Bottoms product slurry and with increased first and second stage temperatures, coal conversion increased to about 96% of maf coal, around 4% higher than obtained with the solids-free recycle solvent. Correlation of coal conversion results indicates that over three-fourths of the increased in conversion was due to the change in solvent recycle characteristics, and the rest of the change was due to the increases in reactor temperatures.

The final operation of Run CC-8 (227-66), with micronized Run-of-Mine coal, had a coal conversion about 89.3%, 2.5% lower than obtained in the earlier comparable Condition 1 operation with the cleaned micronized coal.

These conversion in Run 227-66 (CC-8) were lower than would have been obtained with mine-washed Illinois coal containing about 11 W% ash, as illustrated by the following comparison of the conversions for the OTISCA coal

operations with those projected from the correlation of the mine-washed CTSL results:

Operation	Coal	Exp. Conv.	Proj. Conv.
Run 227-65	Cleaned	94.5	94.2
Run 227-66 Condition 1	Cleaned	92.0	94.2
Run 227-66 Condition 2	Cleaned	96.2	96.0
Run 227-66 Condition 3	R-O-M	89.3	94.4

The microautoclave evaluations of the micronized OTISCA samples, which are summarized in the section below concerning the analyses of the coal samples, did not indicate any substantial deleterious impact of the OTISCA preparation upon convertibility. The relatively poor performance of the micronized materials in Run 227-66 (CC-8) would then be ascribed to the slurry drying conditions used in the run. The Run 227-65 performance indicated that more moderate drying conditions had a lower impact upon coal conversion.

Table 4 summarizes the results of other microautoclave tests which evaluated feed materials (vacuum dried) and product solids from Run 227-66 (CC-8). These tests indicated that 3.0 W% of the maf cleaned coal was virtually unreactive, and that the reactive portion consisted of 87-89% of a high reactivity component, and 8-10% of a low reactivity component. The microautoclave tests of the micronized OTISCA run-of-mine feed and product solids indicated about 1 W% more of the unreactive component, and possibly as much as 10% more of the low reactivity component than the OTISCA cleaned coal.

C₁-C₃ GAS YIELDS

Normalized C₁-C₃ gas yields in Run 227-66 (CC-8) averaged 6.5 W% of dry coal for the Condition 1 operation with the cleaned coal and first and second stage temperatures of 750 and 800°F, respectively. When the stage temperatures were increased to 775 and 810°F in the Condition 2 operation, the gas yield increased by about 1.5 W%. In the Condition 3 operation, with run-of-mine coal and the stage temperatures of 750 and 800°F, the gas yields were about 5.0 W% of dry coal. *Figure 2* summarizes collected gas yields for Runs 227-65 and 227-66 (CC-8). The collected gas yields for the Condition 1 operation, with cleaned coal, averaged 6.2 W% of maf coal, while that of the Condition 3 operation, with run-of-mine coal, averaged 5.8 W% of maf coal, which is not a statistically significant difference (62% statistical confidence level). The slightly higher gas yield for the Run 227-65 operation by 0.6 W% also is not significantly statistically from the yield during the Condition 1 operation of Run 227-66 (CC-8).

The increase of 1.6 W% of dry coal in gas yield with the increased stage temperatures of the Condition 2 operation is consistent with a projected change of 1.8 W% based on correlation of earlier Illinois Coal CTSL results, which

assumed an activation energy of 57 Kcal/gm mole for the secondary reaction of liquid phase components to the gases.

LIQUID PRODUCTS

Figure 3 compares, for the three Conditions of Run 227-66 (CC-8), the cumulative yields, on a moisture-ash-free basis, of the C_4^+ distillate and residuum. *Figure 4* compares the yields of each of the major distillate product fractions. *Figure 5* is a similar comparison of the other major products for the run.

The C_4 -975°F yield for the Condition 2 operation with the washed coal was the highest of the run, 73.8 W% of maf coal, 2.7 W% higher than for the Condition 1 operation, and 9.1 W% higher than for the Condition 3 operation with the run-of-mine coal. The increased distillate yield of the Condition 2 operation compared to that of Condition 1 reflected increased coal conversion, by 2-4 W%, and lower residual oil yield, by 2.5 W%, which was greater than the increased gas yield, by about 2%, of later operation. The lower distillate yield of the Condition 3 operation, with the run-of-mine coal, compared to that of the Condition 1 operation reflected lower coal conversion, by 3 W%, and higher residual oil yield, by 4 W%.

The variation in residual oil yield involves the slightly higher reaction severity of the Condition 2 operation, the impact of catalyst deactivation, and solvent balance considerations. *Figure 6* summarizes the concentration of residual oil in the product slurry from the second reactor as related to the days of coal operations, to reflect the deactivation of the catalyst with respect to the secondary reaction of the residual oil to lighter products. There is a general upward trend in this concentration, increasing by about 5 W% between the Condition 1 and Condition 3 operations, possibly slightly mitigated in the Condition 2 operation at the higher stage temperatures, where the concentration was about the same as in the final Condition 3 operation.

The patterns of the residual oil yield in Run 227-66 (CC-8) correspond to the correlation of the residual oils yields for Run I-12 to I-14 with Illinois No. 6 coal, although the yields projected by the correlation are 1-3 W% higher than the experimental yields. The correlation indicates that the Condition 2 residual oil yields, allowing for the temperature changes, recycle patterns, and catalyst aging would be 4.5 W% below that of Condition 1, with a residual concentration about 3 W% lower (Period 9 against Period 5). Correlated Condition 3 yields were 2.6 W% higher than Condition 1 yields, and the residual oil concentration would be 7 W% higher. The key parameters of the correlation were primary residual oil formation of 60.5 W% of converted coal, a first order rate constant of 11.6 lbs/hr/ft³ at 750°F, and activation energy of 47 kcal/gm mole, and deactivation in the second stage of 0.19% per lb of coal processed/lb of catalyst (a compounded rate of deactivation).

The distribution of the distillate product, *Figure 4*, shows a higher proportion of C⁴-390°F naphtha and of the 390-650°F light gas oil for the Condition 2 operation, by 5-8 W% of maf coal, relative to the other two Conditions, and a corresponding low yield of 650-975°F heavy gas oil. This pattern is consistent with higher hydrocracking rates indicated by the higher gas yields and lower residual oil yield of the Condition 2 operation.

Water yields were calculated by a forced carbon/oxygen balance since the water recoveries were uncertain to give reliable net water formation quantities because of the very high proportion of feed slurry water, around 200% of the dry coal fed. On this basis water yields were virtually identical for the three Conditions of Run 227-66 (CC-8), at 13.8 W% of maf coal.

Hydrogen consumption for the Condition 2 operation, 8.3 W% of dry coal, was slightly higher than for the other two operations, by about 0.7 W% of maf coal. This difference reflects the higher proportion of light gas and lower boiling range liquids, which have relatively high hydrogen contents, that were produced in that operation.

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 227-66 (CC-8) product fractions are summarized in *Table 5*. In addition, *Table 6* 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 heavier liquid product fractions are graphically summarized in *Figure 7*.

The hydrogen contents of the heavy gas oil product fractions were not greatly different for the three conditions of the run, with a range of about 0.3 W% and averages within 0.1 W% and no consistent pattern of the differences from condition to condition. The hydrogen content of the residual oil was progressively lower as the run continued, with a total of 0.4 W% difference between the first and last condition. Such a pattern of residual oil hydrogen contents, reflecting catalyst deactivation, is consistent with those of other operations, but somewhat more moderate than that in Run 227-63 (CC-6), with oil-agglomeration cleaned Illinois Coal, where the change in this hydrogen content was around 1.0 W% over the same span of catalyst age.

The hydrogen contents of the lower boiling product streams from the final Condition 3 operations of Run 227-66 (CC-8) with run-of-mine coal were virtually the same as those of the Condition 1 operation of the run. This contrasts to the pattern of Run 227-63 (CC-6) where these hydrogen contents declined by about 0.3 W%.

The hydrogen contents for the Run 227-66 (CC-8) products were consistently higher than those of the products from Run 227-63 (CC-6), as follows summarizing the hydrogen contents of the two runs:

Fraction	Run 227-63 (CC-6)	Run 227-66 (CC-8)
IBP-650°F	11.08-11.57	11.67-12.04
650-850°F	10.15-10.59	10.92-11.06
850-975°F	8.68-9.63	10.08-10.21
975°F+ Residual Oil	6.88-7.95	8.26-8.69

The hydrogen contents of Run 227-66 (CC-8) products superior hydrogenation performance and a relatively moderate rate of catalyst deactivation during this run.

Nitrogen Contents

The nitrogen contents of the heavier liquid product fractions for Run 227-66 (CC-8) are summarized in *Figure 8*.

The trends in nitrogen contents indicate some catalyst deactivation in the course of the run with nitrogen contents for the final operations of Condition 3 being about 1.5-2 times those of the first operation of Condition 1. However, these nitrogen contents are considerably lower than those for the products of Run 227-63 (CC-6), as follows summarizing the nitrogen contents of the two runs:

Fraction	Run 227-63 (CC-6)	Run 227-66 (CC-8)
IBP-650°F	0.10-0.13	0.07-0.13
650-850°F	0.21-0.35	0.11-0.23
850-975°F	0.29-0.56	0.21-0.32
975°F+ Residual Oil	0.68-1.18	0.47-0.75

In both runs the lowest nitrogen contents were for the initial operations and the highest nitrogen contents for the final operations. Thus, throughout the two runs the nitrogen contents for Run 227-66 (CC-8) were about two-thirds of those of Run 227-63 (CC-6).

Sulfur Contents

The sulfur contents of the distillate products and product fractions were in the range of 0.00-0.03 W%, with no consistent pattern with respect to boiling point and catalyst age. The sulfur content of the residual oil was in the range of 0.04 to 0.33 W%, with the highest content during the final operations with the run-of-mine coal. This pattern of sulfur contents is the same as obtained with the oil-agglomeration cleaned Illinois coal in Run 226-63 (CC-6). The sulfur remaining in the liquid products was less than 1% of the organic sulfur in the cleaned coal and about 1% of the organic sulfur in the run-of-mine coal. The sulfur remaining in the product solids corresponded to 0.59 W% of dry coal for the cleaned coal, and 0.97 W% of dry coal for the run-of-mine coal, which compares to pyritic plus sulfate sulfur contents of the coals fed of 0.67 and 1.29 W%, respectively, indicating incomplete conversion of pyrites to pyrrhotite.

COMPARISON WITH PERFORMANCE OF OTHER CLEANED COALS

Table 7 compares the results of Run 227-66 (CC-8), processing oil agglomeration cleaned coal, with those of earlier runs that processed Illinois No. 6 coal that had been cleaned by float-sink heavy media separation (Runs I-19 and I-27 of the previous CTSL program) or by oil-agglomeration (Run CC-6 of the current CTSL program).

Coal conversions with the OTISCA cleaned coal in Run 227-66 (CC-8) were generally lower than obtained in the runs with the other cleaned coals. With solids-free recycle solvent in Period 5 of Run 227-66 (CC-8) the coal conversion was 2.5-4.0% lower than in comparable operations with the other two cleaned coals. Two factors appeared to contribute to this deficiency. One was an intrinsic low convertibility of the OTISCA processed coal possibly caused by the slurrying procedure used to remove the water from the water slurry in which the coal was shipped. The other was the necessity for using a relatively high proportion of recycle solvent, lowering the coal concentration in the system, with that coal because of the pumping difficulties with lower proportions of recycle solvent. An increase of 1.5% in conversion was effected by recycling solids in Topped Separator Bottoms during the operation with OTISCA processed coal, but it still was 2-3% lower than the values with the other coals. This difference in coal conversion performance was also reflected in the relative results with run-of-mine coals in Run 227-66 (CC-8) and CC-6. The 2.5% higher conversions with the OTISCA processed coal obtained in Run 227-65, discussed above, suggests that more careful slurry drying at lower temperatures could equalize this factor.

The highest C₄-975°F distillate yield with the OTISCA processed coal was 73.8 W% of maf coal about 2 W% below that with the oil-agglomeration cleaned coal, about the difference in coal conversions for those two coals. However, the other factors contributing to this difference were 4 W% higher water yield and 3% lower residual oil yield with the OTISCA processed coal. The difference in water yields was unexpected since the ultimate analysis oxygen-by-difference value for the OTISCA processed coal was virtually the same as for the other cleaned Illinois coals, 11.3 W% compared to 10.1-11.4 W%. There was an exceptionally high amount of water involved in the operations of Run 227-66 (CC-8), with the gross amount of water handled amounting to about 20 times the apparent net water formation, so that the calculation of water yield was based on an oxygen-by-difference balance rather than the actual collected water quantity as in the other runs, possibly causing a bias. The differences in residual oil yields for the operations with the various coals, reflect solvent balance considerations which are difficult to match from run to run. The actual concentration of residual oil in the product oil was virtually the same in the runs with oil-agglomeration cleaned coal and with OTISCA processed coal, so that there would have been little difference in residual oil yield if the solvent balance had been similar for those operations. After these considerations, it is concluded that the OTISCA

processed coal, as operated in Run 227-66 (CC-8), would give C₄-975°F distillate about 2% lower than oil-agglomeration cleaned coal, because of the lower coal conversion.

In Run 227-66 (CC-8) with the OTISCA process coal, the distribution of the distillate product between naphtha, light gas oils, and heavy gas oils was in the range experience with oil-agglomeration and heavy-media cleaned coals.

With respect to product distribution, the principal debit of the OTISCA processed coal is the generally lower coal conversions that were obtained because of the dilution of the solids by the high proportion of recycle solvent required to obtain a pumpable feed slurry. In addition, drying of the water slurry with this coal may result in poor coal convertibility. This factor may be mitigated to a degree by recycling some unreacted solids in the recycled solvent. However, this alternative will result in further additional costs along with the those of water slurry drying and of the higher proportion of recycle solvent that is required to obtain a pumpable feed slurry.

Table 8 compares the hydrogen and nitrogen contents of the product fractions for CTSL operations in Run I-27 (heavy media cleaned Illinois coal), in Run 227-63 (CC-6) (oil-agglomeration cleaned coal, and Run 227-66 (CC-8) (OTISCA process cleaned coal). The products from the CTSL operations with the OTISCA processed coal had consistently higher hydrogen contents (averaging 0.8 W% higher) and lower nitrogen contents (about two-thirds as great) than those of the other two operations cited. Such differences would generally be ascribed to differences in catalytic behavior rather than a property of the variations in coal composition since there were only minor differences in the elemental compositions of the coal feeds to these three runs.

The same lot of Shell S-317 catalyst was used for the three runs. Catalyst presulfiding for Run 227-66 (CC-8) used TNPS (tertiary nonyl poly sulfide) as in Run CC-6, while the I-27 catalyst was presulfided with DMDS (dimethyl disulfide). The recovered catalyst analyses, discussed below, indicate that the Run 227-66 (CC-8) catalysts had sulfur contents corresponding to more complete metal sulfiding than in Run I-27, although not appreciably more complete than in Run CC-6. The hydrogenation/denitrogenation performance of the catalysts would also be affected by contamination. The recovered Run 227-66 catalysts (actually the catalyst after further operations as Run 227-66E (CC-9) as an extension of Run CC-8) had lower carbon contents than those from these other two runs and low metal contamination, comparable to that of Run CC-6 and much lower than that of Run I-27 (see below). Arguably, the OTISCA type cleaning removes contaminating metals and organic coal species that tend to contaminate the catalysts. However, there has been no clear pattern in the variations in metallic contamination and carbon accumulations after various operations with Illinois coals with respect to coal preparation (cleaning).

RUN CC-8 (227-65 & 227-66) DETAILS OF OPERATIONS

Run (CC-8), first attempted as Run 227-65 and finally completed as Run 227-66, evaluated Illinois No. 6 coal reduced to 3.6 W% ash content by OTISCA Industries using their proprietary process. The cleaned coal was provided, as generated, in a water slurry containing about 35% solids.

The principal focus of the program was development of a drying procedure for the water slurry when mixed with recycle oil, while providing a pumpable feed slurry without excessive water inclusion into the high pressure process. Preliminary testing indicated a possible difficulty in using very low ratios of recycle oil to coal, possibly due to enhanced swelling of the extremely fine coal (5 micron median diameter). A conservative value of 2/1 recycle oil/dry coal was selected for use in the balance of the Bench Unit test operations, with relatively brief operations attempted with lower oil/coal ratios. The run plan included demonstration of the process performance of the coal at usual CTSL operating conditions using solids-free filtered recycle oil, and tests with a high proportion of unfiltered solids-containing recycle oil to demonstrate the reduced recycle oil clarification requirements that might be accomplished with such cleaned coals. The run plan also included operations with the run-of-mine Illinois coal similarly micronized in water slurry (the feed to the OTISCA cleaning operation).

SLURRY DRYING PROCEDURE

The coal/water slurry mixed with recycled oil was dried in the slurry pretreatment system, which had been installed for thermal pretreatment in Run 227-62 (CC-5). Eight-hour feed batches of the coal/water slurry along with recycled filtered product (and unfiltered product) were heated for approximately six hours (until almost all of the water was removed) and then pumped to the feed slurry holder for the high pressure CTSL equipment. In the final development of the drying technique sparging nitrogen flow was used equal to the amount of water to be removed. The quantity of water recovered from the drier and the water content of the dried slurry was determined. At the end of drying cycle, the entire inventory of dried slurry was transferred to the unit feed slurry tank for feed to the high pressure equipment during the following eight-hour interval.

For Run 227-65 the temperature in the drying cycle was limited to 210°F. About 85% of the water was removed in the drying operation, but the water remaining in the slurry was very high, corresponding to 20-35% of the dry coal fed. In Run 227-66, with a temperature limit of 275°F and with a nitrogen sparge of 70 SCFH during the eight hour cycle which removed about 20-25 pounds of water, drying was more complete. The final water content was 1-2 W% of the dry coal fed.

Pretesting had indicated possible pumping difficulties with low ratios of oil to coal, so that the operations for the first two days was with higher than target recycle oil to coal ratios. This involved successive 16-hour operations with unit feed of 4/1, 3/1, and 2.5/1 recycle oil/dry coal before the target ratio of 2/1 was used in the third day. The operating experience of Run 227-65 permitted more rapid arrival at the target oil/coal ratio in Run 227-66 after 32 hours of coal operations.

PRELIMINARY WATER SLURRY DRYING TESTS

Prior to the delivery of the OTISCA cleaned Illinois coal that was used in Run CC-8, preliminary small scale tests on slurry preparation were carried out using a Kentucky coal/water slurry provided by OTISCA. These tests indicated that preparation of pumpable slurries with less than 2 parts oil to 1 part of dry coal was unlikely. Drying of the coal/water/oil mixture at atmospheric pressure would require temperatures over 300°F for removal of all the water, with the development of a very plastic and virtually unpumpable mixture. Under moderate vacuum, a high proportion of drying was attained at about 200°F and the resulting water-free coal/oil mixture was sufficiently fluid to permit pumping to the high pressure system. This experience led to the use in the bench unit drying apparatus of a nitrogen sparge at a rate equal to the total amount of water to be vaporized.

These small scale tests indicated the desirability of keeping temperature of the slurry drying/preparation as low as feasible; so this temperature was kept below 220°F during Run 227-65. However, a considerable amount of water corresponding to as much as 35% of the dry coal fed was still unvaporized. This factor may have contributed to the poor operability of Run 227-65.

Further small scale tests after Run 227-65, now with the Illinois coal/water slurry, indicated that the slurry preparation temperature could be raised somewhat while obtaining pumpable dried coal/oil slurries. In Run 227-66, drying temperatures up to 275°F were used, resulting in increased water removal without pumping difficulties, at least with the 2/1 oil/coal slurries.

OPERATIONS

Preoperational Procedures - Operations were started using HRI 5648 vacuum distillate 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 three sets of conditions used during the run is given in *Table 1*. No first stage samples were taken during the runs.

Run 227-65

Operations with coal feed in Run 227-65 started on March 8, 1990 and proceeded for three days successfully completing the program of progressively reducing the proportion of recycled slurrying oil to the target value of 2 lbs/lb dry coal while maintaining the feed of slurry to the high pressure system. In the third day, a persistent increase in pressure drop across the first stage reactor developed, reaching 200 psi, with apparent loss of the ebullating internal recycle oil flow around that reactor and a plugging of its internal recycle oil line. The coal feed was stopped at the end of the third day for inspection of the unit.

Inspection of the unit after the run found the expected blockage in the first stage internal recycle line. The first stage catalyst bed had not settled to the catalyst support, which occurs usually, but was pushed up a distance corresponding to about 60% of the settled bed height. Catalyst was missing from the reactor, with the settled bed volume only 76% of the amount charged, and only 69% recovery of full sized catalyst. Mechanical evaluation showed the attrition loss of the recovered catalyst was 4.6 times that of fresh catalyst, and a crush strength only 75% as great as that of the fresh catalyst. Recovered catalysts after other runs have had about the same mechanical properties as the fresh catalyst. The second stage reactor system was clean (when the catalyst was dumped after the further attempted operations about 7% of the catalyst was missing). Despite the apparent loss of catalyst, there was no indication of catalyst (by molybdenum analyses) in the product filter cake obtained during the coal operations.

On March 14, after replenishing the missing first stage catalyst with fresh catalyst, it was attempted to resume operations using the dried feed slurry remaining after this interruption. Pumping problems appeared immediately when coal/oil feed slurry was introduced to the high pressure system, and the first stage pressure drop started to rise at this time. The operation was aborted and new batches of fresh catalyst were charged to both reactors for the next run.

Despite the relatively small particle size of the coal fed, and presumably of the solids produced, there were no difficulties in filtering the product slurry to obtain the solids-free recycle solvent. The filtration rates were comparable to those of the other CTSL operations, and the filtrate contained minimal amounts of mineral matter.

Run 227-66 (CC-8) Operations

On March 20, testing of the OTISCA cleaned Illinc's coal as Run CC-8 was resumed in Run 227-66 (CC-8) with charges of fresh catalyst to both stages. Fifteen days of operations were completed as Run CC-8. The operations were continued after that time as Run 227-66E (CC-9), to a total of twenty-three days, with both the OTISCA cleaned coal and the OTISCA micronized "run-of-mine"

coal in preparing feeds for coking tests on the bottoms products from the CTSL operations.

During Period 15, a single eight-hour batch of pumpable slurry was produced using an oil/coal ratio of 1.67. When an oil/coal ratio of 1.17 was tried in the next batch, circulation could not be maintained in the slurry preparation system, and additional recycle oil and make-up oil was added, to bring the oil/coal ratio up to 2.43, and restore circulation in the preparation system. In Run 227-66E (CC-9) the oil/coal ratio was 1.8-2.4.

The major difference of Run 227-66 from Run 227-65 was the use of higher temperature, up to 275°F, along with a nitrogen sparge in the slurry preparation operation. Consequently, water remaining in the feed slurry to the high pressure system was lowered to 1-2% of the dry coal content. There were no operating problems in feed slurry preparation or in the reaction system when using an oil/dry coal ratio of 1.67 or higher. However, when the oil/coal ratio was lowered to 1.17 (a ratio used in other coal evaluations) circulation could not be maintained in the slurry preparation system, and dilution with oil to the higher oil/coal ratio was necessary.

After Run 227-66E (CC-9) the catalyst in both stages was found in the normal settled positions in the reactors, at positions that corresponded to 92% and 96% of the original first and second stage catalyst volumes, respectively. The catalysts were easily flushed from the reactors using fuel oil. The reaction system and the downstream lines were easily flushed with wash oil.

COAL FEED

The coal feed for Runs 227-65 and 227-66 (CC-8) were prepared using Burning Star Mine, Illinois No. 6 coal by OTISCA Industries, LTD, Syracuse, NY, by means of their proprietary T-Process coal cleaning process. The cleaned coal was delivered as produced in a water slurry, containing 30-35 W% solids. *Table 9* summarizes the analyses of the cleaned coal, along with those for the micronized coal used in the preparation of the cleaned coal, for the refuse from the cleaning operation, and for the raw coal used (the ash content corresponds to that of mine-washed samples we have received at other times).

The cleaned coal, and the uncleaned micronized coal, were delivered as a slurry with water, containing 65-70 W% water. Both these materials were very finely ground, with over 90% finer than 11.5 microns, and weight median particle sizes of about 4 microns (cleaned) and 5 microns (uncleaned). The cleaned coal contained 3.46 W% ash (dry basis), compared to 10.57 W% ash in the uncleaned feed, and 64.54 W% ash in the cleaning refuse. These ash contents correspond to 88.4 W% recovery of cleaned coal, containing 95.3 W% of the organic content of the original coal, and 29 W% of the ash content. The cleaning removed 34% of the total sulfur, 59% removal of pyritic sulfur, and less than 10% removal of

organic sulfur. The largest change in the mineral analysis was a higher iron content in the cleaned coal, by a factor of 1.5, although the pyritic sulfur to iron atomic ratio was about 0.92 for both the feed and cleaned coals.

Petrographic analysis indicated that there was no selective removal by the cleaning of unreactive macerals. Actually, these analyses indicate slightly higher proportions of inertinite in the cleaned coal (11 V% mm-free), than in the refuse (6 V% mm-free).

Microautoclave coal evaluation tests indicated about the same conversion in catalytic tests (with Shell S-317 catalyst) for the raw, micronized feed, and cleaned coals. However, in tests without catalyst, the conversion of the micronized feed was higher than that of the cleaned coal which, in turn, was higher than that of the raw coal. This pattern indicates some catalytic contribution of the higher mineral matter content of the feed and also some advantage, in the absence of catalyst, of the micronization. The refuse gave relatively low conversions in these microautoclave tests, indicating that the cleaning operation did actually remove a relatively high proportion of unreactive components. The conversion level in these catalytic microautoclave tests of the OTISCA samples, 93.2%, is only slightly lower than that obtained with the oil-agglomeration cleaned coal used in CTSL Run 227-63 (CC-5), 93.7%, and the raw coal used in preparing the oil-agglomeration cleaned coal, 93.4%. These differences are less than the probable experimental variability.

START-UP/MAKEUP OIL

The start-up oil for Run 227-65 and Run 227-66 (CC-8) was a heavy distillate, HRI 5648 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. A small amount of this oil was also used as a makeup oil. *Table 10* summarizes the analyses of the HRI 5648 oil.

The solvent quality evaluations of this oil were relatively high, 70.1% conversion in the test using Illinois No. 6 Coal, compared to a range of 53.4% to 70.2% for other solvent used as start-up oils, and 61.5% conversion in the test using Black Thunder Mine sub-bituminous coal, where the range has been 51.7 to 65.9% for the other solvents.

The HRI 5648 oil has a hydrogen content of 10.01 W%, about 0.4 W% lowered than that of the recycled oils of the same boiling range that were produced in the first operations of Run 227-66 (CC-8). The nitrogen content of HRI 5648 oil, 0.46 W%, was more than twice that of the equivalent fraction of the recycled solvent.

FRESH CATALYST

The catalyst used in both stages for Run 227-65 and Run 227-66 (CC-8) was Shell S-317, 1/32" extrudate, nickel-molybdate on alumina. The designation was HRI No. 5394, the same lot that had been used in previous CTSL operations with Illinois Coal, Ohio Coal and Black Thunder Mine Coal. The inspections on the fresh catalyst are presented in *Table 11*.

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). TNPS was used as the sulfiding agent, in place of DMDS (Dimethyl Disulfide) which had been used in preparing catalyst for earlier CTSL operations with Illinois coal 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 six-hour holding periods with the reactors at 450°F, and at 550°F, and a four-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 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 Run 227-65 are given in *Table 12*, and those of the recovered catalysts after Run 227-66E (CC-9), the extension using OTISCA processed coals of Run 227-66 (CC-8), are given in *Table 13*.

For Run 227-65, the history of the final first stage catalyst was uncharacteristic, in that it was a mixture of catalyst recovered after the first shutdown in the run, of catalysts recovered from earlier runs, and some fresh catalyst that had not been involved in any significant degree in coal operations.

After Run 227-65, the recovery of catalyst from the second stage was 93% (volumetric basis), or 106% (molybdenum content basis), or 106% (nickel content basis). The second stage catalyst from Run 227-65, had a relatively low carbon content, 9.3% compared to values of 13 to 20 W% for catalysts after longer operations with Illinois Coals. The accumulation of iron and calcium was very low, around 0.05 W%. The sulfur content of the recovered catalyst was 80% of that corresponding to the formation of MoS₂ and NiS, which is a relatively low proportion (after Run 227-66E, the sulfur contents of the recovered catalysts corresponded to 108% and 104% of that sulfiding equivalent). This pattern indicates that the presulfiding was only partially complete, and that the catalyst becomes more completely sulfided during the coal operations. This conclusion

is qualified by the discrepancy between the volumetric and metals recoveries noted above. The pore volume of the recovered second stage catalyst was 85% of that of fresh catalyst, which is considerably higher than values as low as 52% after longer operations with Illinois coal. This is consistent with the relatively low proportions of contaminants on the Run 227-65 catalyst, although it does not correlate exactly with carbon content.

After Run 227-66E the recovery of catalyst from the first and second stages were 94% and 102% (volumetric basis), 86% and 90% (molybdenum contents), and 96% and 97% (nickel contents), respectively.

Metals contamination totaled about 1.1% on the recovered catalysts from both stages. This level is about the same as that on the recovered catalysts from Run 227-63 (CC-6), which processed oil-agglomeration cleaned Illinois Coal, but very much lower than the 8.5% and 4.1% levels of the recovered catalysts after Run 227-47 (I-27) which processed heavy-media cleaned Illinois Coal, although it is only slightly below the 2.1% and 1.3% levels for the catalyst from Run 227-37 (I-18) which processed mine-washed (10.6 W% ash) Illinois Coal. A review of the metal contaminants on catalysts from eight other runs with mine-washed Illinois coal showed a range of 1.6-6.1 W% (average 3.6 W%) on first stage catalysts, and a range of 0.7-1.7 W% (average 1.2 W%) on second stage catalysts. A consideration in evaluating the low contamination of the Run 227-66E catalyst is that about half of the operation was with cleaned coal and half with uncleared coal. The contamination of the Run 227-66E catalysts is low, but it is not certain that coal cleaning is necessarily the sole reason for this result.

Carbon accumulation on the recovered first and second stage catalysts after Run 227-66E (CC-9) were 12.6 and 13.6 W%, respectively. These carbon contents are lower than those of the first and second stage catalysts recovered after Run 227-63 (CC-6), 15.1 and 22.2 W%, and after Run 227-47 (I-27), 14.8 and 17.8 W%.

The sulfur contents of the recovered catalysts after Run 227-66E (CC-9) were 108% and 104% of the amount corresponding to formation of MoS_2 and NiS in the catalysts, which is about the same as that of the recovered catalysts after Run 227-63 (CC-6). However, the catalysts recovered after Run 227-47 (I-27) had sulfur contents that corresponded to only 83 and 89% of the formation of the metal sulfides.

TABLE 1

RUN 227-65 AND 227-66(CC-8) OPERATING CONDITIONS

Catalyst - Shell S-317 (HRI 5394) in Both Stages

Coal Feed - Burning Star Mine Illinois No. 6 Coal

OTISCA Process Cleaned, and Run-of-Mine Coals

RUN	227-65	227-66 (CC-8)		
CONDITION	1	1	2	3
PERIOD (DAYS)	1-3	1-5	6-9	10-15
COAL FEED	Cleaned	Cleaned	Cleaned	R-O-M
HRI No.	5738	5738	5738 5742	5739
W % Ash	3.31	3.31	3.31	10.57
NOMINAL CONDITIONS				
Unit Pressure, Psig	2,800	2,800	2,800	2,800
Coal, Lb(dry)/hr/ft ³ (catalyst)				
First Stage	42	45	45	52
Second Stage	42	45	45	52
Coal, Lb(maf)/hr/ft ³ (catalyst)				
First Stage	41	44	44	47
Second Stage	41	44	44	47
Solvent Recycle, Lb/Lb Coal				
Filtered Liquid	3.5-2.2	2.0	0.4	1.8
Makeup Oil (HRI 5648)		0.0	0.0	0.0
Topped Separator Bottoms	0.0	0.0	2.2	0.0
Oil/Solids in Feed	3.5-2.2	2.0	2.0	1.8
Atmos. Still, Temp., °F (Vapor)	480	500	500	500
Reboiler	600	600	600	625
H ₂ S, W% of Dry Coal	0	0	0	0
Reactor Temperatures, °F				
First Stage	750	750	775	750
Second Stage	800	800	810	800
Slurry Drying Conditions				
Water in Slurry Feed, W%	64	64	68	67
Temperature, °F	210	275	275	275
Hours	8	8	8	8
Nitrogen, SCF/Lb Dry Coal	50	50	50	42

TABLE 2
RUN 227-65 OPERATING SUMMARY
BENCH-SCALE TWO STAGE COAL LIQUEFACTION

COAL: ILLINOIS NO. 6 - OTISCA CLEANED (HRI 5738) PERIODS 1-3
CATALYST: BOTH STAGES: SHELL S-317 NIMO 1/32" (HRI 5394)

Period Number	1	2	3
Date (Start of Period)	03/08/90	03/09/90	03/10/90
Hours of Run (End of Period)	24	48	56
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	29	54	62
Moisture in Coal/Water Slurry, W%	67.22	67.22	67.22
Moisture in Feed Slurry, W%	5.91	4.81	10.47
Moisture to Reactor, W% of Dry Coal Feed	28.2	19.2	36.0

TEMPERATURES, °F

First Stage Reaction	730	747	748
Second Stage Reaction	780	799	801
Slurry Mix Tank	142	146	143

PRESSURES, PSIG

Unit Back Pressure	2,791	2,748	2,792
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DRY SPACE VELOCITIES

Stg. 1, Lb/Hr/Ft ³ (catalyst)	46.0	40.4	37.8
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RECYCLES, W% OF DRY COAL

Pressure Filter Liquid	150.9	285.4	213.8
PFL to Buffer - Stage 1	4.3	4.7	5.1
PFL to Buffer - Stage 2	3.6	3.5	3.7
Separator Bottoms	0.0	0.0	0.0
Make-up Oil (HRI-5648)	199.1	0.0	0.0
TOTAL MATERIAL RECOVERY (GROSS)	97.42	96.64	99.03

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C₁-C₃ in Gases
C₄-C₇ 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* Oil
Toluene Insoluble 975°F* Oil
Unconverted Coal
Ash (SO₃-free)
Water
CO
CO₂
NH₃
H₂S
Total (100 + H₂ Reacted)

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal		
975°F* Conversion, W% MAF		
Coal Conversion, W% MAF	93.9	94.5
HDS, W%		
HIDN, W%		

TABLE 3

RUN 227-66 OPERATING SUMMARY
BENCH-SCALE TWO STAGE COAL LIQUEFACTION

Part 1 of 2

COAL: Illinois No. 6 - Otisca Cleaned (HRI 5738) Periods 1-7C, Cleaned New Batch (HRI 5742) Periods 8A-9C,
 Otisca Uncleaned (HRI 5739) Periods 10A-15C
CATALYST: BOTH STAGES: SHELL S-317 NiMo 1/32" (HRI 5394)

Period Number	1	2	3	4	5	6	7
Date (Start of Period)	03/20/90	03/21/90	03/22/90	03/23/90	03/24/90	03/25/90	03/26/90
Hours of Run (End of Period)	24.	48.	72.	96.	120.	144.	168.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	26.	58.	86.	115.	143.	172.	198.
Moisture in Coal/Water Slurry, W%	62.89	62.84	63.31	63.83	63.19	62.52	63.51
Moisture in Feed Slurry, W%	62.89	62.84	63.31	63.80		62.52	63.51
Moisture to Reactor, W% of Dry Coal Fed		1.10	0.82		1.00		1.38

TEMPERATURES, °F

First Stage Reaction	735.	751.	750.	749.	750.	766.	775.
Second Stage Reaction	784.	799.	799.	799.	798.	806.	806.
Slurry Mix Tank	138.	139.	162.	172.	187.	206.	208.
Slurry Drying Max Temp	275	275	275	275	275	275	275

PRESSURES, PSIG

Unit Back Pressure	2799.	2803.	2804.	2797.	2799.	2798.	2799.
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SPACE VELOCITY

Dry Coal Sp. Vel. - Stg. 1, Lb/Hr/Ft ³ (cat.)	41.8	60.9	44.7	45.3	45.1	46.2	41.1
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RECYCLES, W% OF DRY COAL

Pressure Filter Liquid	94.1	205.1	184.7	193.2	190.1	150.0	54.1
PFL to Buffer - Stage 1	3.2	3.7	4.2	4.4	4.4	4.1	4.7
PFL to Buffer - Stage 2	2.4	3.1	4.0	3.4	4.0	3.4	4.2
Topped Separator Bottoms	0.0	0.0	0.0	0.0	0.0	50.1	205.7
Make-up Oil (HRI 5648)	246.9	0.0	6.2	0.0	0.0	0.0	0.0
Oil/Solids In Feed Slurry		2.15	1.98	1.97	1.98		2.15

TOTAL MATERIAL RECOVERY (GROSS)	98.47	96.97	97.05	97.32	97.22	97.32	98.83
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ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases				6.49	6.48		8.19
C ₄ -C ₆ in Gases				5.06	5.06		5.45
IBP-390°F in Liquids				11.70	12.15		15.61
390-500°F in Liquids				9.69	9.57		12.78
500-650°F in Liquids				21.52	20.78		25.94
650-850°F in Liquids				16.25	16.55		10.10
850-975°F in Liquids				4.87	4.48		1.49
Toluene Soluble 975°F Oil				3.67	3.82		1.40
Toluene Insoluble 975°F Oil				0.00	0.07		0.00
Unconverted Coal				7.58	7.84		6.43
Ash	3.31	3.31	3.31	3.31	3.31	3.31	3.31
Water				13.34	13.39		13.37
CO				0.00	0.00		0.00
CO ₂				0.01	0.01		0.01
NH ₃				1.61	1.61		1.66
H ₂ S				2.19	2.20		2.24
Total (100 + H ₂ Reacted)				107.29	107.32		107.99

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal				69.7	69.4		75.8
975°F Conversion, W% MAF				88.6	88.1		91.9
Coal Conversion, W% MAF		91.9	92.2	92.2	91.9		93.3
HDS, W%				78.0	78.3		79.5
HDN, W%				87.5	87.5		89.9

COAL: Illinois No. 6 - Otisue Cleaned (NRI 5738) Periods 1-7C,
(NRI 5742) Periods 8A-9C,
Otisue Uncleaned (NRI 5739) Periods 10A-15C
CATALYST: BOTH STAGES: SHELL S-317 NIMO 1/32" (NRI 5394)

Period Number	8	9	10	11	12	13	14
Date (Start of Period)	03/27/90	03/28/90	03/29/90	03/30/90	03/31/90	04/01/90	04/02/90
Hours of Run (End of Period)	192.	216.	240.	264.	288.	311.	335.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	224.	252.	285.	319.	352.	385.	418.
Moisture in Coal/Water Slurry, Wt	68.08	68.05	66.85	66.22	67.77	67.43	67.80
Moisture in Feed Slurry, Wt	68.08	68.05	66.85	66.22	67.77	67.43	67.80
Moisture to Reactor, Wt of Dry Coal Fed	2.96	1.15		0.97	0.73	0.67	0.83
TEMPERATURES, F							
First Stage Reaction	776.	777.	756.	751.	751.	750.	750.
Second Stage Reaction	807.	808.	799.	799.	799.	799.	800.
Slurry Mix Tank	210.	200.	198.	231.	245.	255.	265.
Slurry Drying Max Temp							
PRESSURE, PSIG							
Unit Back Pressure	2800.	2703.	2704.	2704.	2788.	2785.	2705.
1st Stage Reactor DP	5.6	5.8	5.7	9.9	5.8	5.9	5.8
2nd Stage Reactor DP	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Overall DP	11.5	11.8	11.4	11.9	11.7	11.6	11.9
SPACE VELOCITY							
Dry Coal Sp. Vel. - Stg. 1, Lb/Mr/Ft3	19.0	20.2	23.5	24.3	24.9	23.4	23.7
RECYCLES, Wt OF DRY COAL							
Pressure Filter Liquid	41.9	39.0	185.6	162.5	181.4	161.1	168.8
PFL to Buffer - Stage 1	4.5	4.3	3.5	3.3	3.2	3.5	2.8
PFL to Buffer - Stage 2	3.8	3.6	3.2	3.1	2.9	2.9	2.9
Yoppad Separator Bottoms	235.0	219.5	0.0	0.0	0.0	0.0	0.0
Take-up Oil (NRI 5648)	0.0	0.0	0.0	10.1	0.0	18.3	7.9
Oil/Solids in Feed Slurry	2.19	1.90		1.73	1.81	1.79	1.77
TOTAL MATERIAL RECOVERY (GROSS)	95.72	94.48	96.13	99.63	98.19	101.89	98.13
ESTIMATED UNOVALIZED YIELDS, Wt DRY FRESH FEED							
C1-C3 in Gases		7.70				5.06	4.94
C4-C7 in Gases		4.80				6.37	6.07
180-350 deg-f in Liquids		14.03				9.34	10.08
300-500 deg-f in Liquids		11.34				7.49	7.77
500-650 deg-f in Liquids		26.54				18.80	18.23
650-850 deg-f in Liquids		10.89				15.45	15.15
850-975 deg-f in Liquids		1.70				-1.16	2.00
Toluene Soluble 975F+ Oil		1.51				7.51	6.95
Toluene Insoluble 975F+ Oil		0.04				0.45	0.11
Unconverted Coal		2.97				9.71	9.56
Ash	3.31	3.31	10.57	10.57	10.57	10.57	10.57
Water		17.13				12.99	11.67
CO		0.00				0.00	0.00
CO2		0.01				0.06	0.06
H2S		1.75				1.26	1.24
H2g		2.39				2.84	2.71
Total (CO + H2 Reacted)		108.11				106.94	106.71
PROCESS PERFORMANCE							
C4-975 deg-f Distillates, Wt of HAF Coal		73.6				66.8	65.8
975F+ Conversion, Wt HAF		95.3				79.4	82.0
Coal Conversion, Wt HAF	95.3	96.9		91.1	89.3	89.2	89.3
EOS, Wt		84.9				73.3	72.2
BDU, Wt		94.8				76.4	76.3

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MICROAUTOCLAVE EXPERIMENTS WITH MICRONIZED COALS
FEED AND PRODUCTS FOR RUN CC-8(227-66)

Table 4

Microautoclave Tests - 825 F, 2000 psig Hydrogen
1 gram DMDS Presulfided Shell S-317
per gram of Solid Tested
4 grams L-721 Wilsonville Distillate
per gram of Solid Tested

TESTS ON PERIOD 7C PRODUCT (Oil-free)
(CTSL Feed - Cleaned Micronized Coal)

Autoclave Test Time, Minutes	Solid Composition, W%		-----Organic Content ----- Conversion % of Original MAF Coal
	Ash	Organic	
Feed	36.09	63.91	6.41
30	44.40	55.60	29.27 4.52
60	49.56	50.44	42.52 3.69
Infinite(proj)			52.57 3.04

TESTS ON CLEANED MICRONIZED COAL

Autoclave Test Time, Minutes	Solid Composition, W%		-----Organic Content ----- Conversion % of Original MAF Coal
	Ash	Organic	
Feed	3.49	96.51	100.00
30	36.18*	63.82	93.62 6.38
60	41.90*	58.10	94.98 5.02
Infinite(proj)			(96.96) (3.04)
Est. High React.			87.21, 89.31

TESTS ON PERIOD 14 PRODUCT (Oil-free)
(CTSL Feed - Run-of-Mine Micronized Coal)

Autoclave Test Time, Minutes	Solid Composition, W%		-----Organic Content ----- Conversion % of Original MAF Coal
	Ash	Organic	
Feed	56.42	43.58	9.12
30	71.29	28.71	47.81 4.76
60	73.85	26.15	54.06 4.19
Infinite(proj)			55.00 4.10

TESTS ON RUN-OF-MINE MICRONIZED COAL

Autoclave Test Time, Minutes	Solid Composition, W%		-----Organic Content ----- Conversion % of Original MAF Coal
	Ash	Organic	
Feed	10.57	89.43	100.00
30	64.73*	35.27	93.56 6.44
60	67.51*	32.49	94.31 5.69
Infinite(proj)			(95.90) (4.10)
Est. High React.			78.1

* Ash recovery over 100%, values adjusted for ostensible catalyst content.

PRODUCT FRACTION ANALYSES - RUN 227-66

Operations With Otisca Processed Illinois No. 6 Coal
S-317 Catalyst

Period Number	5	9	14
Coal Feed	---- Cleaned ---		Uncleaned
Catalyst Age, Lb Coal/Lb Catalyst	143	198	418
LGO (IBP-650 F)			
IBP (D-1160 of Solvent)	530	527	538
Gravity, deg-API	18.7	18.0	17.7
Carbon, W%	89.06	88.54	88.13
Hydrogen, W%	11.67	11.97	12.04
Sulfur, W%	0.030	0.006	0.012
Nitrogen, W%	0.07	0.11	0.13
H/C Ratio	1.56	1.61	1.63
VGO (650-850 F)			
Gravity, deg-API	11.9	12.2	12.3
Carbon, W%	89.20	88.06	88.63
Hydrogen, W%	10.93	10.92	11.06
Sulfur, W%	0.006	0.008	0.008
Nitrogen, W%	0.11	0.13	0.23
H/C Ratio	1.46	1.48	1.49
HVGO (850-975 F)			
Gravity, deg-API	6.4	5.1	3.5
Carbon, W%	89.57	89.87	89.44
Hydrogen, W%	10.21	10.12	10.09
Sulfur, W%	0.011	0.014	0.024
Nitrogen, W%	0.21	0.22	0.32
H/C Ratio	1.36	1.34	1.34
RESIDUUM (975 F+)			
Gravity, deg-API	-3.0	-4.4	-5.2
Carbon, W%	89.97	90.46	89.02
Hydrogen, W%	8.69	8.48	3.26
Sulfur, W%	0.038	0.074	0.330
Nitrogen, W%	0.47	0.50	0.75
Cyclohexane Insolubles, W%	9.81	12.01	23.34
Toluene Insolubles, W%	1.87	2.66	1.63
Ash, W%	0.01	0.03	0.03
H/C Ratio	1.15	1.12	1.11

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

PRODUCT STREAM ANALYSES - RUN 227-66(CC-8)

Operations with Otisca Processed Illinois No. 6 Coal (Micronized)

Coal Feed	Cleaned	Uncleaned
Period Number	5	14
Catalyst Age, Lbs Coal/Lb Catalyst(Stage)	143	408
SEPARATOR OVERHEAD		
Volume Average Boiling Point, F	439	443
Gravity, deg-API	33.10	32.60
Watson Characterization Factor	10.95	11.00
ELEMENTAL ANALYSIS, W%		
Carbon, W%	87.81	86.99
Hydrogen, W%	13.22	13.24
Sulfur, W%	0.02	0.01
Nitrogen, W%(Perkin-Elmer)	0.08	0.10
Oxygen, W% (Untersacher)	< 0.05	< 0.05
Total	101.13	100.34
Nitrogen (Kjeldahl), W%	0.02	0.10
H/C Ratio	1.79	1.81
ATMOSPHERIC OVERHEADS		
Volume Average Boiling Point, F	514	515
Gravity, deg-API	25.80	25.20
Watson Characterization Factor	10.95	10.91
ELEMENTAL ANALYSIS, W%		
Carbon, W%	89.38	87.54
Hydrogen, W%	12.57	12.67
Sulfur, W%	0.00	0.00
Nitrogen, W%(Perkin-Elmer)	0.07	0.22
Oxygen, W% (Untersacher)	< 0.05	< 0.05
Total	102.02	100.43
Nitrogen (Kjeldahl), W%	0.04	0.22
H/C Ratio	1.68	1.72
PRESSURE FILTER LIQUID		
Gravity, deg-API	9.80	6.90
COMPOSITION		
500-650 deg-F, W%	8.59	6.26
650-850 deg-F, W%	53.25	49.02
850-975 deg-F, W%	19.78	20.35
975 deg-F+, W%	17.18	23.78
Loss, W%	1.20	0.59
ELEMENTAL ANALYSIS, W%		
Carbon, W%	89.74	88.80
Hydrogen, W%	10.55	10.12
Sulfur, W%	0.01	0.06
Nitrogen, W%	0.24	0.36
Oxygen, W% (Untersacher)	0.39	0.79
Total	100.93	100.13
H/C Ratio	1.40	1.36
FILTER CAKE PRODUCT		
COMPOSITION		
Oil (Quinoline Soluble), W%	52.30	55.29
Unconverted Coal, W%	33.54	21.22
Ash (ASTM), W%	14.16	23.49
ELEMENTAL ANALYSIS		
Carbon, W%	75.88	66.34
Hydrogen, W%	6.58	6.49
Sulfur, W%	2.44	2.19
Nitrogen, W%	0.67	0.61
Oxygen, W% (Untersacher)	3.16	3.44
Total (With Ash)	103.09	102.56
H/C Ratio	1.03	1.17

Table 7

**CTSL PERFORMANCE OF OTISCA MICRONIZED AND OIL AGGLOMERATION CLEANED ILLINOIS NO. 6 COAL
BENCH-SCALE TWO STAGE COAL LIQUEFACTION**

Run CC-8: Otisca Micronized Cleaned Coal, Periods 1-7
 Otisca Micronized Run-of-Mine Coal, Periods 8-14
 Run CC-6: Bechtel Oil Agglomerated Cleaned Coal, Periods 1-9
 Run-of-Mine Coal, Periods 10-12
 Run I-19: Bituminous Coal Research Heavy Media Cleaned Coal
 Run I-27: Bituminous Coal Research Heavy Media Cleaned Coal
 Demonstration Run with Solvent Fractionation for Bottoms Extinction

Run	----- CC-8 -----			----- CC-6 -----			I-19	I-27
Coal Treatment	-----Micronized-----			Oil Agglomeration			Heavy Media	
Condition	----- Cleaned -----			-----Cleaned-----			Cleaned	
Period Number	5	7	ROM 14	4	9	ROM 12	10	8
Hours of Run (End of Period)	120.	168.	335.	96.	213.	285.	240.	192.
Stg 1 Catalyst Age, Lb Dry Coal/Lb Cat	143.	198.	418.	106.	233.	319.	290	209
Moisture in Coal/Water Slurry, W%	63.19	65.51	67.20					
Moisture to Reactor, W% of Dry Coal Fed	1.00	1.38	0.83	6.81	6.81	3.23		
Temperatures, F								
First Stage Reaction	750.	775.	750.	751.	753.	749.	751	753
Second Stage Reaction	798.	818.	800.	800.	811.	812.	800	807
Slurry Mix Tank	187.	208.	265.	191.	299.	283.		
Slurry Drying Max Temp	247	247	287					
Unit Back Pressure, psig	2799.	2799.	2795.	2529.	2521.	2524.	2463	2488
Space Velocity Stage								
Lb Dry Coal / Hr / Ft ³ Catalyst	45	41	53	44	41	46	44	43
RECYCLES, W% OF DRY COAL								
Pressure Filter Liquid	198.5	63.0	174.5	177.7	131.0	114.3	194.0	149.0
Topped Separator Bottoms	0.0	205.7	0.0	0.0	0.0	0.0	0.0	0.0
Make-up Oil	0.0	0.0	7.9	2.0	4.2	4.6	0.0	0.0
Oil/Solids In Feed Slurry	1.98	2.15	1.77	1.69	1.23	1.08		1.17
Material Recovery, W%	97.22	98.83	98.13	99.35	96.97	100.51	100.08	973.7
Normalized Yields, W% of dry Coal								
C1-C3 in Gases	6.48	8.19	4.94	7.57	7.28	7.57	5.78	6.76
C4-390 deg-f in Liquids	17.21	21.06	16.15	19.82	22.30	17.63	17.13	17.75
390-650 deg-f in Liquids	30.35	33.85	26.00	33.49	33.07	29.15	33.07	41.21
650-975 deg-f in Liquids	21.03	11.58	17.15	18.19	17.32	11.57	18.44	15.91
975 F+ Oil	3.89	1.39	6.66	1.94	4.88	5.99	8.16	2.94
Unconverted Coal	7.84	6.43	9.56	5.28	4.43	5.34	3.75	3.63
Ash	3.31	3.31	10.57	4.62	4.62	15.21	5.33	5.77
Water	13.39	13.36	11.67	12.04	8.96	9.59	11.27	9.37
CO	0.00	0.00	0.00	0.04	0.05	0.07	0.24	0.04
CO ₂	0.01	0.01	0.06	0.04	0.04	0.04	0.08	0.00
NH ₃	1.61	1.66	1.24	1.67	1.56	1.35	1.49	1.62
H ₂ S	2.20	2.24	2.71	2.52	2.51	2.74	2.34	2.51
Total (100 + H ₂ Reacted)	107.32	107.99	106.71	107.23	106.99	106.25	107.07	107.19
Process Performance								
W% of MAF Coal								
C4-975 deg-f Distillates	69.4	73.8	65.8	75.0	76.2	68.8	72.5	79.6
975F+ Conversion	88.1	91.9	82.0	92.4	90.2	86.6	87.4	93.5
Coal Conversion	91.9	93.3	89.3	94.5	95.4	93.7	94.0	96.2
Hydrosulfurization, W%	78.3	79.5	72.2	81.6	81.3	67.9		
Hydrodenitrogenation, W%	87.5	89.9	76.3	90.1	83.8	83.8	82.9	88.3

Table 8

PRODUCT FRACTION ANALYSES WITH CLEANED ILLINOIS COALS

Operations using Shell S-317 Catalyst

RUN	I-27	CC-6	CC-8
Cleaning Process	Heavy Media	Oil-Agglom.	Otisca
Day of Operation	9	9	9
Catalyst HRI No	5394	5394	5394
Presulfiding Agent	DMDS	TNPS	TNPS
Product Fration			
IBP-650 F			
Hydrogen, W%	11.33	11.39	11.97
Nitrogen, W%	0.21	0.10	0.13
650-850 F			
Hydrogen, W%	10.29	10.29	10.92
Nitrogen, W%	0.18	0.23	0.13
850-975 F			
Hydrogen, W%	9.07	9.20	10.12
Nitrogen, W%	0.31	0.32	0.22
975 F+ Residuum			
Hydrogen, W%	7.62	7.29	8.48
Nitrogen, W%	0.77	0.92	0.50

Run664763prod.tab

2 of 3

Table 9
Part 1 of 2

FEED COAL ANALYSES FOR RUN 227-66(CC-8)

Run 227-66 Feed: Otisca Processed Illinois No. 6 Coal

FEED DESIGNATION, HRI No.	5738 5742	5739	5761	5762
TYPE	Cleaned	Uncleaned	Refuse	Raw
FEED FOR PERIODS	1-9	10-15		
MOISTURE CONTENT				
As Received Slurry, W%	67.22	67.01	76.03	
Analyzed Sample, W%	1.25	1.61	2.20	3.19
PROXIMATE ANALYSIS, W%				
Moisture, W%	61.86			
Volatile Matter (MAF Basis)	44.78	43.91		
Fixed Carbon (MAF Basis)	55.22	56.09		
ULTIMATE ANALYSIS (W%, Dry Basis)				
Carbon	75.87	69.27	23.50	69.68
Hydrogen	5.17	4.53	1.87	4.76
Sulfur	2.65	3.53	6.84	3.62
Nitrogen	1.52	1.34	0.44	1.37
Chlorine	0.04	0.07		
Ash	3.46	10.57	64.54	9.95
Oxygen (By Difference)	11.33	10.69	2.81	10.62
Oxygen (Unterzaucher)	13.24	16.02		
SULFUR FORMS (W%, Dry Basis)				
Sulfate	0.07	0.11		
Pyrite	0.60	1.28		
Organic	2.07	1.97		
HEATING VALUE, Btu/lb(Dry)	13124	12303	3650	11003
Btu/Lb MAF	13594	13757	10293	12219
MINERAL ANALYSIS OF ASH (W%, Ignited)				
Silica, SiO ₂	33.50	44.57	51.57	
Alumina, Al ₂ O ₃	16.50	19.79	20.24	
Titania, TiO ₂	1.90	0.78	0.19	
Ferric Oxide, Fe ₂ O ₃	33.16	22.40	16.58	
Lime, CaO	5.98	5.00	4.49	
Magnesia, MgO	1.20	0.88	0.87	
Potassium Oxide, K ₂ O	1.30	1.80	1.91	
Sodium Oxide, NaO	0.44	0.42	0.26	
Sulfur Trioxide, SO ₃	5.20	3.43	3.56	
Phosphorous Pentoxide, P ₂ O ₅	0.10	0.70	0.16	
Strontium Oxide, SrO		0.03	0.00	
Barium Oxide, BaO		0.05	0.02	
Manganese Oxide, Mn ₃ O ₄		0.01	0.15	
Undetermined	0.76	0.14	0.00	

FEED COAL ANALYSES FOR RUN 227-66(CC-8)

Run 227-66 Feed: Otisca Processed Illinois No. 6 Coal

FEED DESIGNATION, HRI No.	5738 5742	5739	5761	5762
TYPE	Cleaned	Uncleaned	Refuse	Raw
FEED FOR PERIODS	1-9	8-15		
PARTICLE SIZE DISTRIBUTION, W%				
>11.5 microns	4.9	9.7		
11.5	3.7	1.8		
10.5	1.6	5.2		
9.5	2.4	3.3		
8.5	5.2	4.7		
7.5	4.8	6.6		
6.5	7.8	8.85		
5.5	10.3	8.35		
4.5	11.3	9.9		
3.5	12.7	11.5		
2.5	14.0	12.85		
1.5	17.2	13.35		
0.5	4.8	3.85		
MICROAUTOCLAVE RESULTS **				
Thermal Coal Conversion	85.7	90.0	76.4	74.1
Catalytic Coal Conversion	93.4	93.3	81.1	93.2
** 1989 tests - 800 F, 30 minutes, 2000 psig H ₂ , 4/1/(1) Solvent/Coal/(Shell S-317 Catalyst) Solvent - Wilsonville coal liquefaction distillate product.				
MACERAL ANALYSIS, V%				
Reactives				
Vitrinites	81.1	76.8	59.9	
Liptinite	3.4	4.3	2.0	
Exinite				
Resinite				
1/3 Semifusinite				
Total	84.5	81.1	61.9	
Unreactive				
2/3 Semifusinite				
Micrinite				
Fusinite				
Inertinite	10.7	8.8	4.0	
Total		8.8		
Pyrite	3.1	5.7	20.4	
Other Mineral	1.7	4.4	13.7	

Table 10

INSPECTION OF STARTUP AND MAKEUP OIL
FOR RUNS 227-65 AND 227-66(CC-8)

Designation	HRI 5648
Gravity, API	6.4
Distillation, F	
IBP	696
5 V%	769
10 V%	789
20 V%	807
30 V%	820
40 V%	831
50 V%	841
60 V%	875
70 V%	892
80 V%	909
90 V%	950
E.P.	975
V% @ 650 F	76
V% @ 850 F	96
V% @ 975 F	94
IBP-650 F, W%	0.0
650-850 F, W%	52.5
850-975 F, W%	41.1
975 F+, W%	5.9
Loss, W%	0.5
Carbon, W%	89.27
Hydrogen, W%	10.01
Sulfur, W%	0.01
Nitrogen, W%	0.46
Solvent Quality Test*	
Illinois Coal	70.1
Black Thunder Coal	61.5

* Coal conversion, 750 F, 30 Minutes,
2000 psig N₂, 2/1 solvent/coal

TABLE 11**FRESH CATALYST PROPERTIES - RUNS 227-65 AND 227-66 (CC-8)**

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°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 12
RECOVERED CATALYSTS ANALYSES
RUN 227-65

STAGE	First	Second
CATALYST AGE, LB COAL/LB	62	62
CATALYST RECOVERY, Vol. %	86.7	93.3
Bulk Density, Gm/cc	0.87	0.84
ANALYSES OF OIL-FREE		
+20 MESH CATALYST, W%		
Carbon	9.66	9.28
Hydrogen	1.13	0.88
H/C Ratio	1.40	1.14
Nitrogen	0.27	0.27
Sulfur	5.84	5.89
Molybdenum	9.54	9.49
Cobalt		
Nickel	1.82	1.82
Titanium	0.03	0.04
Iron	0.12	0.06
Calcium		
Sodium		
Total Metal Contaminants		
Loss on Ignition, W%		
Particle Density, Gm/cc particle*	1.1951.44	1.18
	5	
Pore Volume (D>30 [°] A), cc/gm	0.46	0.47
cc/cc particle	0.55	0.56
Surface Area (calc.), M ² /gm	189	182
M ² /cc particle	226	215
Modal Pore Diameter, Angstrom		
Macro-pores	2,600	2,100
Mini-pores	78	76
ANALYSES OF IGNITED CATALYST		
Particle Density, gm/cc particle*		
Pore Volume (D>30 [°] A, cc/gm		
cc/cc particle		
Surface Area (Calc.), M ² /gm		
M ² /cc particle		
Modal Pore Diameter, Angstrom		
Macro-pores		
Mini-pores		
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS		
Weight, Grams	63.0	12.8
Molybdenum, W%	7.23	8.60
Nickel, W%		

* In mercury at 10 psia.

TABLE 13
RECOVERED CATALYSTS ANALYSES
RUN 227-66E (CC-9) EXTENSION OF RUN 227-66 (CC-8)

STAGE	First	Second
CATALYST AGE, LB COAL/LB	327	329
CATALYST RECOVERY, Vol. %	94.4	102.2
Bulk Density, Gm/cc	0.840	0.83
ANALYSES OF OIL-FREE		
+20 MESH CATALYST, W%		
Carbon	12.56	13.61
Hydrogen	1.23	0.93
H/C Ratio	1.18	0.82
Nitrogen	0.36	0.19
Sulfur	6.32	6.02
Molybdenum	7.47	7.39
Cobalt		
Nickel	1.62	1.55
Titanium	0.32	0.30
Iron	0.47	0.09
Calcium	0.18	0.17
Sodium	0.20	0.56
Total Metal Contaminants	1.17	1.12
Loss on Ignition, W%	17.54	17.19
Particle Density, Gm/cc particle*	1.27 1.445	1.33
Pore Volume (D>30*A), cc/gm	0.37	0.39
cc/cc particle	0.47	0.52
Surface Area (calc.), M ² /gm	168	158
M ² /cc particle	213	210
Modal Pore Diameter, Angstrom		
Macro-pores	2,000	1,020
Mini-pores	70	73
ANALYSES OF IGNITED CATALYST		
Particle Density, gm/cc particle*	1.15	1.14
Pore Volume (D>30*A, cc/gm	0.57	0.58
cc/cc particle	0.66	0.66
Surface Area (Calc.), M ² /gm	168	158
M ² /cc particle	213	210
Modal Pore Diameter, Angstrom		
Macro-pores	2,000	1,020
Mini-pores	70	73
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS		
Weight, Grams	47.0	24.1
Molybdenum, W%	3.08	0.82
Nickel, W%	0.68	0.18

* In mercury at 10 psia.

FIGURE 1

COAL CONVERSION – OTISCA PROCESSED ILLINOIS COALS

Runs 227-65 and 227-66(cc-8)

FIGURE 2

COLLECTED GAS YIELDS – OTISCA PROCESSED ILLINOIS COAL

Runs 227-65 and 227-66(CC-8)

FIGURE 3

LIQUID YIELDS - RUN 227-66(CC-8)

FIGURE 4

DISTILLATE YIELDS – RUN 227-66(CC-8)

FIGURE 5

YIELDS - RUN 227-66(CC-8)

FIGURE 6

RESIDUAL OIL CONCENTRATION IN PRODUCT SLURRY

Run 227-66(CC-8)

FIGURE 7

HYDROGEN CONTENTS OF PRODUCT FRACTIONS

Run 227-66(CC-8)

FIGURE 8

NITROGEN CONTENTS OF PRODUCT FRACTIONS

Run 227-66(CC-8)

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SECTION III

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SECTION III

RUN 227-62E (CC-9) - PREPARATION OF PRODUCT SLURRY FOR DELAYED COKING 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 delayed coking. This operation, as practiced in the petroleum industry, involves partial conversion of a heavy liquid into lighter liquid by rejecting carbon with the formation of solids and simultaneous separation of solids from liquids by vaporization. For it to be used effectively as a solids separation technique in coal liquefaction, it would have to be modified to give more emphasis to liquid recovery (less coke formation) relative to liquid quality.

Illinois No. 6 bituminous coal (of two different ash contents) was liquefied at a space velocity of 67 lb/hr/ft³ of catalyst in an eight-day extension of Run 227-66 (CC-8). Atmospheric bottoms were collected at two conditions: first with the first and second reactor temperatures at 750 and 800°F, and then with the reactor temperatures at 775 and 810°F.

The coking tests were conducted at Foster Wheeler Development Corporation in a four-inch diameter minicoker. They found that coal liquefaction bottoms could be processed by delayed coking; however, the coking temperature had to be significantly lower and the steam-to-feed ratio significantly higher than practiced commercially in the petroleum industry. About 85 W% of the liquid present in the coking feed was recovered. The liquid product had a low residuum content as most of the resid present in the feed was either converted to a lighter product or to coke.

The liquid product from delayed coking showed good coal liquefaction quality in microautoclave tests and would be suitable as recycle solvent. Using delayed coking as a solids separation operation would lead to overall higher residuum conversion if the residuum conversion in the liquefaction reactors is maintained. The major disadvantage of delayed coking is the conversion of resid, which could be converted to distillate in a CTSL extinction operation, to solids.

SCOPE OF WORK

Typically, CTSL bench runs are in solvent balance, i.e. the entire amount of atmospheric bottoms is used to provide the necessary amount of recycle solvent. However, in this run, in order to obtain 20 kg of bottoms for coking tests, a similar quantity of make-up oil had to be added over the course of the run.

Run 227-66E (CC-9) was an extension of Run 227-66 (CC-8), which had examined the performance of OTISCA-cleaned Illinois No. 6 coal. The same aqueous coal slurries were used for feed in this run extension. The run plan for this eight-day extension is shown in *Table 1*. The space velocity was 67 lb/hr/ft³ of catalyst per stage and the recycle-to-fresh-coal ratio was kept high, at about 2:1, because of the operational problems that had been encountered in the preceding operations with higher coal concentrations in the slurry-drying system. The original run plan included two conditions, to obtain CAS bottoms of two different characteristics. The first condition, with uncleaned coal and first and second stage reactor temperatures at 750 and 800°F, was completed as planned. Condition 2, with cleaned coal and first and second stage reactor temperatures at 775 and 810°F, also prescribed recycle of the CAS bottoms solids-containing stream. However, the feed slurry was too viscous with these conditions and the run plan was modified, first to reduce the quantity of CAS bottoms in the recycle and later to use makeup oil for the entire recycle oil requirements.

Delayed coking tests, using the CAS bottoms, were conducted by Foster Wheeler Development Corporation to determine its applicability as a solids-separation technique for CTSL slurry products. The suitability of the delayed-coker liquid product as recycle solvent was evaluated by conducting microautoclave tests to estimate the solvent quality for liquefaction.

PROGRAM RESULTS AND ANALYSES - RUN 227-66E (CC-9)

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 average yields and process performance for Condition 1. The yield information was not calculated for Condition 2 because the process was not at steady state due to changes in the feed composition.

The average coal and 975°F+ resid conversions for Condition 1 were 87.3 and 75.8 W% of maf coal, respectively. Mostly due to the 29% higher space velocity in Run 227-66E (CC-9), these values are somewhat lower than the 89.3 and 80.7 W% achieved at the end of Run 227-66(CC-8). The C₄-975°F distillate yield, 65.2 W% (maf), and the denitrogenation, 71.2%, were also lower at the higher space velocity. The C₁-C₃ gas yield in Run 227-66E (CC-9), 4.0 W% (dry coal) was lower by 1.0 W%.

DELAYED-COKING TESTS

Table 4 shows the analyses of the two atmospheric still bottoms (ASB) products that were tested at Foster Wheeler. The composition of the two ASB's was fairly similar even though they were produced at different conditions. Apparently, the differences in process severity, makeup oil rate, and catalyst age were approximately offsetting.

Two coking tests, one for each ASB sample, were conducted in a four-inch diameter mini-coker. The Foster Wheeler test report is appended to this section. Two key parameters, temperature and steam/feed ratio, were selected as the variables in order to meet the objective of producing high liquid yields. The effects of other potential variables are either known (pressure and throughout ratio) or have a lesser effect on yield (coking cycle time, feed rate, and steamout period); so they were held constant. Initially, a scoping test was done at high coking temperature and a steam rate significantly above the normal commercial ratios. The feedstock (Condition 1 product) was not thermally stable at these conditions, and the coil quickly plugged. A test (Run 1) was then successfully completed at a lower temperature. For Run 2, a lower coking temperature and a higher steam/feed ratio were chosen.

The tests showed that it is possible to operate a delayed coker to process liquefaction bottoms. The nature of the feedstock requires that the operating variables be different than practiced commercially for the petroleum based feeds. The coker temperature should be significantly lower and the steam/feed ratio should be significantly higher than those used for petroleum feedstocks.

The yields from the coking tests are shown in *Table 5*. In the second part of *Table 5*, the conversions and net yields are expressed as a weight percent of the 975°F⁺ oil in the feed as if this were the only reactive component. The performance of the two coking runs was quite similar. In each of the coking tests, about 40 W% of the 975°F⁺ liquid was converted to 975°F⁻ product, and 39 W% was converted to coke. The net C₄-975°F distillate yield was around 30 W% of the 975°F⁺ liquid in the coker feed. The analyses of the coke and oil produced in these coking tests are listed in *Tables 6 and 7*.

The conversion of 975°F⁺ liquid to 975°F⁻ product is, of course, desirable; however, its conversion to coke is very undesirable because the valuable coal liquid product is converted to an undesired byproduct. For using delayed coking as a solids separation operation, the most ideal situation would be a more physical operation (viz. vaporization of liquid) rather than chemical conversion to coke. The liquid product obtained in these tests had very little resid content. A better operation would have yielded more liquid with higher resid content. The higher resid content would not be undesired because this liquid would be used as recycle anyway, and the resid conversion could then occur in the liquefaction reactors.

To understand the effect of integrating delayed coking with the liquefaction section (by recycling the coker liquid to slurry the coal), the liquefaction yields obtained in Condition 1 were combined with the delayed coker performance obtained in the above tests. (Although coking Run 2 was obtained from Condition 2, the yields from Condition 1 were assumed applicable.) The following bases were assumed. Coal is slurried with a portion of the delayed coker product (650°F⁺ liquid) in a 1:1.1 ratio and fed to the liquefaction section. The yields in the liquefaction section were considered to be identical to those obtained in Condition 1, despite the different quality and composition of the recycled coker oil. In fact, the resid conversion using the coker liquid as the recycle solvent would be lower due to the decreased resid concentration in the reactors. The resid content of the coker solvent would be lower than that of a solvent obtained through a physical separation process such as filtration. The 650°F⁺ product from the reaction section, including the solids, is then sent to the delayed coker. The net yields in coking were assumed to be the same as obtained in the above tests as reported in *Table 5*. A portion of the coker 650°F⁺ liquid product, including the entire 975°F⁺ liquid and the portion of the 650-975°F liquid required for the 1.1:1 solvent:coal ratio, is then recycled.

Table 8 shows the product yields and the performance of the integrated process. The yields for case I and case II are based on the yields observed in the first and the second coking tests, respectively. The integrated process gives higher resid conversion, by 5.6 W% (maf) and also higher C₄-975°F product, by 4.4 W% (maf). Coal conversion is, of course, lower because a portion of the liquefied coal is converted to coke. Coal and resid conversions are identical as there is no net yield of 975°F⁺ liquid. These predicted yields represent a

best-case scenario, in which no detriment is obtained due to the quality of the recycled coker oil and extinction of the resid is assumed possible. But these yields were not as attractive as the yields that had been attained in the extinction recycle operation of the CTSL process demonstration Run 227-47 (I-), in which 77.9 W% (maf) distillate was produced. The liquefaction conditions of the two operations were quite different, and Run 227-47 (I-) relied on solvent extraction for solids separation, but the demonstration run indicates what is ultimately achievable with the CTSL process.

If delayed coking, or any other solids separation process is to be used in coal liquefaction to produce recycle oil, the quality of the liquid product should have certain beneficial properties. First of all, it should be effective in liquefying coal. Secondly, the separation process should not alter the chemical nature of the liquid in an undesirable way whereby its reactivity towards conversion to distillate is diminished. Also, the nature of the liquid product should not increase catalyst deactivation. The first, and probably the most important, of these concerns was addressed by performing microautoclave solvent and coal reactivity tests, using coker liquid products.

These reactivity tests were conducted in a 20-cc microautoclave unit at 800°F for 30 minutes under 2000 psig hydrogen pressure. A run-of-mine Illinois No. 6 coal was used. The tests measured the coal conversion under catalytic and non-catalytic conditions. For each test, 1 gm of coal was added to 8 gm of solvent and 2 gm of aged catalyst (if used). Four solvents (2 coker liquid products and 2 PFL's) were compared.

The results from the microautoclave tests are shown in *Table 9*. By these tests the solvent qualities of the coker liquid products and of the coker feed liquids (PFL) are very similar. The average coal conversion for the coker products (89.3 W%) was only 0.6 W% less than the coal conversion for the coker feeds. The solvent properties are compared in *Table 10*. The hydrogen contents are quite similar (except the hydrogen content of the liquid from the second coking run is higher). By H-NMR analysis, the coker liquid products have a higher aromatic hydrogen content, indicating dehydrogenation of some of the components during coking. These results suggest that the liquid products obtained from delayed coking should be suitable for use as recycle oils for slurrying coal to liquefaction reactors.

DETAILS OF OPERATION

OPERATIONS

Run 227-66E (CC-9) started at the conclusion of Run CC-8. The same slurry-drying system was used to remove water from the coal slurry feed. The aqueous coal slurry and the oil solvent were charged to the slurry-drying vessel, which held enough slurry for eight hours of operations. Under flowing nitrogen, the contents were heated for about six hours, during which almost all the water evaporated, leaving a dried slurry of less than 2 W% moisture (coal basis). The dried slurry was then charged to a feed vessel from which it was pumped continuously to the liquefaction reactors.

Condition 1 was executed as planned. When the operating conditions were changed to Condition 2 target levels, operating problems were encountered. The feed slurry became too viscous with the specified recycle of Topped Separator Bottoms (TSBs), which contained unreacted coal solids. The viscosity did not improve significantly when the recycle was changed back to Pressure Filter Liquid (PFL); so the entire recycle solvent was then changed to lighter make-up oil. Although operations were again successful, steady-state liquefaction data could not be obtained in this condition due to the frequent changes that had preceded.

COAL FEED

Since Run CC-9 was an extension of Run 227-66(CC-8), the cleaned and uncleaned coals used in Run CC-8 were also used in Run CC-9. The uncleaned coal (10.36 W% ash) was used in Periods 16-19, and the cleaned coal (3.44 W% ash) was used in Periods 20-23. The feed coal supplied by OTISCA Industries was an aqueous slurry containing around 30 W% coal in micronized form. The analyses of the feed coals are given in *Table 9* of the CC-8 section.

MAKE-UP OIL

No start-up oil was required for this run because it was a continuation of Run CC-8, but make-up oil was added continuously to replace the solvent removed with the TSB samples for coking tests. For most of the run L-756, a composite of PFL's from earlier CTSL operations, was used. As described above, more makeup oil had to be used in Condition 2, and the stock of L-756 was exhausted. For the last day of the run, HRI 5648, a Wilsonville derived heavy gas oil, which had been used during the start-up of Run CC-8, was used. The analyses of the L-756 makeup oil are listed in *Table 11*, and the analyses of the HRI 5648 makeup oil are listed in *Table 10* of the CC-8 section.

CATALYST

The same Shell S-317, HRI 5394, 1/32-inch extrudate NiMo catalyst that had been used throughout the program was used in both liquefaction stages. In Run 227-66E(CC-9) the catalysts started with the 418 lb coal/lb catalyst (each stage) age that they had at the end of Run CC-8. There was no additional sulfiding during the transition from Run CC-8 to Run CC-9. The analyses of the fresh catalyst had been previously presented in *Table 11* of the CC-8 section.

RECOVERED CATALYST

The analyses of the recovered catalyst had been discussed in the CC-8 section, and they are listed in *Table 12* of that section.

- (1) Kimber, G., "The Development of Filtration for Coal Liquefaction," British Coal Liquefaction Project, EPRI Conference, 1991.

TABLE 1**Run Plan for 227-66E (CC-9)**

Condition	1	2
Run 227-66E Periods	16-19	20-23
Space Velocity Lb/hr/ft ³ catalyst)	67	67
1st Stage Temperature, °F	750	775
2nd Stage Temperature, °F	800	810
Coal Type (Illinois #6) HRI No.	Uncleaned 5739	Cleaned 5743
Oil to Solids Ratio	2	2
Recycle (Planned), W% Coal		
PFL	1.74	0.00
Make-up Oil	0.26	2.00
CAS Bottoms	0.00	0.00

TABLE 2 - Operating Summary - Solids Separation Run 227-66E (CC-9)

COAL: Illinois No. 6 - OTISCA Uncleaned (HRI 5739) Periods 16-19
 OTISCA Cleaned (HRI 5743) Periods 20-23

CATALYST: Shell 317 NiMo

Period Number (227-66)	16	17	18	19
Date (Start of Period)	4/4/90	4/5/90	4/6/90	4/7/90
Hours of Run (End of Period)	383.	407.	431.	455.
Catalyst Age, Lb.Dry Coal/Lb.Cat. Per Stage	495.	540.	578.	624.
Moisture in Coal/Water Slurry, W%	67.01	67.01	70.78	67.01
Moisture in Feed Slurry, W%			0.23	0.19
Moisture to Reactor, W% Dry Coal Fed			0.67	0.54
First Stage Temperature (°F)	750.	752.	752.	751.
Second Stage Temperature (°F)	801.	802.	801.	800.
Unit Back Pressure (psig)	2802.	2803.	2799.	2797.
Space Velocity, (Lb/Hr/Ft ³ Cat)	72.4	70.9	61.6	72.9

W% DRY COAL

PFL Recycle	153.7	148.8	163.4	151.5
PFL To Buffer - Stage 1	2.7	3.1	3.2	2.5
PFL to Buffer - Stage 2	2.3	2.7	3.8	2.0
CAS Bottoms	0.0	0.0	0.0	0.0
Make-Up Oil	24.4	35.6	44.7	34.3
TOTAL MATERIAL RECOVERY (GROSS)	100.45	99.72	99.5	99.60

ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED

C ₁ -C ₃ in Gases		4.79	3.29
C ₄ -C ₇ in Gases		6.66	5.32
IBP-390°F in Liquids		8.94	8.92
390-500°F in Liquids		9.84	9.84
500-650°F in Liquids		11.20	14.88
650-850°F in Liquids		15.63	12.27
850-975°F in Liquids		7.62	5.83
Toluene Soluble 975°F ⁺ Oil		9.42	9.81
Toluene Insoluble 975°F ⁺ Oil		0.60	0.79
Unconverted Coal		10.57	12.27
Ash		10.36	10.36
Water		6.72	8.65
CO		0.00	0.00
CO ₂		0.07	0.06
NH ₃		1.17	1.17
H ₂ S		2.59	2.55
Total (100 + H ₂ Reacted)		106.18	105.99

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal		66.8	63.6
975°F ⁺ Conversion, W% MAF		77.0	74.5
Coal Conversion, W% MAF	88.1	88.2	86.3
HDS, W%		72.4	71.1
HDN, W%		71.3	71.1

TABLE 2 - (Continued)

COAL: Illinois No. 6 - OTISCA Uncleaned (HRI 5739) Periods 16-19
OTISCA Cleaned (HRI 5743) Periods 20-23

CATALYST: Shell 317 NiMo

Period Number (227-66)	20	21	22	23
Date (Start of Period)	4/8/90	4/9/90	4/10/90	4/11/90
Hours of Run (End of Period)	479.	503.	527.	551.
Catalyst Age, Lb.Dry Coal/Lb.Cat. Per Stage	672.	717.	761.	800.
Moisture in Coal/Water Slurry, W%	67.01	66.16	66.16	70.00
Moisture in Feed Slurry, W%		0.30	0.94	0.41
Moisture to Reactor, W% Dry Coal Fed		1.00	2.86	1.20
First Stage Temperature (°F)	768.	772.	773.	773.
Second Stage Temperature (°F)	806.	808.	811.	809.
Unit Back Pressure (psig)	2806.	2807.	2800.	2812.
Space Velocity, (Lb/Hr/Ft ³ Cat)	68.9	71.1	70.7	62.0

W% DRY COAL

PFL Recycle	21.6	72.4	17.2	0.0
PFL To Buffer - Stage 1	2.9	3.1	2.5	3.0
PFL to Buffer - Stage 2	2.3	2.3	2.4	2.7
CAS Bottoms	184.4	158.0	42.3	0.0
Make-Up Oil	62.8	16.4	151.7	211.0
TOTAL MATERIAL RECOVERY (GROSS)	92.97	100.53	89.04	101.21

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 ⁺ Oil				
Toluene Insoluble 975°F ⁺ Oil				
Unconverted Coal				
Ash		3.31	3.31	3.31
Water				
CO				
CO ₂				
NH ₃				
H ₂ S				
Total (100 + H ₂ Reacted)				

PROCESS PERFORMANCE

C ₄ -975°F Distillates, W% of MAF Coal			
975°F ⁺ Conversion, W% MAF			
Coal Conversion, W% MAF	94.4	93.6	92.1
HDS, W%			
HDN, W%			

TABLE 3**Liquefaction Performance
Run 227-66E (CC-9)**

Condition	1	2
Periods (227-66E)	18/19	22/23
Catalyst Age (Per Stage) Lb Coal/Lb Cat.	601	773
1st Stage Temperature, °F	752	773
2nd Stage Temperature, °F	801	810
Space Velocity (Per stage) Lb/Hr/Ft ³ Catalyst	67.2	66.3
Recycle/Coal Ratio	2.01	2.16
NORMALIZED YIELDS (W% COAL)		
C ₁ -C ₃	4.04	
C ₄ -390°F	14.92	
390-500°F	9.84	
500-650°F	13.04	
650-850°F	13.95	
850-975°F	6.73	
975°F+ Liquid	10.31	
IOM	11.42	
Ash	10.36	
CO + CO ₂	0.07	
H ₂ S	2.57	
NH ₃	1.17	
H ₂ O	7.74	
TOTAL (100 + H ₂ CONS)	106.09	
PERFORMANCE (W% MAF)		
Coal Conversion	87.3	93.0
Resid (975°F+) Conversion	75.8	
C ₄ -975°F Yield	65.2	
HDS	71.8	
HDN	71.2	

TABLE 4**Coking Feedstock Properties
ASBS from Run 227-66E (CC-9)**

HRI No.	LO-5274/75	LO-5276
CONDITION	1	2
API Gravity	-1.5	-0.5
IBP, °F	549	500
IBP-650°F, W%	10.00	15.00
650-850°F, W%	41.51	40.09
850-975°F, W%	12.40	10.74
975°F+, W%	36.09	34.17
Carbon, W%	84.18	85.69
Hydrogen, W%	9.22	9.27
Nitrogen, W%	0.49	0.55
Sulfur, W%	0.56	0.52
Oxygen, W%	0.68	0.86
Ash, W%	4.87	3.11
Quinoline Insol, W%	11.35	8.46
Toluene Insol, W%	13.10	12.05
Pentane Insol, W%	23.77	21.83
CCR (Liquid), W%	8.54	7.64

TABLE 5
Delayed Coking Tests

Run	1	2
Coking Feed	LO-5274/75	LO-5276
Normalized Yields		
Gas	3.65	3.07
Oil	75.53	78.56
Coke (IOM + Ash)	20.82	18.37
H ₂	0.33	0.22
H ₂ S	0.02	0.01
CO + CO ₂	0.06	0.15
C ₁ -C ₃	2.37	1.83
C ₄	0.60	0.58
C ₅	0.27	0.29
IBP-650°F	19.86	17.38
650-850°F	38.81	44.12
850-975°F	11.66	11.40
975°F+ Liquid	5.19	5.66
IOM	15.95	15.26
Ash	4.87	3.11
W% of 975°F+ in Liquid in Feed		
Resid Conversion	40.75	39.44
Conversion to Coke	38.28	38.53
Net C ₄ -975°F Yield	29.51	30.87
Net H ₂	1.33	0.87
Net H ₂ S	0.08	0.03
Net CO + CO ₂	0.23	0.57
Net C ₁ -C ₃	9.60	7.10
Net C ₄	2.44	2.26
Net C ₅	1.07	1.11
Net IBP-650°F	39.87	9.25
Net 650-850°F	-10.89	15.68
Net 850-975°F	-2.98	2.57
Liquid Yield (W% feed)	75.53	78.56
Liquid Recovery (W% liquid)	85.20	85.83

TABLE 6
Coker Oil Analysis

Run	1	2
Coking Feed	LO-5274/75	LO-5276
API	9.5	10.2
IBP, °F	346	419
IBP-650°F, W%	26.30	22.12
650-850°F, W%	51.39	56.16
850-975°F, W%	15.44	14.51
975°F+, W%	6.87	7.21
Carbon, W%	89.00	88.95
Hydrogen, W%	10.13	10.51
Nitrogen, W%	0.36	0.29
Sulfur, W%	0.39	0.11

TABLE 7 - Coke Analysis

Run	1	2
Coking Feed	LO-5274/75	LO-5276
Carbon, W%	71.51	78.26
Hydrogen, W%	2.83	3.07
Nitrogen, W%	1.02	1.23
Sulfur, W%	1.86	1.89
Ash, W%	21.05	15.24

TABLE 8
Integration of CTSL With Delayed Coking

Yields, W% Coal	Base	Case I	Case II	CTSL with Extinction Recycle*
C ₁ -C ₃	4.04	5.29	4.98	8.1
C ₄ -390°F	14.92	15.38	15.37	18.6
390-500°F	9.84	9.84	9.84	10.0
500-650°F	13.04	18.24	14.26	23.9
650-850°F	13.95	12.53	16.02	19.3
850-975°F	6.73	6.34	7.07	1.7
975°F+ Liquid	10.31	0.00	0.00	2.4
IOM	11.42	16.42	16.52	3.0
Ash	10.36	10.36	10.36	5.8
Heterogases	11.50	11.54	11.58	14.1
Performance, W% (MAF)				
Coal Conversion	87.26	81.69	81.58	96.8
Resid Conversion	75.76	81.69	81.58	94.1
C ₄ -975°F Yield	65.24	69.53	69.79	78.0

Basis for Calculations:

1. Coal was slurried with a portion of the coker liquid product in 1:1.1 proportion.
2. Yields in liquefaction section were unaffected by the quality or composition of the recycled coker liquid.
3. 650°F+ product from liquefaction is sent to coker.
4. A portion of the 650°F+ product from coker is recycled. Entire 975°F+ cut is recycled; balance recycle contains 650-850°F and 850-975°F portion in the same ratio as in the coker product.
5. Base yields are from condition 1. Case I and Case II consider yields from coking tests I and II, respectively.

* *CTSL Process Demonstration Run 227-47 (I-27) periods 14-18 average.*

TABLE 9
Quality of Coker Liquid Towards Coal Liquefaction

Coal: Illinois No. 6 (HRI-5715)
 Liquefaction Temperature: 800°F
 Time: 30 Minutes
 Pressure: 2000 psig (H₂)
 Catalyst: Recovered CTSL Catalyst
 Solvents: Coker Feed 1 (227-69-18 PFL)
 Coker Product 1 (HRI-5765, Coking Run 1)
 Coker Feed 2 (227-69-22 PFL)
 Coker Product 2 (HRI-5778, Coking Run 2)

Solvent	Coal Conversion (W% MAF)	
	Non-Catalytic	Catalytic
Coker Feed 1	90.4	89.8
Coker Product 1	89.7	89.4
Coker Feed 2	87.7	91.8
Coker Product 2	87.9	90.4

TABLE 10
Comparison Between Coker Feeds and Products

Sample	Coker Feed 1	Coker Product 1	Coker Feed 2	Coker Product 2
Liquid Analyses				
API Gravity	5.2	9.5	4.3	10.2
Carbon, W%	88.69	89.00	89.25	88.95
Hydrogen, W%	10.11	10.13	10.06	10.51
Nitrogen, W%	0.42	0.36	0.40	0.29
Sulfur, W%	0.09	0.39	0.05	0.11
H/C Ratio	1.37	1.37	1.35	1.42
Hydrogen Type (H-NMR)				
Paraffinic	58.18	56.82	54.58	56.10
Naphthenic	32.03	28.64	33.45	29.70
Aromatic	9.80	14.55	11.97	14.19

TABLE 11
Analysis of Make-Up Oil
Run 227-66E (CC-9)

HRI-No.	L-756
Type:	Composite CTSL PFL
API Gravity	12.9
Carbon, W%	87.99
Hydrogen, W%	11.04
Nitrogen, W%	0.33
Sulfur, W%	0.01
D1160 Distillation	Temperature, °F
IBP	
5 V%	
10 V%	519
20 V%	564
30 V%	599
40 V%	627
50 V%	656
60 V%	690
70 V%	723
80 V%	762
90 V%	850
93 V%	975
IBP-650°F, W%	48.56
650-850°F, W%	41.84
850-975°F, W%	4.80
975°F+, W%	5.10

APPENDIX

FOSTER WHEELER TEST REPORT

HRI, INC.

DELAYED COKING PROJECT

PREPARED BY:
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FWDC PROJECT 9-61-2128
JUNE 1990

FOSTER WHEELER DEVELOPMENT CORPORATION

12 Peach Tree Hill Road, Livingston, New Jersey 07039

The contents of this report have been reviewed and approved by:

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INTRODUCTION

Foster Wheeler Development corporation (FWDC) has conducted two delayed coking screening tests for HRI, Inc., in support of their ongoing, DOE-sponsored, coal liquefaction program. HRI supplied two similar residue feedstocks from the atmospheric distillation unit of their coal liquefaction test facility for testing. Their liquefaction work was conducted with Illinois No. 6 bituminous coal.

The primary objectives of the delayed coking tests were to achieve the maximum coker liquid yield and produce liquid samples for evaluation by HRI. They will cut out a distillate product and recycle the heavier material as a coal solvent. The recycled material will be evaluated for properties such as solvent quality, conversion to light distillates (reactivity), and catalyst deactivation.

FWDC's 4-in.-diameter mini-delayed coking pilot plant was selected for this preliminary evaluation because it requires modest amounts of feedstock, provides operating flexibility, and is relatively inexpensive to run.

DELAYED COKING TEST PROCEDURE

FWDC's 4-in. mini-delayed coking pilot plant, depicted in Figure 1, has the following features:

■ Coking pressure to 150 psig	■ Two drums
■ Once-through operation	■ 7-lb coke/drum
■ Preheated feedstock	■ Feed rate: 0.25 to 0.5 gal/h
■ Coke drum steamout	

Figure 1 4-in. Mini-Delayed Coking Pilot Plant

The minicoker is normally operated on a once-through basis over a 6- to 8-hour test period.

Feed is weighed into the feed tank hourly and pumped through the fluidized bed sand heater to the coke drum. Temperature is controlled in the sand heater and in the coke drum. The coke drum is housed in a three-zone tubular electric heater. Vapor effluents from the coke drum pass through a knockout pot, a cooler/condenser, and a light distillate receiver. A heavy distillate collects in the knockout pot. The uncondensed vapor leaving the receiver is metered, and an adequate sample is taken for analysis. After the coke drum is filled, it is immediately steamed out.

The coke drum is then cooled, and the coke is removed, weighed, and sampled. All other products are weighed, a material balance is determined, and product inspections are made according to the specific requirements of each project.

TEST RESULTS

Feedstock Characteristics

FWDC did not provide any direct characterization of the feedstocks. HRI supplied the analyses as presented in Table 1.

Delayed Coking Results

To meet the objective of producing a high liquid yield, two key parameters--temperature and steam/feed ratio--were selected as the variables for this two-test program. The effects of other potential variables are either known (pressure and throughput ratio) or have a lesser effect on yield (coking cycle

Table 1 Feedstock Characteristics (Source HRI)

	<u>HRI No.</u>	
	<u>10-5274/5275</u>	<u>10-5276</u>
*API Gravity	-1.5	-0.5
IBP, °F	549	500
IBP-650, wt%	10.00	15.00
650-850, wt%	41.51	40.09
850-975, wt%	12.40	10.74
975°F+, wt%	36.09	34.17
Carbon, wt%	84.18	85.69
Hydrogen, wt%	9.22	9.27
Nitrogen, wt%	0.49	0.55
Sulfur, wt%	0.56	0.52
Ash, wt%	4.87	3.11
Quinoline Insoluble, wt%	11.35	8.46
Pentane Insoluble, wt%	23.77	21.83
Toluene Insoluble, wt%	13.10	12.05
CCR (on liquid portion), wt%	8.54	7.64

time, feed rate, and steamout period); therefore, these variables were held constant.

The initial test was done at high coking temperatures and a steam rate significantly above normal commercial ratios. These levels were chosen to determine the effect of competing distillation and thermal cracking/polymerization mechanisms at extremely severe conditions. The peak coke drum temperature first chosen is at or near the top of standard commercial operation. The feedstock was not thermally stable enough to pass through the sand bath heating coil upstream of the coke drum; it quickly plugged the coil--possibly because of the cracking reactions being promoted by residual catalyst in the feedstock. A successful test (Run 1) was then completed at a somewhat lower

peak coking temperature. This run was designated as the base case (bc). This level was now considered at or near the maximum practical coking temperature of the feedstock for these tests, although it is possible to design facilities with higher throughputs to compensate for premature thermal cracking.

Tables 2 through 4 report the test results. The normalized liquid yield was 75.5 wt% (including steamout oil). The coke, which contained 20.6 wt% ash, had a yield of 20.9 wt%. The balance (3.6 wt%) was gas. While this constituted a very high liquid yield for delayed coking, there appeared room for improvements.

Lower coking temperatures and an even higher steam-to-feed ratio were chosen for the second test (Run 2) to reduce coke-producing reactions and either maintain or enhance distillation. As a point of reference, the steam-to-feed ratios selected for this program fall between those of conventional delayed coking and thermal cracking of liquid hydrocarbons for ethylene production.

Table 2 Operating Conditions (Relative Basis)

	<u>HRI Feedstock No.</u>	
	<u>LO-5274/5275</u>	<u>LO-5276</u>
FWDC Run No.	1	2
Coke Drum Pressure, psig	bc*	bc
Steam/Feed Ratio, w/w	bc	2(bc)
Average Temperature Profile in Drum, °F	bc	(bc)-25

*bc = base case.

Table 3 Material Balance

<u>Run 1</u>			
<u>Yield, wt%</u>			
	<u>Grams</u>	<u>As Measured</u>	<u>Normalized</u>
Feed (LO-5274/5275)	8830	---	---
Products			
Gas	312	3.5	3.6
Distillate Oil	6356	72.0	74.4
Steamout Oil*	98	1.1	1.1
Coke	<u>1780</u>	<u>20.2</u>	<u>20.9</u>
Recovery	8546	96.8	100.0

<u>Run 2</u>			
<u>Yield, wt%</u>			
	<u>Grams</u>	<u>As Measured</u>	<u>Normalized</u>
Feed (LO-5276)	11,335	---	---
Products			
Gas	361	3.2	3.1
Distillate Oil	9,195	81.1	78.1
Steamout Oil*	45	0.4	0.4
Coke	<u>2,160</u>	<u>19.1</u>	<u>18.4</u>
Recovery	11,761	103.8	100.0

*This amount represents oil portion of steamout emulsion.

Table 4 Product Inspections

	<u>HRI Feedstock No.</u>	
HRI Feedstock No.	<u>10-5274/5275</u>	<u>10-5276</u>
FWDC Run No.	1	2
<u>Gas</u>		
Compound: Air-Free, mol%		
Hydrogen	60.77	57.75
Carbon Monoxide	0.30	0.29
Carbon Dioxide	0.29	1.53
Hydrogen Sulfide	0.21	0.12
Methane	16.23	14.90
Ethane	6.41	4.71
Ethylene	1.95	1.29
Propane	5.18	8.92
Propylene	3.38	3.20
Isobutane	0.26	0.53
n-Butane	1.90	3.21
Propadiene	---	---
Butene-1 and/or Isobutene	1.19	1.03
trans-Butene-2	0.24	0.27
Methyl Acetylene	---	---
cis-Butene-2	0.22	0.18
Butadiene	0.10	---
Acetylene	---	---
Iso Pentane	0.20	0.31
n-Pentane	0.46	0.81
Pentenes	0.72	0.96
Average Molecular Weight	13.50	15.89
<u>Coke</u>		
Volatile Matter, wt%	6.48	6.09
Ash, wt%	20.63	15.55
Total Carbon, wt%	72.83	78.57

The combination of lower temperatures and a higher steam rate did increase the liquid yield (78.5 wt% on a normalized basis). Both the gas yield and coke yield were lowered to 3.1 wt% and 18.4 wt% respectively.

Calculating the yields of coke by using their ash content as a marker confirmed that Run 2 produced less coke (20.0 wt%) than Run 1 (23.6 wt%). The calculated yields were both about 2 wt% (absolute) higher than the material balance data and are considered in good agreement with these data given the difficulties of obtaining perfectly representative samples of coke for analysis and the "normal" differences one can expect from experimental discrepancies.

CONCLUSIONS AND RECOMMENDATIONS

The two runs that were completed demonstrated that delayed coking can be used to produce high liquid yields and reject entrained solids in the coke drum where they can be effectively removed from a coal liquefaction operation. Delayed coking has thus been proved a viable option of an integrated liquefaction process.

Additional testing is now warranted to further explore the recovery of coal-derived liquids. Such testing at the minicoker level can be used to investigate even higher liquid yields (>80 wt%) and explore the range of applicable operating parameters.

At this time FWDC recommends three additional minicoker tests (described in Table 5), with the same set of variables held constant as in the completed program, to expand the partial test matrix already undertaken. Conditions for

Table 5 Recommended Test Work

Steam Rate, lb/lb feed	Temperature, °F		
	Base Case	Base Case - 25	Base Case - 50
2 Base Case	•	■	•
Base Case	■	•	▲
0.5 Base Case	▲	▲	▲

Legend

- Completed
- Recommended
- ▲ Not recommended at this time

a fourth test should then be selected from among the completed tests. The coking cycle time (run interval) should be doubled (to 12 hours) to determine the impact of this variable, held constant until now, on the yield distribution. Because the coke drum was about half filled in these runs, the coking cycle time could probably be lengthened in this manner without a significant reduction in throughput rate. However, approximately twice the amount of feedstock would be needed.

These recommendations will allow us to explore higher yields and generate data for judging the sensitivity of the process to temperature, steam rate, and coking cycle time.

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SECTION IV

RUN 227-72 (CC-14) EVALUATION OF A PRE-DISPERSED IRON CATALYST IN TWO-STAGE LIQUEFACTION

SUMMARY

The objective of this run was to investigate the performance of predispersed iron oxide hydroxide catalyst in a thermal/catalytic reactor configuration, comparing it with the performance of dispersed molybdenum catalyst and with no catalyst in the first (thermal) reaction stage.

The initial work with Illinois #6 coal and this highly dispersed FeOOH catalyst was performed at PETC over several years by A. V. Cugini et al (1). Tests were conducted in 40-ml microreactors and then scaled to 1-liter bench-scale continuous units. The highly dispersed FeOOH catalyst showed very good activity at low concentrations (2,500 ppm) when compared with other dispersed iron and molybdenum catalysts.

The catalyst comparisons in Run 227-72(CC-14) were conducted with a pretreater at 527°F, the first liquefaction stage (without supported catalyst) at 825°F, and the second liquefaction stage (with Shell S-317 supported catalyst) at 775°F. The space velocity was 44 lb/hr/ft³ catalyst.

The results from Run 227-72 (CC-14) indicated some catalytic effect for the FeOOH and Ammonium Tetrathiomolybdate dispersed catalysts; however, there were essentially no differences in the coal conversions, which ranged from 94 to 95 W% (maf). Distillate yields, which decreased from 75 W% of maf coal at the beginning of the run to 66 W% at the end of the run, were relatively high, but still less than the 77 W% that had been sustained in the process demonstration run 227-47(I-27). After considering the deactivation of the supported catalyst, the 975°F conversions were slightly higher in the operations with the dispersed iron catalyst and in the operations with the dispersed molybdenum catalyst, compared to the operations with no dispersed catalyst. The nitrogen removal declined at a slow, steady rate from 88% in Period 8 to 83% in Period 20, except that it was lower than this trend, 79%, when no dispersed catalyst was used in Period 17. In general, the product quality of the distillation fractions from the first liquefaction stage (with only dispersed catalyst) was the highest in operations with the molybdenum catalyst and lowest in operations without any dispersed catalyst, but the differences were small.

SCOPE OF WORK

In Run 227-72(CC-14) an iron-based predispersed catalyst was evaluated in a three-reactor configuration that included a pretreater at 527°F, a first (liquefaction) stage without supported catalyst, and a second (liquefaction) stage at 775°F with Shell S-317 catalyst. Each of the three equal-volume reactors were backmixed, and the expansion of the catalyst in the second stage was controlled as an ebullated bed.

The run plan for this 20-day, 5-condition run with Illinois #6 coal is shown in *Table 1*. The space velocity was 44 lb/hr/ft³ of catalyst, and the first and second stage reactor temperatures were 825°F and 750°F, respectively, in Conditions 2 through 5. Iron-treated coal was used in the first two conditions. After Condition 1 the first stage temperature was increased from 800 to 825°F. In Condition 3 untreated coal was used, and the dispersed catalyst was ammonium tetrathiomolybdate added as a 9.91 W% water solution at the rate of 1500 ppm Mo (dry coal basis). No dispersed catalyst was used in Condition 4, and the iron-treated coal was used again in Condition 5 to check the influence of supported-catalyst deactivation on the performance parameters. H₂S was injected continuously at 3 W% (of feed coal).

PROGRAM RESULTS AND ANALYSES

RUN 227-72 (CC-14)

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 that were attained in the last period of each of the five conditions.

COAL AND 975°F CONVERSION

Figure 1 shows the coal and resid (975°F) conversions obtained in the run. During the run, there were only small changes in the coal conversion, which ranged from 94 to 95 W% (maf). The increase from 94.0 % in Condition 1 to 94.6 % in Condition 2 with the first stage temperature increased from 800°F to 825°F is close to the 0.7 W% increase that is predicted based on previous performance with the Illinois #6 coal. The coal conversions for all of this run were lower by about 1 W% than the coal conversions predicted by models based on previous Illinois #6 coal CTSL. This difference could be due to the different reactor configurations. Analyses of samples from the first stage indicated that, when the first stage was at 825°F, no significant additional coal conversion occurred in the second stage.

The 975°F conversion increased by 2.4 W% (maf) when the first stage temperature was increased from 800 to 825°F. In Conditions 2 through 5, at constant severity, the 975°F conversion decreased from 90.4 W% (maf) to 87.5 W%. The iron and molybdenum dispersed catalysts followed this trend, but in Condition 4, with no dispersed catalyst, the 975°F conversion was about 2 W% below this trend.

NORMALIZED PRODUCT DISTRIBUTION

Figure 2 shows the C4-975 F distillate yield. The indicated distillate yields were highest in Condition 1 with the iron-treated coal and with the first stage temperature at 800°F, and the second highest distillate yields were in Condition 3 with the molybdenum dispersed catalyst. However, the distillate yield is not as accurate of a catalyst-activity indicator because it includes the variabilities of the gas and water yields. In this run the water yields were more variable than usual. In particular, the lowest water yields occurred in Conditions 1 and 3, causing much of the indicated high distillate yields for these conditions.

Figures 3 and 4 show the effect of the first stage temperature on the distillate yield and selectivity with the iron catalyst. Increasing the temperature from 800°F to 825°F led to an increase in the yields of C₄-390°F and 390-500°F fractions

(both as a percentage of feed and as a percentage of the total distillate product) and a decline in the formation of 500-650°F, 650-850°F, and 850-975°F fractions.

The comparisons of the individual distillate fraction yields and selectivities indicate more about the hydrocracking activities of the dispersed catalysts. These comparisons are shown in *Figures 5 through 8*. The comparisons have been made on adjacent conditions (i.e. Condition 2 compared with Condition 3 and Condition 4 compared with Condition 5) in order to minimize the effect of deactivation of the supported catalyst in the second stage. Although the molybdenum-based catalyst gave an indicated higher total distillate yield, the iron-based catalyst showed a higher hydrocracking activity, resulting in a higher yield of the naphtha (C₄-390°F) fraction. The distillate slate was heavier with the molybdenum catalyst. Comparing Condition 4 (no dispersed catalyst) with Condition 5 (Fe catalyst), a lighter product slate was produced with the iron catalyst.

The C₁-C₃ gas yield increased from an average of 7.3 W% of dry coal in Condition 1, with the first stage at 800°F, to an average of 11.0 W% for all of the periods with the second stage at 825°F. The average gas yield for operations with the dispersed iron catalyst was 0.8 W% higher than the gas yield with no dispersed catalyst, but this difference might not be significant.

The hydrogen consumption for each condition is shown in *Figure 9*. As a result of the changes in product yields, discussed above, the hydrogen consumption was lowest in Conditions 1 (800°F first stage temperature) and 4 (no dispersed catalyst).

Figure 10 shows the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) observed during the run. The HDN declined at a slow, steady rate from 88% in Period 8 to 83% in Period 20, except that it was lower than this trend, 79%, when no dispersed catalyst was used in Period 20. The HDS was highest in Condition 3 with the dispersed molybdenum catalyst. It was 77% in this condition, compared with 70% in Condition 4 with no dispersed catalyst. One possible reason for the lower HDS in all of the operations with iron-dispersed catalyst was the capture of more sulfur by the additional iron in the unconverted coal.

PRODUCT QUALITY

The analyses of the SOH and ASOH products are shown in *Table 4*. Among the conditions at the same reactor temperature, these products from operations with the dispersed molybdenum catalyst had the lowest nitrogen contents and the highest H/C ratios.

The analyses of the PFL distillation fractions are listed in *Table 5*, and *Figures 11 through 13* show the H/C ratios, nitrogen contents, and sulfur contents of these

fractions. There are only small deviations from the general trend of slow product-quality deterioration as the catalyst aged. Possibly, the products from operations with dispersed molybdenum catalyst were of slightly higher quality than this trend. The activity of the supported catalyst was the primary influence on these product properties.

With less influence of the second stage supported catalyst, the product properties of the first stage distillation fractions (*Table 6* and *Figures 14 through 16*) provide a better indication of the activity of the dispersed catalyst. The slightly superior performance of the dispersed molybdenum catalyst is clear by these three measures of product quality. The sulfur content of these products from operations with the dispersed iron catalyst were significantly lower than those from operations without any dispersed catalyst.

Table 7 shows the analyses of the first stage solids. Notably, the solids from the operations with dispersed catalyst had H/C ratios significantly lower than the solids from Condition 4 with no dispersed catalyst (0.44 vs. 0.57). All of these H/C ratios are lower than the typical value of 0.7 for both the first and second stage solids from catalytic/catalytic, low temperature/high temperature operations.

COMPARISON WITH CTSL

The results from this run with the iron dispersed catalyst are compared with results from the CTSL Process Demonstration Run 227-47 (I-27) in *Table 8*. The comparison is between Condition 5 of this run and Period 21 of Run 227-47 (I-27), which was at the same catalyst age and similar overall severity. Although the Illinois coals were different in these two operations and additional resid conversion was attained in Run 227-47 (I-27) by concentrating the resid in the recycle, the relatively large differences in resid conversion and distillate yields indicate the benefit of the CTSL process. The higher denitrogenation activity in Run 227-72 (CC-14), however, demonstrates the activity of the dispersed iron catalyst that does not decrease with time. However, at similar catalyst ages the qualities of the liquid products from CTSL operations, in terms of nitrogen and hydrogen content, were superior (especially for the higher boiling fractions) to the qualities of the liquid products from operations with the dispersed iron catalyst.

DETAILS OF OPERATION

Three 2000-cc reactors were used in this run. The first reactor was a pretreater for activating the dispersed-iron 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 the first stage were circulated at a high rate to obtain complete back-mixing.

OPERATIONS

The operations were smooth in Conditions 1 and 2, and a first-stage sample was withdrawn after Condition 2. The initial run plan had called for lowering the pretreater temperature to below 400°F to effectively eliminate the pretreatment, but as the temperature was lowered, the pressure drop in the pretreater started increasing, and the circulation in it became difficult. The unit had to be shut down in Period 11 because it was no longer possible to pump the feed into the pretreater. The problem might have been the result of coal slurry swelling at the conditions of the pretreater.

The pretreater was opened and cleaned and the run restarted in Period 11. It was decided to maintain the pretreater temperature at 527°F throughout the run. No more operational problems were encountered. The first stage samples were withdrawn after Conditions 3, 4, and 5.

COAL FEED

Illinois No. 6 bituminous coal was used as feedstock. *Table 9* shows the analyses of the untreated coal and the iron-impregnated coal.

The iron-impregnated coal was prepared by DOE-PETC using an incipient wetness impregnation/precipitation method(1). A solution of one part ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) dissolved in 40 parts distilled water was used to wet 50 parts of -200 mesh coal to incipient wetness (paste). The wet coal paste was then added into a solution containing 20 parts ammonium hydroxide (29% NH_3) and 200 parts distilled water. This mixture was then pressure-filtered through 0.45 micron media to obtain a clear filtrate. The iron catalyzed coal was then vacuum dried at 104°F. The target iron content of the impregnated coal was 2500 ppm, and the difference between the analyzed iron oxide contents of the iron-impregnated and untreated coals agreed approximately with this level of impregnation.

START-UP OIL

The run was started using HRI 5868, an Illinois No. 6 coal-derived heavy distillate produced at Wilsonville. The analyses of this oil is shown in *Table 10*. This oil was also used for the restart in Period 11 and once, in Period 8, as a small amount of make-up oil when there was insufficient process-derived pressure filter liquid to slurry the feed coal.

FRESH CATALYST

The same Shell S-317, HRI 5394, 1/32-inch extrudate NiMo catalyst that had been used throughout the program was used in the second liquefaction stage. The Shell S-317 analyses are shown in *Table 11* in the section on Run 227-66 (CC-8). The catalyst was sulfided during startup by holding the reactor at several intermediate temperatures for several hours in the presence of H₂S. There was no supported catalyst in the first stage.

The dispersed catalyst for Condition 3 was Ammonium Tetrathiomolybdate (NH₄)₂MoS₄. It was added to the feed coal slurry as a 9.91 W% water solution at the rate of 1500 ppm Mo (coal basis). The predispersed iron catalyst was discussed in the "Coal" section above.

RECOVERED CATALYST

Table 11 shows the analyses of the catalyst recovered from the second stage. The catalyst recovery was 79% based on the relative volumes of charged and recovered +20 mesh oil-free catalyst, and 74% 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 2% of the amount of the molybdenum in the catalyst charged.

The carbon accumulation on the recovered catalyst, 14.9 W%, was somewhat higher than on most of the low-temperature stage catalysts after earlier operations with Illinois coal and S-317 catalyst, which ranged from 9.5 to 15.1. Metals contaminants accumulation was low, a total of 0.88 W%, with sodium as the largest component. This level of metals contaminants is lower than the range of metal contaminants for first stage catalysts from operations with mine-washed Illinois coal (1.6 to 6.1 W%) and on the low end of the range of metal contaminants for second stage catalysts from similar operations (0.7 to 1.7 W%). Apparently, the dispersed catalysts acted as effective scavengers of the contaminant metals. The pore volume decreased from 0.70 cc/cc (particle) for the fresh catalyst to 0.39 cc/cc (particle) for the recovered catalyst. The sulfur content of the recovered catalyst was 94% of the amount corresponding to formation of MoS₂ and NiS.

TABLE 1
Run Plan for 227-72 (CC-14)

Condition	1	2	3	4	5
Periods*	1-5	6-10A	10B-15A	15B-18A	18B-21A
Coal Type (HRI No.)	5876	5876	5857	5857	5857
Dispersed* Catalyst	Fe	Fe	Mo	None	Fe
Nominal Conditions					
Space Velocity, lb coal/ft ³ (cat)	44	44	44	44	44
Backpressure, psig	2,500	2,500	2,500	2,500	2,500
Temperatures, °F					
Pretreater	527	527	527	527	527
First Stage***	800	825	825	825	825
Second Stage***	775	775	775	775	775
Recycle Ratio****	1.6	1.6	1.6	1.6	1.6
H ₂ S Rate, W% Coal	3.0	3.0	3.0	3.0	3.0

* Each Period (day) is subdivided into three subperiods, A, B, and C. The run was suspended in Period 10B due to operability problems and was restarted at Period 11A.

** Fe was impregnated on coal to obtain Fe at 2,500 ppm (coal). Mo was added to the feed tank at 1,500 ppm (coal) by adding partially dissolved ammonium tetrathiomolybdate in H₂O (9.91 W% solution).

*** First stage and second stage reactors were of equal volume. First stage contained no supported catalyst, while second stage contained Shell S-317 NiMo catalyst and was operated as an ebullated bed reactor.

**** Coal was fed into the reactors after recycling with pressure filter liquid (PFL) at PFL/coal ratio of 1.6. In addition, small amount of PFL was used as buffer flows in all three reactors.

TABLE 2

PART 1 OF 3

RUN CC-14 OPERATING SUMMARY
DISPERSED CATALYST RUN

AL: ILLINOIS NO. 6 - HRI-5876 (FE TREATED) (PERIODS 1-9, 18-20)

HRI-5856 (UNTREATED) (PERIODS 10-17)

CATALYST: 2ND STAGE-- S-317 NiMo CATALYST

AMMONIUM THIOMOLYBDATE IN PERIODS 10-14

FE IMPREGNATED ON HRI-5876

Period Number	2	3	4	5	7
Date (Start of Period)	05/30/91	05/31/91	06/01/91	06/02/91	06/04/91
Hours of Run (End of Period)	48.	72.	96.	120.	168.
Stage 2 Catalyst Age, Lb Dry Coal/Lb Cat	57.	86.	116.	145.	205.
Pretreater Temperature (F)	525.	525.	525.	525.	527.
1st Stage Temperature (F)	799.	798.	798.	799.	825.
2nd Stage Temperature (F)	775.	775.	775.	776.	770.
Unit Back Pressure (PSIG)	2488.	2484.	2483.	2495.	2497.
Space Velocity, Lb Coal/Hr/Ft ³ (2nd Stage) Cat	46.4	45.8	46.0	45.8	46.2
WT OF DRY COAL					
PFL Recycle + Buffer to Pretreater	150.9	158.9	161.2	161.1	160.6
PFL to Buffer to Stage 1	3.9	4.1	3.9	3.3	3.6
PFL to Buffer to Stage 2	4.1	4.4	4.1	3.1	3.7
Make-up Oil	0.0	0.0	0.0	0.0	0.0
H ₂ S	2.5	2.5	2.9	3.0	2.4
Additive	0.0	0.0	0.0	0.0	0.0
MATERIAL BALANCE (t) (GROSS)	99.88	102.29	98.43	100.74	103.02

ESTIMATED NORMALIZED YIELDS, Wt DRY FRESH FEED

C1-C3 in Gases	6.94	7.60
C4-C7 in Gases	4.19	4.58
IBP-390 deg-f in Liquids	13.70	13.78
390-500 deg-f in Liquids	10.12	10.17
500-650 deg-f in Liquids	21.12	20.86
650-850 deg-f in Liquids	14.23	13.88
850-975 deg-f in Liquids	3.58	3.85
Toluene Soluble 975F+ Oil	4.18	5.07
Toluene Insoluble 975F+ Oil	0.32	0.18
Unconverted Coal	5.40	5.34
Ash	11.00	11.00
Water	7.27	6.19
CO	0.20	0.17
CO ₂	0.16	0.20
NH ₃	1.66	1.66
H ₂ S	2.19	2.31
Total (100 + H ₂ Reacted)	106.25	106.84

PROCESS PERFORMANCE

C4-975 deg-f Distillates, Wt of MAP Coal	75.2	75.4
975F+ Conversion, Wt MAP	88.9	88.1
Coal Conversion, Wt MAP	93.5	94.5
HDS, Wt	64.6	68.3
HDN, Wt	86.3	86.3

TABLE 2

PART 2 OF 3

RUN CC-14 OPERATING SUMMARY

DISPERSED CATALYST RUN

COAL: ILLINOIS NO. 6 - HRI-5876 (FE TREATED) (PERIODS 1-9, 18-20)

HRI-5856 (UNTREATED) (PERIODS 10-17)

CATALYST: 2ND STAGE-- S-317 NiMo CATALYST

AMMONIUM TRIMOLYBDATE IN PERIODS 10-14

FE IMPREGNATED ON HRI-5876

Period Number	8	9	12	13	14
Date (Start of Period)	06/05/91	06/06/91	06/12/91	06/13/91	06/14/91
Hours of Run (End of Period)	192.	216.	280.	304.	328.
Stage 2 Catalyst Age, Lb Dry Coal/Lb Cat	234.	265.	343.	374.	403.
Pretreater Temperature (F)	530.	525.	520.	525.	523.
1st Stage Temperature (F)	827.	824.	819.	822.	822.
2nd Stage Temperature (F)	775.	775.	773.	774.	774.
Unit Back Pressure (PSIG)	2495.	2496.	2504.	2503.	2496.
Space Velocity, Lb Coal/Hr/Ft ³ (2nd Stage) Cat	46.7	48.2	48.4	47.8	46.2
WT OF DRY COAL					
PFL Recycle + Buffer to Pretreater	153.3	161.7	158.4	159.7	158.1
PFL to Buffer to Stage 1	3.7	4.6	3.5	3.7	3.2
PFL to Buffer to Stage 2	3.7	4.6	3.7	3.7	3.7
Make-up Oil	6.2	0.0	0.0	0.0	0.0
H ₂ S	2.9	2.7	2.7	2.7	2.8
Additive	0.0	0.0	0.4	0.4	0.4
MATERIAL BALANCE (%) (GROSS)	99.39	98.49	98.09	98.47	102.90
ESTIMATED NORMALIZED YIELDS, WT DRY FRESH FEED					
C1-C3 in Gases	11.44	10.92			10.19
C4-C7 in Gases	5.60	6.21			5.90
IBP-390 deg-f in Liquids	17.82	16.42			15.26
390-500 deg-f in Liquids	12.53	11.32			12.11
500-650 deg-f in Liquids	16.10	15.58			17.23
650-850 deg-f in Liquids	7.65	9.82			11.12
850-975 deg-f in Liquids	1.96	2.83			2.39
Toluene Soluble 975F+ Oil	3.09	4.45			3.93
Toluene Insoluble 975F+ Oil	0.33	0.41			0.28
Unconverted Coal	5.19	4.84			4.90
Ash	11.00	11.00			10.72
Water	10.11	8.86			8.38
CO	0.27	0.29			0.30
CO ₂	0.41	0.37			0.45
NH ₃	1.69	1.67			1.29
H ₂ S	2.29	2.31			2.75
Total (100 + H ₂ Reacted)	107.48	107.29			107.20
PROCESS PERFORMANCE					
C4-975 deg-f Distillates, WT of MAP Coal	69.3	69.9			71.8
975F+ Conversion, WT MAP	90.3	89.1			89.8
Coal Conversion, WT MAP	94.2	94.6	94.0	94.3	94.5
HDS, WT	67.6	68.1			76.5
HDM, WT	88.0	86.6			84.3

TABLE 2

PART 3 OF 3

RUN CC-14 OPERATING SUMMARY

DISPERSED CATALYST RUN

COAL: ILLINOIS NO. 6 - HRI-5876 (FE TREATED) (PERIODS 1-9,18-20)

HRI-5856 (UNTREATED) (PERIODS 10-17)

CATALYST: 2ND STAGE-- S-317 NiMo CATALYST

AMMONIUM THIOSULFATE IN PERIODS 10-14

FE IMPREGNATED ON HRI-5876

Period Number	16	17	19	20
Date (Start of Period)	06/16/91	06/17/91	06/19/91	06/20/91
Hours of Run (End of Period)	376.	400.	448.	472.
Stage 2 Catalyst Age, Lb Dry Coal/Lb Cat	463.	493.	553.	581.
Pretreater Temperature (F)	528.	528.	526.	527.
1st Stage Temperature (F)	824.	822.	824.	825.
2nd Stage Temperature (F)	774.	774.	775.	774.
Unit Back Pressure (PSIG)	2483.	2507.	2520.	2505.
Space Velocity, Lb Coal/Hr/Ft ³ (2nd Stage) Cat	46.9	47.3	46.9	44.9
WT OF DRY COAL				
PFL Recycle + Buffer to Pretreater	158.4	158.4	161.3	163.4
PFL to Buffer to Stage 1	3.7	3.6	3.4	3.8
PFL to Buffer to Stage 2	4.0	3.7	3.8	4.1
Make-up Oil	0.0	0.0	0.0	0.0
H ₂ S	2.8	2.8	2.8	2.9
Additive	0.0	0.0	0.0	0.0
MATERIAL BALANCE (t) (GROSS)	100.63	103.95	100.11	100.70
ESTIMATED NORMALIZED YIELDS, Wt DRY FRESH FEED				
C1-C3 in Gases		10.57		11.82
C4-C7 in Gases		6.00		6.25
IBP-390 deg-f in Liquids		13.14		14.55
390-500 deg-f in Liquids		11.33		12.27
500-650 deg-f in Liquids		16.86		15.00
650-850 deg-f in Liquids		10.00		7.88
850-975 deg-f in Liquids		2.43		2.36
Toluene Soluble 975F+ Oil		5.52		5.36
Toluene Insoluble 975F+ Oil		1.13		1.02
Unconverted Coal		5.19		4.44
Ash		10.83		11.00
Water		9.08		10.56
CO		0.25		0.33
CO ₂		0.54		0.47
NH ₃		1.20		1.59
H ₂ S		2.53		2.21
Total (100 + H ₂ Reacted)		106.61		107.11
PROCESS PERFORMANCE				
C4-975 deg-f Distillates, Wt of MAP Coal		67.0		65.5
975F+ Conversion, Wt MAP		86.7		87.8
Coal Conversion, Wt MAP	94.6	94.2	94.7	95.0
HDS, Wt		70.4		65.2
HDM, Wt		78.9		83.0

TABLE 3**Yields and Performance Summary
Run 227-72 (CC-14)**

Condition	1	2	3	4	5
Additive	FeOOH	FeOOH	ATTM	None	FeOOH
Amount	2,800 ppm	2,800 ppm	1,500 ppm	--	2,800 ppm
Reaction Temp., °F					
Pretreater	525	527	523	528	527
First Stage	799	825	822	822	825
Second Stage	775	775	775	774	774
Yields, W% MAF Coal					
C ₁ -C ₃	8.6	12.3	11.5	12.0	12.5
C ₄ -390°F	20.7	26.5	24.0	21.7	23.3
390-650°F	34.9	32.3	33.1	31.9	30.6
650-975°F	19.5	10.2	14.7	13.6	11.8
975°F*	5.7	3.6	4.6	7.3	7.4
Performance, W% MAF Coal					
C ₄ -975°F	75.1	69.0	71.8	67.2	65.7
975°F* Conversion	88.0	90.4	89.5	86.4	87.5
Hydrogen Consump.	7.5	8.2	8.1	7.4	7.8
Coal Conversion	94.0	94.6	94.5	94.2	95.0
Denitrogenation, W%	86.3	86.6	84.3	78.9	83.0

TABLE 4**Analyses of Distillate Products
Run 227-72 (CC-14)**

Condition	1	2	3	4	5
Period	5	9	14	17	19
Separator Overhead					
API Gravity	35.7	37.0	36.9	35.9	35.8
Carbon, W%	86.49	86.71	86.36	86.24	86.33
Hydrogen, W%	12.50	12.52	12.54	12.27	12.35
Nitrogen, W%	0.09	0.11	0.09	0.12	0.16
Sulfur, W%	0.01	0.01	0.02	0.10	0.12
H/C Ratio	1.73	1.73	1.74	1.71	1.72
Watson K Factor	11.04	11.07	11.07	10.97	10.96
Atmospheric Still Overhead					
API Gravity	23.9	25.0	25.8	23.0	22.9
Carbon, W%	87.42	87.20	86.98	86.93	86.87
Hydrogen, W%	11.62	11.41	11.66	11.22	11.10
Nitrogen, W%	0.14	0.19	0.15	0.20	0.25
Sulfur, W%	0.00	0.02	0.04	0.11	0.13
H/C Ratio	1.60	1.57	1.61	1.55	1.53
Watson K Factor	10.82	10.75	10.83	10.69	10.65

TABLE 5
Analyses of PFL Cuts
Run 227-72 (CC-14)

Condition Period	1 5	2 9	3 14	4 17	5 21
API Gravity	3.8	0.8	2.1	-2.1	-3.4
IBP-650°F	9.08	11.87	13.13	11.33	10.59
650-850°F	50.48	46.17	51.37	43.51	39.46
850-975°F	17.11	15.42	12.84	12.07	13.48
975°F*	23.33	26.54	22.66	33.09	36.47
Carbon, W%	89.70	90.07	89.16	89.11	89.17
Hydrogen, W%	9.27	8.49	8.76	7.74	7.78
Sulfur, W%	0.09	0.14	0.17	0.26	0.31
Nitrogen, W%	0.42	0.54	0.49	0.74	0.82
H/C Ratio	1.24	1.13	1.18	1.04	1.05
IBP-650°F Cut					
API Gravity	16.6	15.0	17.2	15.0	14.7
Carbon, W%	88.03	88.37	87.82	88.07	87.80
Hydrogen, W%	10.80	10.41	10.77	10.46	10.28
Sulfur, W%	0.01	0.02	0.01	0.10	0.08
Nitrogen, W%	0.14	0.21	0.14	0.20	0.22
H/C Ratio	1.47	1.41	1.47	1.43	1.05
650-850°F Cut					
API Gravity	10.5	7.6	10.1	7.4	6.8
Carbon, W%	89.55	90.35	89.56	89.73	89.32
Hydrogen, W%	10.15	9.56	9.95	9.37	9.21
Sulfur, W%	0.02	0.05	0.04	0.11	0.12
Nitrogen, W%	0.22	0.26	0.24	0.29	0.34
H/C Ratio	1.36	1.27	1.33	1.25	1.24
850-975°F Cut					
API Gravity	0.4	-4.1	-2.2	-5.5	-6.0
Carbon, W%	90.07	91.00	90.44	90.08	89.56
Hydrogen, W%	8.88	8.11	8.35	7.87	7.40
Sulfur, W%	0.04	0.07	0.10	0.20	0.30
Nitrogen, W%	0.40	0.58	0.49	0.76	0.84
H/C Ratio	1.18	1.07	1.11	1.05	0.99
975°F Cut					
API Gravity	-9.2	-11.2	-11.1	-14.0	-13.0
Carbon, W%	89.67	90.47	88.37	89.08	88.62
Hydrogen, W%	7.05	6.26	6.39	5.98	5.80
Sulfur, W%	0.35	0.28	0.53	0.51	0.63
Nitrogen, W%	1.01	1.18	1.33	1.51	1.56
H/C Ratio	0.94	0.83	0.87	0.81	0.79
Cyclohexane Insol., W%	23.13	43.80	83.54	88.14	74.89
Toluene Insol, W%	3.40	8.52	6.75	16.97	16.00

TABLE 6
Analyses of Liquid Cuts from First Stage Samples
Run 227-72 (CC-14)

Condition (After) Period	2 9	3 14	4 17	5 21
API Gravity	-6.1	-2.6	-7.4	-7.1
IBP-650°F	11.88	13.11	9.38	9.57
650-850°F	36.08	38.53	34.83	26.80
850-975°F	13.56	14.94	14.47	22.50
975°F*	38.48	33.42	41.32	41.13
Carbon, W%	89.53	88.46	88.72	88.72
Hydrogen, W%	7.42	7.24	7.52	7.26
Sulfur, W%	0.34	0.97	0.42	0.39
Nitrogen, W%	1.05	0.79	1.09	1.17
H/C Ratio	1.00	0.99	1.02	1.05
IBP-650°F Cut				
API Gravity	12.5	13.7	12.9	12.7
Carbon, W%	87.48	86.45	86.59	86.81
Hydrogen, W%	9.78	10.28	9.77	9.74
Sulfur, W%	0.22	0.17	0.28	0.21
Nitrogen, W%	0.45	0.40	0.47	0.53
H/C Ratio	1.34	1.43	1.35	1.35
650-850°F Cut				
API Gravity	2.9	5.9	4.3	5.2
Carbon, W%	89.07	88.81	89.40	89.05
Hydrogen, W%	8.39	9.07	8.74	8.76
Sulfur, W%	0.17	0.14	0.20	0.16
Nitrogen, W%	0.58	0.40	0.51	0.58
H/C Ratio	1.13	1.23	1.17	1.18
850-975°F Cut				
API Gravity	-7.9	-4.9	-10.5	-8.5
Carbon, W%	89.40	88.08	89.24	89.02
Hydrogen, W%	7.19	7.57	7.24	7.42
Sulfur, W%	0.27	0.28	0.38	0.27
Nitrogen, W%	1.02	0.80	0.98	1.04
H/C Ratio	0.97	1.03	0.97	1.00
975°F Cut				
API Gravity	-14.1	-11.4	-14.3	-14.2
Carbon, W%	88.67	86.73	88.21	88.61
Hydrogen, W%	5.77	6.10	5.69	5.69
Sulfur, W%	0.53	0.62	0.66	0.52
Nitrogen, W%	1.57	1.57	1.68	1.83
H/C Ratio	0.78	0.84	0.77	0.77
Cyclohexane Insol., W%	21.72	88.39	88.92	91.17
Toluene Insol, W%	2.23	21.94	25.92	25.46

TABLE 7**Analyses of Solids From First Stage Samples
Run 227-72 (CC-14)**

Condition (After) Period	2 9	3 14	4 17	5 21
Solids, W% (THF Insolubles)	12.26	9.82	9.71	9.21
Analysis of Solids				
Carbon, W%	22.53	21.39	23.88	21.07
Hydrogen, W%	0.82	0.79	1.15	0.79
Sulfur, W%	6.39	6.27	5.38	5.87
Nitrogen, W%	0.33	0.32	0.34	0.34
Ash, W%	71.35	72.23	69.26	71.56
H/C Ratio	0.44	0.44	0.57	0.45

TABLE 8
Liquefaction Results
Dispersed Iron and CTSL
Run 227-72 (CC-14)

	Thermal/Catalytic with Predispersed FeOOH 227-72 (CC-14)	CTSL with NiMo Catalyst 227-47 (I-27)
	Period 20	Period 21
Catalyst Age, lbs coal/lb cat (1 stage)	581	585
Conditions		
Coal Rate, lbs/hr/ft ³ (stage)	44.9	44.2
Pretreater Temp., °F	527	--
1st Stage Temp., °F	825	767
2nd Stage Temp., °F	774	823
Liquid Recycle, lb/lb coal	1.71	1.51
Yields, W% MAF Coal		
C ₁ -C ₃	12.5	9.2
C ₄ -390°F	23.3	21.6
390-650°F	30.6	35.0
650-975°F	11.8	21.0
975°F+ Residuum	7.4	2.7
Performance, W% MAF Coal		
C ₄ -975°F	65.7	77.6
975°F+ Conversion	87.5	94.4
Coal Conversion	95.0	97.1
Hydrodenitrogenation	83.0	75.1
Hydrogen Consumption	7.8	7.9

TABLE 9

**Feed Coal Analyses
Run 227-72 (CC-12)**

HRI No.	5876	5857
Coal Type	Illinois No. 6	
Treatment		
	Fe-Treated	Untreated
Maceral Analysis, V%		
Vitrinite		78.2
Liptinite		5.8
Inertinites		9.8
Pyrites		4.2
Other Minerals		2.0
Ultimate Analysis, W% (Dry Basis)		
Carbon	68.78	68.61
Hydrogen	4.32	4.29
Sulfur	3.19	3.39
Nitrogen	1.58	1.26
Ash	11.00	10.83
Sulfur Types, W% (Dry Basis)		
Sulfate	0.01	0.01
Pyritic	1.26	1.50
Organic	2.26	2.00
Ash Analysis, W% (Dry Basis)		
Silicon Dioxide	46.29	47.05
Aluminum Oxide	18.12	17.85
Titanium Dioxide	0.85	0.84
Iron Oxide	20.58	17.18
Calcium Oxide	5.57	6.44
Magnesium Oxide	0.92	0.93
Potassium Oxide	1.17	1.77
Sodium Oxide	0.27	0.39
Sulfur Trioxide	5.42	7.27
Phosphorous Pentoxide	0.11	0.12
Strontium Oxide	0.01	0.01
Manganese Oxide	0.15	0.15
Undetermined	0.00	0.00

TABLE 10**Analyses of Start-Up/Make-Up Oil
Run 227-72 (CC-14)**

HRI No.	5868
Type	Coal (Illinois) Derived Heavy Distillate from Wilsonville
API	7.2
Elemental Analysis, W%	
Carbon	86.51
Hydrogen	9.56
Sulfur	0.47
Nitrogen	0.26
D-1160 Distillation	
IBP	466
5 V%	650
10 V%	736
20 V%	771
30 V%	786
40 V%	805
50 V%	819
60 V%	838
66 V%	850

TABLE 11
Recovered Catalyst Analyses
Run 227-72 (CC-14)

Stage	Second
Catalyst Age, lb coal/lb	590
Catalyst Recovery, V%	78.9
Bulk Density, Gm/cc	84.5
Analyses of Oil-Free +20 Mesh Catalyst, W%	
Carbon	14.94
Hydrogen	0.94
H/C Ratio	0.74
Nitrogen	0.22
Sulfur	5.49
Molybdenum	7.45
Cobalt	
Nickel	1.61
Titanium	0.19
Iron	0.10
Calcium	0.09
Sodium	0.50
Total Metal Contaminants	0.88
Loss on Ignition, W%	18.70
Particle Density, Gm/cc particle*	1.327
Pore Diameter (D>30°A), cc/gm	0.291
cc/cc particle	0.387
Surface Area (calc.), M ² /gm	123
M ² /cc particle	163
Analyses of Ignited Catalyst	
Particle Density, Gm/cc particle*	1.058
Pore Diameter (D>30°A), cc/gm	0.529
cc/cc particle	0.560
Surface Area (calc.), M ² /gm	162
M ² /cc particle	171
Analysis of 20-100 Mesh Oil-Free Solids	
Weight, grams	36.4
Molybdenum, W%	2.95
Nickel, W%	0.72

* In mercury at 10 psia.

DISPERSED CATALYST RUN (CC-14)

COAL AND 975 F+ CONVERSIONS

FIGURE 1

DISPERSED CATALYST RUN (CC-14)

DISTILLATE YIELD

FIGURE 2

DISPERSED CATALYST RUN (CC-14)

DISTILLATE YIELD WITH FE CATALYST

FIGURE 3

DISPERSED CATALYST RUN (CC-14)

DISTILLATE SELECTIVITY WITH FE CATALYST

FIGURE 4

DISPERSED CATALYST RUN (CC-14)

DISTILLATE YIELD AT 825 F

FIGURE 5

DISPERSED CATALYST RUN (CC-14)

DISTILLATE SELECTIVITY AT 825 F

FIGURE 6

DISPERSED CATALYST RUN (CC-14)

DISTILLATE YIELD AT 825 F

FIGURE 7

DISPERSED CATALYST RUN (CC-14)

DISTILLATE SELECTIVITY AT 825 F

FIGURE 8

DISPERSED CATALYST RUN (CC-14) HYDROGEN CONSUMPTION

FIGURE 9

DISPERSED CATALYST RUN (CC-14)

HDS AND HDN

FIGURE 10

DISPERSED CATALYST RUN (CC-14)

H/C RATIO OF PFL CUTS

FIGURE 11

DISPERSED CATALYST RUN (CC-14)

NITROGEN CONTENT OF PFL CUTS

FIGURE 12

FIGURE 13

DISPERSED CATALYST RUN (CC-14)

H/C RATIO OF 1ST STAGE SAMPLE CUTS

FIGURE 14

DISPERSED CATALYST RUN (CC-14)

NITROGEN CONTENT OF 1ST STAGE SAMPLE

FIGURE 15

DISPERSED CATALYST RUN (CC-14)

SULFUR CONTENT OF 1ST STAGE SAMPLE

FIGURE 16

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SECTION V

RUN 227-76 (CC-16) EVALUATION OF AKZO AO-60 NICKEL-MOLY CATALYST

SUMMARY

Run 227-76(CC-16) completed, as scheduled, 13 days of operation with Illinois No. 6 coal, testing the activity of Akzo AO-60 1/16" nickel molybdate extrudate catalyst in the CTSL process. The conditions for the run duplicated the conditions of three previous catalyst evaluation runs, which had tested 1/32" Amocat 1C extrudates, 1/20" UOP RCM4 spheres, and 1/32" Shell S-317 extrudates. These three catalysts had performed similarly and very well in Runs 227-35, -36, and -37 (I-16, -17, and -18).

The resid conversions and distillate yields for the AO-60 and the other catalysts were very similar. In Condition 1 (750°F first stage, 800°F second stage, and 46 lb/hr/ft³ catalyst/stage), resid conversion decreased from 88.4 to 82.9 W% of maf coal, and the C₄-975°F distillate yield decreased from 73.7 to 68.6 W% between periods 4 and 9. In the higher severity Condition 2 (775 F first stage, 810°F second stage, and increased feed coal concentration the resid conversion averaged 90.0 W%, and the distillate yield averaged 72.7 W%. The AO-60 catalyst did selectively produce slightly more naphtha and less vacuum gas oil and residuum than the other three catalysts.

In general, the product quality in Run 227-76(CC-16) with AO-60 catalyst was not quite as high as had been attained with the other three catalysts. The H/C ratio of the three heaviest oil fractions averaged 0.04 lower, and the nitrogen content of the two gas oil fractions averaged 0.03 W% higher for the AO-60 catalyst. However, the nitrogen content of the resid was only 0.68 W% in operations with the AO-60 catalyst compared to an average of 0.81 W% with the other three catalysts.

Overall, the AO-60 catalyst performed very well in the CTSL process. The slightly lower product-quality-improvement activity was somewhat offset by its slightly higher selectivity for lighter product formation. There was no apparent excessive physical degradation of the catalyst in this 13-day operation. Based on the information from this run, the AO-60 catalyst would be an appropriate catalyst for future CTSL operations.

SCOPE OF WORK

The coal for this run was an Illinois No. 6 coal, and the catalyst was Akzo AO-60 1/16" extrudates for both stages. The startup oil was a blend of pressure filter liquids derived from previous runs using Illinois No. 6 coal or Black Thunder Mine coal.

The operating conditions for this run were chosen so as to duplicate the operating conditions used in the previous runs 227-35, 36, 37 (I-16, I-17, I-18). These were a series of runs performed for catalyst evaluation using Amocat 1C 1/32" extrudates, UOP RCM4 1/20" spheres, and Shell S-317 1/32" extrudates. This allows a direct comparison of the results of this run with the results of the previous runs so as to evaluate the AO-60 catalyst in the CTSL process.

The operating conditions are given in *Table 1*. The run consisted of only two conditions, the first lasting nine days and the second lasting four days. The first and second stage reactor temperatures were 750°F and 800°F in Condition 1 and 775°F and 810°F in Condition 2. The dry coal space velocity was 46 lbs/hr/ft³ catalyst (per stage) throughout the run. The oil (recycled PFL) purge of the ebullating lines was kept at the 15 W% (of dry coal) rate that had been used in the comparison runs instead of the now more typical lower rate of 4 W%.

PROGRAM RESULTS AND COMPARISONS TO OTHER CATALYSTS

This section discusses the conversions, product yields, process performance and product quality for Run 227-76 (CC-16). *Table 2* part I & II is an 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. These results are summarized in *Figures 1-4*.

This section will also compare the results of this run in terms of conversions and product yields with three previous runs using Illinois No. 6 coal and different catalysts: Run 227-35 with Amocat 1C 1/32" extrudate, Run 227-36 using UOP RCM4 1/20" spheres, and Run 227-37 using Shell S-317 1/32" extrudate. These comparisons are summarized in *Table 3* and *Figures 5-13*. In addition a more detailed comparison is given on a daily basis between the results of this run and the previous run with Shell S-317, a standard catalyst used in most of the runs in this program.

COAL CONVERSION

Daily coal conversion is summarized in *Figure 1* for this run and run 227-37 with Shell S-317 catalyst. For the Condition 1 operation coal conversion is in the 91.0% to 92.5% range of maf coal. For the Condition 2 operation, when reactor temperature were 25°F higher in reactor 1 and 10°F higher in reactor 2 and the slurry oil/coal ratio was decreased from 1.5 to 1.1, coal conversions increased to the 93.4% to 94.1% range of maf coal.

The coal conversions for Run 227-76 (CC-16) were lower than had been attained in Run 227-37 (I-18) by an average of about 1.0 W%. There was no apparent explanation for the lower coal conversion in this operation than in previous operations with mine-washed Illinois No. 6 coal. Microautoclave tests indicated that the HRI 6081 coal was as reactive as previous shipments (see "Coal Feed" section), and its analyses were similar. The AO-60 catalyst was not likely the cause of the lower coal conversion because the coal conversion is not typically a function of catalyst activity in CTSL operations and the AO-60 catalyst activity by other indicators was similar to the Shell S-317 catalyst. Most likely the coal feed was less reactive than previous Illinois No. 6 coals despite the microautoclave results.

975°F+ CONVERSION

Daily 975°F+ conversion is summarized in *Figure 2* for this run and for Run 227-37 with Shell S-317 catalyst. For the condition 1 operation 975°F+ conversion is in the 98.4% to 82.9% range of maf coal, and shows the typical downward trend in conversion as the catalyst deactivates. For the Condition 2 operation, when reactor temperatures were 25°F higher in reactor 1 and 10°F

higher in reactor 2 and the slurry oil/coal ratio was decreased from 1.5 to 1.1, 975°F conversion rose to about 90.0 W% as a result of the more severe reactor conditions.

The daily 975°F conversion from this run, taking into account the scattering of the data, are very similar to the 975°F conversions from Run 227-37. The 975°F conversions at the end of each condition (Periods 9 & 13) for Run 227-76 (CC-16) were almost the same as the conversions for runs using Amocat 1C, RCM4 and S-317 catalyst (*Figure 6*).

These results indicate that in terms of 975°F conversion the AO-60 performs nearly the same as Amocat 1C, RCM4 and S-317 catalysts.

PRODUCT DISTRIBUTION

C₁-C₃ Gas Yields

The normalized C₁-C₃ gas yields are summarized in *Figure 3* for this run and for run 227-37 with Shell S-317 catalyst. The gas yields for this run were slightly higher than the S-317 run for condition 1, an average of 0.5 W%, and also higher for condition 2, 0.5 W% to 2 W%. *Figure 7* shows a comparison of the gas yields at the end of each condition for this run and for the previous runs with Amocat 1C, UOP RCM4, and Shell S-317. In general the AO-60 catalyst gave a higher gas yield than the other catalysts by an average of 0.7 W% of dry coal.

C₄-390°F Naphtha Yields

The end-of-condition normalized C₄-390°F naphtha yields are presented in *Figure 8* for this run, using AO-60 catalyst, and for the three previous runs using Amocat 1C, UOP RCM4, and Shell S-317 catalysts. The AO-60 catalyst gave higher naphtha yield, by 0 w% to 3.5 w%.

390-650°F Light Distillate Yields

The end-of-condition normalized 390-650°F light distillate yields are presented in *Figure 9* for this run, using AO-60 catalyst, and for the three previous runs using Amocat 1C, UOP RCM4, and Shell S-317 catalyst. For the less severe operating condition (Condition 1) Amocat 1C produces slightly higher, 1.6 W%, light distillate yield than the other three, which are virtually identical. For the more severe operating condition all four catalysts produced about the same 33 W% light distillate yield.

650-975°F Heavy Distillate Yields

The end-of-condition normalized 650-975°F heavy distillate yields are presented in *Figure 10* for this run, using AO-60 catalyst, and for the three previous runs

using Amocat 1C, UOP RCM4, and Shell S-317 catalyst. The three previous runs all had a heavy distillate yield of 18 W% for the less severe condition (Condition 1) while the AO-60 run was 2 W% lower. For the more severe condition, AO-60 gave a heavy distillate yield of 11.5 w% which was 0.5 W% to 2.5 W% lower than the heavy distillate yields for the other three catalysts.

975°F Residual Oil Yields

The end-of-condition normalized 975°F residual oil yields are presented in *Figure 11* for this run, which uses AO-60 catalyst, and for the three previous runs using Amocat 1C, UOP RCM4 and Shell S-317 catalyst. For the less severe operating condition (Condition 1) AO-60 gave a slightly lower residual oil yield than any of the other three catalysts. For the more severe operating condition AO-60 gave a residual oil yield of 0.4 W% higher than RCM4, 0.6 W% lower than Amocat 1C and 2.4 W% lower than S-317.

C₄-975°F Distillate Yields

The normalized C₄-975°F distillate yields are summarized in *Figure 4* for this run and for Run 227-37 (I-18) with Shell S-317 catalyst. The distillate yields for Run 227-76 (CC-16) decreased during Condition 1 from 73.7 W% of maf coal in Period 4 to 68.6 W% in Period 9. At the higher severity in Condition 2, the distillate yield averaged 72.7 W% of maf coal. These distillate yields were not significantly different than the distillate yields for Run 227-37 (I-18) with the Shell S-317 catalyst. The largest deviations from the general trend of lower distillate yield with increased catalyst age occurred in Periods 6 and 13 of Run 227-76 (CC-16). These periods also had the lowest indicated water yields, which would have caused the distillate yields to be biased high.

Figure 12 shows the distillate yields at the end of each condition for this run with AO-60 catalyst and for the previous runs with Amocat 1C, UOP RCM4, and Shell S-317. None of the distillate yields being compared was different by more than 2 W%.

Hydrogen Consumption

The hydrogen consumption (or H₂ reacted) for the last six periods of condition 1 was very consistent with an average value of 6.6%. For condition 2 the hydrogen consumption was also very consistent with an average value of 7.1%, 0.5% higher than condition 1 due to the more severe operating conditions. *Figure 13* shows a comparison of the hydrogen consumption at the end of condition for this run and the previous runs with Amocat 1C, UOP RCM4, and Shell S-317. From this figure it can be seen that there is very little difference among the three in terms of hydrogen consumption.

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PRODUCT QUALITY

The elemental analyses of the products were performed at the end of each of the two conditions, Periods 9 and 13. These analyses are summarized in *Table 4*. In addition the pressure filter liquids were separated into various boiling range fractions, and these fractions were also analyzed. These analyses are summarized in *Table 5*.

Hydrogen Contents

The hydrogen content of the various product fractions of the pressure filter liquid for periods 5, 9 and 13 are summarized in *Table 5* and presented graphically in *Figures 14, 15, and 16*. *Table 6* compares the product qualities from operations with the four different catalysts.

The hydrogen-to-carbon ratios for all the liquid product fractions listed in *Table 6* were slightly lower for the products from operations with the AO-60 catalyst. Similarly, the product quality in terms of nitrogen content was a little poorer for the 650-850 and 850-975°F fractions from operations with AO-60 catalyst. However, the AO-60 catalyst produced a 975°F⁺ oil with lower nitrogen and sulfur content. These trends for the Period 9 product fractions also held true for the Period 13 product fractions. The overall levels of denitrogenation from operations with the AO-60 catalyst, 83% in Period 9 and 89% in Period 13, were very similar to the levels of denitrogenation attained with the other three catalysts. The cyclohexane insoluble contents of the 975°F⁺ fraction were similar for all catalysts, and the toluene insolubles were lowest for the AO-60 catalyst.

These product quality results indicate that the hydrogenation activity and the distillate denitrogenation activity for the AO-60 catalyst are slightly lower than for the other nickel-molybdenum catalysts. However, this slightly lower product-improvement activity is somewhat offset by the higher selectivity of lighter products by the AO-60 catalyst.

Nitrogen Contents

Tables 4 and 5 summarize the nitrogen content in the various product streams and *Figure 15* graphically represents the nitrogen content of the various fractions in the pressure filter liquid. The nitrogen content of the various liquid products increases from period 9 to 13 by factors of 1.04 to 1.5. The nitrogen content of the various fractions of the pressure filter liquid also increase from Period 9 to 13. The following table compares the nitrogen content of the heavy fractions of the PFL of this run with the three previous runs for Period 9. The AO-60 catalyst gives a slightly higher nitrogen content for the 650-950°F and 850-875°F fractions and a lower content for the 975°F⁺ fraction.

	AO-60	Amocat 1C	RCM4	S-317
650-850°F	0.13	0.12	0.10	0.09
850-975°F	0.29	0.24	0.24	0.27
975°F+	0.68	0.75	0.86	0.81

Sulfur Contents

Sulfur content of all the light liquid streams (separator overhead, atmospheric still overhead and the IBP-850°F fraction of the pressure filter liquid) were very low, generally below 0.02%. The sulfur content of the heavy fraction of the pressure filter liquid was much higher, from 0.07% to 0.2%. Figure 16 summarizes the sulfur content in the product fractions of the pressure filter liquid. The sulfur in the solid products was also higher at 0.67%. These numbers show the expected trend of concentrating the sulfur in the heavy products and removing the sulfur from the lighter distillates.

DETAILS OF OPERATION

This report summarizes the operation of Run 227-76 (CC-16) in the CTSL bench unit, using Illinois No. 6 coal and Akzo AO-60 1/16" extrudate catalyst in both reactors.

OPERATIONS

Preoperational Procedures - Operations were started using L-786 as start up oil. This was also the oil used whenever a makeup oil was needed for this run. This oil was blended from 2 parts PFL derived from previous runs using an Illinois No. 6 coal and 1 part PFL from previous runs using Black Thunder Mine coal. At the time of coal introduction, the slurring oil was recycle material produced during heatup.

Operating Summary - A summary of the two conditions used for this 14 day run are given in *Table 1*. Beyond the normal samples taken for in-house analysis and storage, additional samples of PFL, PFC, ASOH, SOH and recycle solvent were taken for shipment to CONSOL for their determination of hydrogen utilization in coal liquefaction.

Condition 1 (Periods 1 through 9) - The operating conditions (as given in *Table 1*) were the same as those given for Condition 1 in runs 227-35, 36, and 38 (I-16, 17 and 18). These runs were part of a previous catalyst evaluation program. The recycle rate of Pressure Filter Liquid (PFL) was higher in this condition than in most of the operations in this program. The combined PFL recycle used to slurry the coal and to purge the ebullating-pump lines was 1.8 times the coal feed.

Condition 2 (Periods 10 through 13) - The operating conditions were the same for Condition 2 in runs 227-35, 36, and 38 (I-16, 17, and 18). The first stage temperature was increased from 750 to 775°F, and the second stage temperature was increased from 800 to 810°F. The coal was concentrated in the feed slurry by using a 1.1:1 recycle PFL: coal ratio. The recycle purge rates were kept at the relatively high rates used in the comparison runs, giving an overall solvent:coal ratio of 1.4:1.

During inspection after the run, the catalyst from both stages flowed freely from the reactors. Reactor 1 catalyst was found in a normal settled position in the reactor at a level that corresponded to 94% of the original catalyst volume. Reactor 2 had catalyst and solids stuck onto the screen which fell off while removing the top head. The rest of the catalyst was found at a normal settled position in the reactor at a level that corresponded to 96% of the original catalyst level.

In this study, the process performance of Akzo AO-60 1/16" NiMo extrudates was found to be very similar to that of Shell S-317 1/32" NiMo catalyst; however, they have different hydrodynamic behavior. Larger diameter 1/16" catalyst are favored for the rigors of PDU scale-operation whereas due to equipment (pump) limitations the 1/32" catalysts perform with more safety at the Bench-Scale. Also, an extensive Bench-Scale data base exists with S-317, thus this catalyst will probably continue to be utilized at the Bench-Scale.

At the Bench-Scale with 1/32" catalyst, and the Moyno Ebullating pumps available, one pump provides sufficient flow for ebullation with a second pump as spare, generally with 1/16" catalysts more flow than one pump can deliver is required.

COAL FEED

The analyses of the Illinois No. 6, Burning Star Mine, coal (HRI 6081) used in this run are listed in *Table 7* along with the analyses of the HRI 5174 coal that had been used in the comparison Runs 227-35, -36, and -37 (I-16, -17, and -18). These analyses do not indicate any differences that would explain the lower coal conversions in Run 227-76 (CC-16). The coal conversions in the microautoclave tests were even slightly higher for the HRI 6081 coal.

FRESH CATALYST

The catalyst used in both stages for Run 227-76(CC-16) was AO-60, 1/16" extrudate, nickel-molybdate on alumina produced by Akzo Chemicals, Inc. The designation was HRI No. 6043. This catalyst is a prospective replacement for the S-317 catalyst, which had been used in most of the previous runs of this program. The S-317 catalyst is no longer available from Shell. The inspections of the AO-60 catalyst and the catalysts that were tested in the comparison Runs 227-35, -36, and -37 (I-16, -17, and -18) are presented in *Table 9*.

The AO-60 catalyst had a somewhat higher pore volume than the other catalysts. It had a pore volume of 0.874 cc/gm (0.762 cc/cc particle), and the modal pore diameter was 82 Angstroms, compared to a slightly larger modal pore diameter of 95 Angstroms for the Shell S-317 catalyst. There were also concentrations of pores at about 400 and 1000 Angstroms in the AO-60 catalyst. These are smaller than the macropores in the Shell S-317 catalyst, which have a modal pore diameter of about 2500 Angstroms.

RECOVERED CATALYST

Analyses of the catalysts recovered from the two stages after Runs 227-76 (CC-16) are given in *Table 10*.

The catalyst recovery from the first stage reactor was 83% based on the relative volumes of charged and recovered +20 mesh oil-free catalyst, and 72.5% 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 recovered catalyst from the first stage reactor, was 12.43 W%. Metals contaminants accumulation was 1.94%. The sulfur content of the recovered catalyst was 5.59%, corresponding to formation of MoS_2 and NiS .

The catalyst recovery from the second stage reactor was 92% based on the relative volumes of charged and recovered +20 mesh oil-free catalyst, and 83.8% based on the reported molybdenum contents for the charged and +20 mesh oil-free recovered catalyst. There was also some catalyst in the 20/100 mesh material recovered, with the molybdenum content corresponding to 0.94% of the amount of molybdenum in the catalyst.

The carbon accumulation on the recovered catalyst from the first stage reactor was 16.38 W%. Metals contaminants accumulation was 1.31 W%. The sulfur content of the recovered catalyst was 5.56 W%, corresponding to formation of MoS_2 and NiS .

TABLE 1
OPERATING CONDITIONS
RUN 227-76

CONDITION PERIODS	1 1-9	2 10-13
NOMINAL CONDITIONS		
COAL SPACE VELOCITY (LBS/HR/FT ³ CAT)	46	46
SLURRY OIL/COAL RATIO	1.5	1.1
SOLVENT/COAL RATIO **	1.8	1.4
UNIT PRESSURE (PSIG)	2500	2500
TEMPERATURES (°F)		
REACTOR 1	750	775
REACTOR 2	800	810
ATMOSPHERIC STILL REBOILER	610	625
HOT SEPARATOR LIQUID	560	600
RECYCLES (WT% DRY COAL)		
COAL	680	680
PRESSURE FILT. LIQ TO SLURRY	150	110
BUFFER 1ST STAGE	15	15
BUFFER 2ND STAGE	15	15
TOPPED SEPARATOR BOTTOMS	0	0

** Includes buffer oil to first and second stages.

TABLE 2 PART 1
RUN 227-76 OPERATING SUMMARY

COAL : ILLINOIS NO. 6 HRI-6081
CATALYST : AKZO AO 60 HRI-6043

Period Number	1	2	3	4	5	6
Date (Start of Period)	12/02/92	12/03/92	12/04/92	12/05/92	12/06/92	12/07/92
Hours of Run (End of Period)	24.	48.	72.	96.	120.	144.
Stage 2 Catalyst Age, Lb Dry Coal/Lb Cat	13.	33.	53.	72.	93.	113.
1st Stage Temperature (F)	707.	749.	751.	750.	751.	749.
2nd Stage Temperature (F)	741.	799.	800.	799.	800.	801.
Unit Back Pressure (PSIG)	2476.	2497.	2493.	2493.	2495.	2492.
Space Velocity, Lb Coal/Hr/Ft ³ catalyst/stage	30.0	44.9	45.1	44.4	46.0	45.8
Wt OF DRY COAL						
PFL Recycle	368.7	152.7	125.0	139.9	148.6	148.6
PFL to Buffer to Stage 1	41.0	16.3	19.2	19.3	15.2	13.7
PFL to Buffer to Stage 2	41.2	14.3	17.1	20.9	18.3	18.2
Make-up Oil	0.0	0.0	27.7	12.8	0.0	0.0
MATERIAL BALANCE (%) (GROSS)	88.83	95.11	101.22	99.06	100.59	99.43
ESTIMATED NORMALIZED YIELDS, Wt DRY FRESH FEED						
C1-C3 in Gases				5.64	5.85	5.70
C4-C7 in Gases				3.88	4.06	4.13
IBP-390 deg-f in Liquids				14.41	12.41	12.46
390-500 deg-f in Liquids				11.01	8.85	8.67
500-650 deg-f in Liquids				25.82	21.52	20.99
650-850 deg-f in Liquids				8.11	11.70	13.92
850-975 deg-f in Liquids				2.62	3.47	4.26
Toluene Soluble 975F+ Oil				2.31	5.64	6.99
Toluene Insoluble 975F+ Oil				0.00	0.04	0.06
Unconverted Coal				8.03	7.11	7.04
Ash				10.61	10.61	10.61
Water				9.96	10.96	7.30
CO				0.13	0.10	0.10
CO2				0.11	0.07	0.04
NH3				1.39	1.33	1.31
H2S				2.99	3.03	2.98
Total (100 + H2 Reacted)				107.00	106.73	106.56
PROCESS PERFORMANCE						
C4-975 deg-f Distillates, Wt of MAF Coal				73.7	69.4	72.1
975F+ Conversion, Wt MAF				88.4	85.7	84.2
Coal Conversion, Wt MAF		91.2	92.2	91.0	92.0	92.1
HDS, Wt				76.6	77.5	76.2
HDN, Wt				91.3	87.3	86.4

TABLE 2 PART 2
RUN 227-76 OPERATING SUMMARY

COAL : ILLINOIS NO. 6 HRI-6081
CATALYST : AKZO AO 60 HRI-6043

Period Number	7	8	9	10	11	12	13
Date (Start of Period)	12/08/92	12/09/92	12/10/92	12/11/92	12/12/92	12/13/92	12/14/92
Hours of Run (End of Period)	168.	192.	216.	240.	264.	288.	312.
Stage 2 Catalyst Age, Lb Dry Coal/Lb Cat	133.	154.	174.	194.	214.	235.	254.
1st Stage Temperature (F)	750.	752.	752.	768.	775.	777.	777.
2nd Stage Temperature (F)	799.	799.	800.	807.	809.	811.	810.
Unit Back Pressure (PSIG)	2496.	2504.	2504.	2502.	2504.	2502.	2496.
Space Velocity, Lb Coal/Hr/Ft ³ catalyst/stage	46.0	46.7	46.4	44.4	45.3	46.9	44.9
Wt OF DRY COAL							
PFL Recycle	148.6	148.6	147.1	109.9	109.0	104.8	96.7
PFL to Buffer to Stage 1	12.2	12.0	14.3	16.4	14.7	16.1	14.3
PFL to Buffer to Stage 2	19.3	35.0	16.4	16.1	14.5	15.3	14.3
Make-up Oil	0.0	0.0	0.0	0.0	0.0	2.5	10.6
MATERIAL BALANCE (%) (GROSS)	99.35	97.72	98.47	95.54	99.27	96.53	98.22
ESTIMATED NORMALIZED YIELDS, Wt DRY FRESH FEED							
C1-C3 in Gases	5.29	5.60	5.76		8.21	7.93	7.71
C4-C7 in Gases	3.38	3.88	3.75		4.03	4.09	4.04
IBP-390 deg-f in Liquids	12.91	12.74	13.43		17.59	17.69	17.64
390-500 deg-f in Liquids	8.86	8.72	9.07		10.92	10.84	10.91
500-650 deg-f in Liquids	18.02	18.21	18.96		22.60	22.18	22.30
650-850 deg-f in Liquids	13.48	12.59	12.41		7.82	7.40	9.33
850-975 deg-f in Liquids	3.91	3.67	3.72		1.72	1.60	2.13
Toluene Soluble 975F+ Oil	7.40	7.26	7.15		3.29	2.82	3.76
Toluene Insoluble 975F+ Oil	0.08	0.08	0.13		0.05	0.09	0.22
Unconverted Coal	7.81	6.89	6.67		5.80	5.88	5.24
Ash	10.61	10.61	10.61		10.61	10.61	10.61
Water	10.16	11.79	10.44		10.00	11.60	8.63
CO	0.14	0.12	0.08		0.17	0.10	0.17
CO ₂	0.04	0.04	0.04		0.04	0.04	0.04
NH ₃	1.26	1.27	1.26		1.34	1.35	1.35
H ₂ S	3.00	3.00	2.97		2.86	2.91	2.93
Total (100 + H ₂ Reacted)	106.37	106.47	106.46		107.04	107.12	107.02
PROCESS PERFORMANCE							
C4-975 deg-f Distillates, Wt of MAF Coal	67.8	66.9	68.6		72.4	71.4	74.2
975F+ Conversion, Wt MAF	82.9	84.1	84.4		89.8	90.2	89.7
Coal Conversion, Wt MAF	91.3	92.3	92.5		93.5	93.4	94.1
HDS, Wt	76.8	76.8	76.0		73.1	74.4	75.1
HEN, Wt	83.0	83.4	83.3		88.6	89.2	89.3

TABLE 3
COMPARISON OF AO-60, AMOCAT 1C, UOP RCM4, SHELL 317

PERIOD 9

	AO60	AMOCAT 1C	RCM4	S-317
Coal Conversion (W% maf)	92.5	93.41	93.67	93.73
975°F ⁺ Conversion (W% maf)	84.4	84.97	84.91	84.38
H ₂ Consumption (W% dry)	6.46	6.47	6.26	6.26

YIELDS (W% dry basis)

C ₁ -C ₃ gases	5.76	5.00	5.28	5.15
C ₄ -390°F	17.18	15.01	15.51	15.17
390-650°F	28.03	30.06	28.75	28.06
650-975°F	16.13	17.91	18.37	18.26
975°F ⁺	7.28	7.55	7.84	8.36
C ₄ -975°F	61.34	62.99	62.62	61.48

PERIOD 13

	AO60	AMOCAT 1C	RCM4	S-317
Coal Conversion (W% maf)	94.1	94.6	95.07	94.91
975°F ⁺ Conversion (W% maf)	89.7	89.42	90.97	87.72
H ₂ Consumption (W% dry)	7.02	6.99	7.20	6.77

YIELDS (W% dry basis)

C ₁ -C ₃ gases	7.71	7.04	8.42	6.13
C ₄ -390°F	21.68	20.13	21.73	18.13
390-650°F	33.21	33.11	32.55	32.66
650-975°F	11.46	12.95	12.04	14.05
975°F ⁺	3.98	4.64	3.66	6.43
C ₄ -975°F	66.35	66.18	66.32	64.85

TABLE 4**PRODUCT STREAM ANALYSIS RUN 227-76 (CC-16)**

CONDITION	1	2
PERIOD	9	13
CATALYST AGE (lbs coal/lb cat)	174	253
SEPARATOR OVERHEAD		
GRAVITY (API)	40.2	41.1
ELEMENTAL ANALYSIS		
CARBON (W%)	86.40	86.40
HYDROGEN (W%)	13.11	12.98
SULFUR (W%)	0.03	0.02
NITROGEN (W%)	0.04	0.06
TOTAL	99.58	99.46
H/C RATIO	1.82	1.80
ATMOSPHERIC OVERHEAD		
GRAVITY (API)	26.4	25.6
ELEMENTAL ANALYSIS		
CARBON (W%)	87.43	87.52
HYDROGEN (W%)	11.82	11.54
SULFUR (W%)	0.01	0.01
NITROGEN (W%)	0.075	0.078
TOTAL	99.33	99.15
H/C RATIO	1.62	1.58
PRESSURE FILTER SOLIDS		
ASH (W%)	30.24	39.08
ELEMENTAL ANALYSIS (ash free)		
CARBON (W%)	87.26	86.60
HYDROGEN (W%)	7.35	6.63
SULFUR (W%)	3.78	5.86
NITROGEN (W%)	0.67	0.64
TOTAL	99.06	99.73
SULFUR/ASH	0.125	0.150

TABLE 5
PRESSURE FILTER LIQUID PRODUCT FRACTION ANALYSIS
RUN 227-76 (CC-16)

CONDITION	1	2
PERIOD	9	13
CATALYST AGE (lbs coal/lb cat)	174	253
TOTAL LIQUID		
GRAVITY (API)	4.9	2.8
ELEMENTAL ANALYSIS (W%)		
CARBON	89.08	89.66
HYDROGEN	9.25	8.60
SULFUR	0.07	0.08
NITROGEN	0.30	0.40
TOTAL	98.70	98.74
IBP-650°F (W%)	10.13	5.88
650-850°F (W%)	45.71	48.29
850-975°F (W%)	14.75	15.37
975°F+ (W%)	28.83	29.79
LOSS (W%)	0.58	0.67
LGO (IBP-650°F)		
GRAVITY (°API)	17.6	17.1
CARBON (W%)	88.14	89.06
HYDROGEN (W%)	11.30	10.99
SULFUR (W%)	0.01	0.01
NITROGEN (W%)	0.07	0.10
VGO (650-850°F)		
GRAVITY (°API)	11.3	10.0
CARBON (W%)	89.08	89.59
HYDROGEN (W%)	10.17	9.84
SULFUR (W%)	0.01	0.02
NITROGEN (W%)	0.13	0.17
HVGO (850-975°F)		
GRAVITY (°API)	1.1	-1.5
CARBON (W%)	89.67	90.74
HYDROGEN (W%)	8.92	8.49
SULFUR (W%)	0.05	0.04
NITROGEN (W%)	0.29	0.39
RESID (975°F+)		
GRAVITY (API)	-7.4	-10.3
CARBON (W%)	89.48	90.22
HYDROGEN (W%)	7.28	6.67
SULFUR (W%)	0.16	0.20
NITROGEN (W%)	0.68	0.83

TABLE 6
COMPARISON OF OIL PROPERTIES
PERIOD 9 SAMPLES FROM RUNS CC-16, I-16, I-17, & I-18

RUN	CC-16	I-16	I-17	I-18
CATALYST	AO-60	AMOCAT 1C	RCM4	S-317
650-850°F				
H/C RATIO	1.37	1.41	1.41	1.40
NITROGEN, W%	0.13	0.12	0.10	0.09
850-975°F				
H/C RATIO	1.19	1.25	1.23	1.20
NITROGEN, W%	0.29	0.24	0.24	0.27
975°F*				
H/C RATIO	0.98	1.03	1.02	1.03
NITROGEN, W%	0.68	0.75	0.86	0.81
SULFUR, W%	0.16	0.22	0.29	0.25
CYCLOHEXANE INSOL, W%	24.2	23.6	25.0	23.3
TOLUENE INSOL, W%	1.8	3.4	7.1	2.2

TABLE 7**ILLINOIS NO. 6 FEED COAL ANALYSES FOR RUNS 227-76 (CC-16)
AND 227-35, 36, & 37 (I-16, 17 & 18)**

FEED DESIGNATION, HRI NO	6081	5174
RUNS	CC-16	I-16, 17, & 18
MOISTURE, W%	2.97	2.57
PROXIMATE ANALYSIS, W% (DRY BASIS)		
VOLATILE MATTER	39.05	
FIXED CARBON	50.34	
ASH	10.61	
ULTIMATE ANALYSIS, W% (DRY BASIS)		
CARBON	69.48	70.39
HYDROGEN	4.39	4.49
SULFUR	3.68	3.60
NITROGEN	1.25	1.44
ASH	10.61	10.55
OXYGEN (DIFFERENCE)	10.59	9.54
MICROAUTOCLAVE RESULTS *		
THERMAL CONVERSION	86.5	79.9
CATALYTIC COAL CONVERSION	91.7	91.0

* 800°F, 30 MINUTES AND 2000 PSIG H₂

TABLE 8
INSPECTION OF START-UP AND MAKE-UP OIL
FOR RUN 227-76 (CC-16)

DESIGNATION	L-786
GRAVITY, °API	2.0
DISTILLATION	
IBP	537
5 V%	619
10 V%	650
20 V%	700
30 V%	737
40 V%	778
50 V%	809
60 V%	850
70 V%	950
EP	975
V% @ 650°F	10
V% @ 850°F	60
V% @ 975°F	74
IBP-650°F, W%	9.2
650-850°F, W%	46.4
850-975°F, W%	14.3
975°F+, W%	29.3
LOSS, W%	0.8
ELEMENTAL ANALYSES, W%	
CARBON	89.5
HYDROGEN	8.69
SULFUR	0.14
NITROGEN	0.55

TABLE 9
FRESH CATALYST PROPERTIES

HRI NO.	5337	5339	5359	6043
Run No.	I-16	I-17	I-18	CC-16
Catalyst	Amocat 1C	UOP RCM4	S-317	AO-60
Nominal Size	1/32"	1/20" sphere	1/32"	1/16"
CHEMICAL ANALYSIS				
Molybdenum	10.95	9.60	10.76	12.25
Nickel	1.91	1.79	2.86	2.6
PHYSICAL PROPERTIES				
Bulk Density, Compacted (gm/cc)	0.646	0.602	0.638	0.557
Particle Dens, 10psi Hg (gm/cc)	0.811	0.866	0.990	0.872
Skeletal Den, 60,000psi Hg (gm/cc)	1.776	2.164	3.031	3.547
Surface Area, calc. (m2/gm)	273	260	263	286
(m2/cc particle)	221	225	260	249
Pore Volume (cc/gm)	0.670	0.772	0.681	0.874
(cc/particle)	0.543	0.668	0.674	0.762
Average Crush Strength (lb/mm)	2.17	6.70	1.78	2.67
Average Diameter (mm)	0.90	1.55	1.00	1.59
Length, average (mm)	3.3		3.8	3.8
< 2.5 mm (w%)	18.7		2.8	6.0
2.5 to 6.3 mm (w%)	78.8		70.0	74.1
> 6.3 mm (w%)	2.4		27.2	19.9
PORE SIZE DISTRIBUTION (cc/gm)				
Diameter > 30 A	0.67	0.77	0.68	0.873
Diameter > 100 A	0.41	0.69	0.37	0.54
Diameter > 250 A	0.12	0.04	0.17	0.24
Diameter > 500 A	0.10	0.015	0.16	0.12
Diameter > 1500 A	0.06	0.005	0.14	0.008
Diameter > 4000 A	0.00	0.00	0.04	0.008
PORE DIAMETER (A)				
At Median Pore Volume	110	156	105	125
4*[Pore Vol./Calc Surf Area]	98	119	104	122

TABLE 10
RECOVERED CATALYSTS ANALYSES
RUN 227-76 (CC-16)

STAGE	FIRST	SECOND
CATALYST AGE, LB COAL/LB CAT *	253	253
CATALYST RECOVERY, V%	82.8	92.2
Bulk Density, gm/cc	0.758	0.763
ANALYSES OF OIL FREE +20 MESH CATALYST, W%		
Carbon	12.43	16.38
Hydrogen	0.90	0.74
H/C Ratio	0.87	0.54
Nitrogen	0.32	0.27
Sulfur	5.59	5.56
Molybdenum	7.588	7.910
Nickel	1.798	1.642
Titanium	1.021	0.215
Iron	0.372	0.042
Calcium	0.056	0.021
Sodium	0.493	1.029
Total Metal Contaminants	1.94	1.31
Loss on Ignition, w%	20.82	25.38
Particle Density, gm/cc particle **	2.412	2.600
Pore Volume (D>30 A), cc/gm	0.489	0.481
cc/cc particle	1.18	1.25
Surface Area (calc.), m2/gm	189.96	185.67
m2/cc particle	458.20	482.74
Modal Pore Diameter, Angstrom		
Macro-pores	875	600
Mini-pores	80	80
ANALYSES OF IGNITED CATALYST		
Particle Density, gm/cc particle **	3.278	3.186
Pore Volume (D>30 A), cc/gm	0.808	0.844
cc/cc particle	2.65	2.69
Surface Area (calc.), m2/gm	236.90	249.60
m2/cc particle	776.47	795.30
Modal Pore Diameter, Angstrom		
Macro-pores	1100	850
Mini-pores	110	100
ANALYSIS OF 20-100 MESH OIL-FREE SOLIDS		
Weight, gm	28.9	9.5
Molybdenum, w%	4.16	5.93

* Catalyst age is for operations through period 13; coal feed was continued for another 20 hours with reactors at reduced T.

** In mercury at 10 psia.

COAL CONVERSION RUN 227-76 (CC-16) AO-60 & SHELL S-317

FIGURE 1

975F + CONVERSION (MAF)
RUN 227-76 (CC-16) AO-60 & SHELL S-317

FIGURE 2

C1-C3 GAS YIELD RUN 227-76 (CC-16) AO-60 & SHELL S-317

FIGURE 3

C4-975F YIELD (MAF)
RUN 227-76 (CC-16) AO-60 & SHELL S-317

FIGURE 4

COAL CONVERSION

FIGURE 5

975F+ CONVERSION

FIGURE 6

C1-C3 GAS YIELD

FIGURE 7

C4-390F YIELD

FIGURE 8

390F-650F YIELD

FIGURE 9

650F-975F YIELD

FIGURE 10

975F+ YIELD

FIGURE 11

C4-975F YIELD

FIGURE 12

H2 CONSUMPTION

FIGURE 13

HYDROGEN CONTENT OF PRODUCT FRACTIONS

FIGURE 14

NITROGEN CONTENT OF PRODUCT FRACTIONS

FIGURE 15

FIGURE 16

REFERENCES

REPORTS

1. Comolli, A.G., P. Ganguli, E. Harris, J.B. MacArthur, J.B. McLean and T.O. Smith, "New Technology Concept for Two-Stage Liquefaction of Coal - Illinois Coal Program", DE-60017-TOP-1, August 1985.
Hydrocarbon Research, Inc. for the Department of Energy, Contract No. DE-AC22-83PC-60017.
2. Abrams, L.M., R. Caruso, J.E. Duddy, J.B. MacArthur and M. Srouji, "New Technology Concept for Two-Stage Liquefaction of Coal - Conceptual Commercial Plant Design and Economics", DE-60017-TOP-2, December 1985.
Hydrocarbon Research, Inc., for the Department of Energy, Contract No. DE-AC22-83PC-60017.
3. Burke, F.P., R.A. Winshel and G.A. Robbins, "Recycle Slurry Oil Characterization - Final Report", October 1980 through March 1985. Issued March 1985 by Conoco, Inc. under DOE Contract No. DE-AC22-80PC-300027.
4. Burke, F.P. et al, "Recycle Oil Characterization - Quarterly Report April 1985 and Final Report December 1986, to be issued under DOE Contract No. DE-AC22-84PC-70018.
5. Comolli, A.G., J.E. Duddy, E.S. Johanson, J.B. McLean, G.A. Popper and T.O. Smith, "Low-Severity Catalytic Two-Stage Liquefaction Process, Illinois Coal Studies, DE-80002-TOP-2, for the U.S. Department of Energy, Contract No. DE-AC22-85PC80002.
6. Abrams, L.M., A.G. Comolli, G.A. Popper, C. Wang and G. Wilson, "Low-Severity Catalytic Two-Stage Liquefaction Process, Illinois Coal Conceptual Commercial Plant Design and Economics", DE-80002-TOP-3, for the U.S. Department of Energy, Contract No. DE-AC22-85PC80002.
7. Department of Energy, PETC and EPRI "Advanced Physical Fine Coal Cleaning Spherical Agglomeration Process, Proof of Concept Plant, Bechtel National, August, 1989.

PAPERS

1. Comolli A.G., Johanson E.S., Panvelker S.V., Stalzer R.H., "Close Coupled Two-Stage Catalytic Liquefaction Continuous Bench-Scale and Support Studies". DOE Contractor's Conference, September 3-5 1991, Pittsburgh, Pa.
2. Comolli A.G., Johanson E.S., "Recent Advances in Direct Coal Liquefaction" International Conference in Coal and Slurry Technologies, April 22-25 1991.
3. Comolli A.G., Johanson E.S., Panvelker S.V., " CTSL™ Process Studies" DOE Contractor's Conference, Pittsburgh, Pa., September 24-26 1990.
4. Comolli A.G., "CTSL Catalytic Two-Stage Liquefaction Coupled @ Coal Cleaning", ACS, Atlanta, Ga., April 1991
5. Comolli A.G., Panvelker S.V., Johanson E.S., Stalzer R.H., "A Two-Stage Coal Liquefaction Evaluation of a Pre-Dispersed, Iron Oxide, Hydroxide Catalyst", AIChE Meeting, Pittsburgh, Pa., August 18-21, 1991.

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