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**DOE/PC/88818-T4
(DE94007958)**

**CATALYTIC TWO-STAGE LIQUEFACTION (CTSL™) PROCESS—LABORATORY
SCALE STUDIES MODELLING AND TECHNICAL ASSESSMENT**

Final Topical Report

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June 1993

Work Performed Under Contract No. AC22-88PC88818

**For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania**

**By
Hydrocarbon Research, Inc.
Princeton, New Jersey**

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ABSTRACT

Reported herein are the details and results of Laboratory-Scale experiments using sub-bituminous and bituminous coal concluded at Hydrocarbon Research, Inc., under DOE Contract No. DE-AC22-88PC88818 during the period October 1, 1988 to June 30, 1993. The work described in this report is primarily concerned with tests on a Laboratory Scale primarily using microautoclaves. Experiments were conducted evaluating coal, solvents, start-up oils, catalysts, thermal treatments, CO₂ addition and sulfur compound effects.

Other microautoclave tests are included in the companion topical reports for this contract, DE-88818-TOP-01 & 02 on Sub-Bituminous and Bituminous Bench-Scale and PDU activities.

In addition to the Laboratory Scale Studies, kinetic data and modelling results from Bench-Scale and Microautoclave tests are interpreted and presented along with some economic updates and sensitivity studies.

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

- 5.1 Kinetic Modelling
- 5.2 Economic Screening Studies

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. 3, microautoclave test results, kinetic CTSL™ interpretations and economic updates on two stage sub-bituminous and bituminous coal processing are presented. When the laboratory tests were integral with Bench-Scale Studies results are included in the Bench-Scale Topical Reports.

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 sub-bituminous and bituminous coal consists of Laboratory Microautoclave Studies, Kinetic Modelling of the CTSL™ Process and Economic Screening Studies.

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 provides a sample required to independently assess the performance 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 line-out 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

MICROAUTOCLAVE DESCRIPTION

The microautoclave (MA) is composed of two tubular reactor bombs which are mechanically shaken in a heated, fluidized sand bath. The reactors are charged with specified quantities of materials and can be pressurized to 2000 psig or greater. The bombs are plunged into a sand bath maintained at a predetermined temperature, then agitated for a specified amount of time. The heating of the reactors is very rapid with internal temperatures within 3-5°F of the bath temperature in 2-3 minutes. After the end of the scheduled time, the bombs are removed, plunged into a water bath for cooling, and the contents analyzed. Products are analyzed primarily by solvent extractions and ash determination.

The microautoclave is routinely used to evaluate candidate coals and oils, and to determine coal reactivity, solvent quality, catalyst quality, coal blending, and coal cleaning effects.

DESCRIPTION

The microautoclave unit to be used in this coal program is HRI's fourth generation microreactor, as shown in *Figure 3*. It is constructed of 347 ss and has a 20 cc internal volume, into which the catalyst-charge basket can be inserted. N₂ or H₂ at up to 3000 psig are added to this system through 1/8" O.D. Tubing, which serves as feed and vent lines. The entire assembly is shaken with approximately one-inch strokes at 460 rpms and lowered into a preheated, temperature-controlled sand bath. A cold trap is located in the gas outlet line to collect the material that escapes from the reactor when pressure is released at the end of the run. Two identical microautoclave reactor systems are operated side-by-side. Two identical sand baths, which can be heated to different temperatures, can be used to simulate close-coupled two-staged reactions.

HRI has run both thermal and catalytic tests with this equipment with different charges, feed ratios, temperatures and times. Operation and data work-up procedures are described below.

PROCEDURES

Typically, reactants (solvent and/or coal) and catalyst (if any) are charged to the microautoclave (MA) reactor. All materials are carefully prepared, stored and sampled prior to their use (or upon arrival at HRI). The coal is ground, riffled and sealed in single-charge containers under N₂. Prior to use in the MA, the coal sample is dried in a 100°F vacuum oven with a N₂ purge for one hours. It is then stored in a desiccator for up to one week. The well-mixed solvent is charged to the reactor first. Its weight, most typically 8.0 g, is the difference between the reactor-plus-solvent weight and the empty reactor weight.

After the solvent is charged, the catalyst, if any, is inserted into the previously tared catalyst-charged basket. The coal is charged last to attain proper contact

between coal and solvent. Careful attention is paid to ensure that all the coal that has been weighed out is actually charged to the reactor. Since coal conversions are calculated by ash balance using very small numbers, accuracy is very important. Reactor loadings of reactant (coal/oil), solvent, and catalyst can be varied but in general the attempt is made to approximate the back-mixed composition of a continuous ebullated bed in the batch reactor charge.

The charged reactor is connected to the MA apparatus and pressure tested with N_2 . After the sand bath has attained a temperature of 25°F higher than the test temperature the reactor is pressured to 500 psig hydrogen and slowly immersed into the sand bath, taking two minutes. At this time, the hydrogen pressure is established (typically at 2000 psig), shaking is begun, and the sand bath temperature is adjusted. At the end of the run the shaking is discontinued; the reactor is quenched in a water bath and depressured. Both the reactor and the cold trap are removed and weighed for material balance determination.

A number of different product work-up procedures can be used, depending on the nature and objectives of the experiment performed. It is anticipated that the following will be included (not all for all runs, however).

- a. Coal conversion via THF extraction and ash balance.
- b. Oils, asphaltenes and preasphaltenes via solvent extraction of THF soluble oils. (This may be done gravimetrically or by liquid column fractionation.)
- c. Coal and oil 975°F+ conversion by TGA (Thermogravimetric Analysis), simulated distillations of feed and products, and material balance.
- d. Elemental analysis of product oil to determine hydrogenation, desulfurization, and denitrogenation efficiency.
- e. Characterization of product oils by proton NMR to determine hydrogenation efficiency.
- f. Analysis and quantification of gases collected by the use of impermeable gas collection bags.

FIGURE 3

MICROAUTOCLAVE REACTOR

MECHANICAL DESIGN

- 20cc INTERNAL VOLUME
- MAXIMUM INLET HYDROGEN PRESSURE 3000psi
- OPERATIONS TO LIQUEFACTION TEMPERATURE
- THERMAL AND GAS INLET COUPLING
- 347ss MATERIAL OF CONSTRUCTION
- EXTERNAL CAP THREADS
- REACTOR CAP REDESIGN
- COLD TRAPS
- CATALYST BASKET
- UTILIZES WHOLE EXTRUDATE CATALYST
- GAS COLLECTION
- SHAKEN VERTICALLY IN A SAND BATH

TESTING CAPABILITIES

- THERMAL TESTS VARYING CHARGE, FEED RATIOS, TEMPERATURE, TIME
- CATALYTIC TESTS VARYING CHARGE, FEED RATIOS, TEMPERATURE, TIME

RESULTS AND CONCLUSIONS

LABORATORY SUPPORT - MICROAUTOCLAVE STUDIES

As an integral part of the Laboratory Support task of this program, microautoclave tests were carried out to support the operation of the continuous bench unit in the following applications:

- a. Coal Feedstock Qualification
- b. Catalyst Qualification
- c. Catalyst Deactivation Studies
- d. Solvent Quality Testing
- e. Product Reactivity Testing

Some of the observations, results and conclusions from this work are summarized below and others are contained in the reports for the continuous bench-scale runs as they apply.

- ◆ Wyoming - Dakota sub-bituminous coals generally have coal conversions in the range of 86 to 92%; however, some coal samples from the Powder River Basin did show coal conversions to 94%.
- ◆ Cleaned bituminous coals are more convertible than uncleaned coals, in a catalytic environment; however, thermally they are poorer probably due to the removal of catalytic components of the ash.
- ◆ The three agents tested DMDS, TNPS and elemental sulfur are all effective sulfiding agents. Dimethyldisulfide (DMDS) was found to be less effective in presulfiding than di-tertiary nonyl polysulfide (TNPS); however, the TNPS complicates the interpretation of results by producing additional naphtha range product.
- ◆ Of four supported catalysts evaluated in the microautoclave, a UOP microporous NiMo bead catalyst showed the highest activity and an Iron-Moly catalyst showed equivalent activity to the baseline NiMo Shell 317 on an equal weight basis.
- ◆ Tests for coal and resid conversion on a microautoclave scale of three disperseable iron catalysts, a pyrrhotite from INCO, a magnetic pigment from Wright Industries and a pyrite from Pea Ridge Iron had some catalytic activity. An Fe_2O_3 sample from Wilsonville showed retrogressive reaction of residual oils whereas at Wilsonville it had exhibited higher coal conversion and distillate yields⁽⁸⁾.
- ◆ The activity of recovered first and second stage catalysts can be correlated with carbon content; at approximately 13% carbon 80% of the activity remains, at 19% only 72% remains.

- ◆ In thermal coal pretreatment tests at 400, 500 and 600°F, some oxygen removal is indicated and the pretreatment does not degrade the ultimate coal convertibility.
- ◆ Coal and residual oil conversion improved with the addition of CO₂; however, water and methane conversion increased indicating a water-gas shift and hydrocarbon synthesis reactions.
- ◆ Tests with different gas oil fractions (600-975°F) indicate that the 900-975°F range oils produce the highest gas yields and the 600-700°F the lowest.
- ◆ Microautoclave testing of "Molyvan" molybdenum additive as a catalyst were conducted to examine coal and residual oil conversion and catalyst behavior. In general, coal conversion appears to be higher with the addition of molyvan whereas residual oil conversion is undetected. Although there is some evidence of molybdenum lay down on the supported catalyst, the supported catalyst activity is unaffected.
- ◆ The dispersion of iron catalyst precursor (FeOOH) on coal matrix, according to an incipient wetness procedure developed by PETC, increases coal conversion by 9 W%, but has no significant (< 1 W%) impact on resid conversion. However, such improvement also becomes less important when the iron treated coal is processed in the presence of highly active NiMo supported catalyst.

Technical Assessment

The test results from Microautoclave and Bench-Scale studies were evaluated along with data from previous studies (Ref. 1, 5, & 7) and kinetic models were developed defining the interrelationship of the various reaction operating parameters and product species from sub-bituminous and bituminous coals. Correlations and modelling studies are summarized below and detailed in Sections II through VI of this report.

Correlations of Illinois Coal Yields

Correlations for residual oil and coal yields were based on first order kinetics, with respect to weight fraction concentration in the slurry phase in the first and second stage reactors.

- ◆ Coal was considered as containing three species, a high reactivity component, a low reactivity component, a small amount of an inert component, following a common activator energy for temperature dependance.
- ◆ Residual oil yields were correlated as resulting from a portion of the primary reaction of the coal less secondary reaction of the residual oil following first order kinetics. Several mechanisms for residual oil conversion are postulated.

- **C₁-C₃ Gas Yields**

Gas yields are correlated as partly derived from the primary reaction of coal and the balance as secondary formation from the reactor slurry phase. Catalyst deactivation and slurry phase composition are considered to have minimal impact on gas yields.

- **C₄-390°F Naphtha Yields**

Reaction models used are similar to those for C₁-C₃ gas yields. Some deactivation of the catalyst for naphtha formation was evident, and naphtha yields were lower when there was no catalyst in the second stage.

- **390-975°F Gas Oil Yields**

Yields are estimated based on the difference of coal conversion and other correlated yields including by-product yields. Preliminary estimates of the reactivity of the gas oil fractions reasonably predicted the feasibility of the "extinction" of the heavy gas oil components by selective recycle.

- **By-Product Yields and Hydrogen Consumption**

By product yields and hydrogen consumption and content are correlated considering catalyst deactivation and averaged product formation.

CORRELATION OF CLOVIS POINT MINE AND BLACK THUNDER WYOMING COAL YIELDS

Correlations are presented for these Wyoming Coals based on first order kinetics, with respect to weight fraction concentration in the slurry phase in the respective first and second stage reactors. Differences in Coal conversion basis due to more detailed analysis of Black Thunder Mine coal are noted.

◆ Process Modelling - Illinois No. 6 and Wyoming Coals

The conversion of Illinois No. 6 coal was modelled using three coal components of high, low and no reactivity over first and second stage temperature ranges of 725-775°F and 800-825°F. Petrographic and reflectance analysis by Penn State to a large degree support this premise i.e. high = vitrinite, low = liptinite and semi-vitrinite, none = inertinite.

Clovis Point Wyoming coal was modelled using two species for coal conversion, a reasonable data fit was obtained, with a three coal species model was developed for the Black Thunder Coal, Black Thunder coal showed the reaction rate constants that were 66% that of those of Clovis Point coal.

◆ Modelling of the Formation and Conversion of Residual Oils

Early modelling efforts of residual oil yields from two stage CTSL™ liquefaction of Illinois No. 6 coal were made on the basis of a single resid waste oil species of uniform composition and reaction behavior; Microautoclave tests indicated a system involving two residual oil species of different reactivity. Parameters developed using 60.5% primary resid formation considering catalyst deactivation with the second stage at 800-825°F were:

Rate Constant, lb/hr/ft ³ @ 750°F	= 11.6
Activation Energy, Kcal/mole	= 32.0
Deactivation Factor (D), lbs catalyst/lb coal	= 0.0019

Results of the kinetic correlations for Clovis Point coal are presented using initial two stage bench processing results and as a result there is considerable scatter evident in the correlations. The summary of this modelling effort shows no deactivation in the first stage for this residual oil function and definite second stage deactivation.

Bench-Scale and Microautoclave tests on Black Thunder coal indicate that the correlating parameters differ considerably from those for Clovis Point coal. i.e. (the primary formation of residuum was taken as 80-100% of converted coal versus 43% for Black Thunder). The Black Thunder results for residual oil yields

in microautoclave tests could not be fit with a single species thus two were assumed, one from the more reactive coal species and the balance from the less reactive (liptinite and semi-vitrinite).

◆ **Evaluation of Recovered CTSL™ Catalysts**

The relative effectiveness of the recovered catalyst that was tested corresponded to their carbon contents with the least effective catalyst containing 18.8% carbon, and the most effective 10.0% carbon, and the catalysts of intermediate effectiveness having intermediate carbon contents. Within this range, catalytic activity is inversely proportional to carbon content.

◆ **Modelling (C₄-390°F) Naphtha Yields**

This correlation development predicated a model of naphtha formation as a portion of the products from the primary reaction of the coal, plus additional formation from the first-order reaction of the slurry phase liquids in each stage. The correlation actually was in terms of a total slurry phase secondary naphtha formation rates. With catalyst in both stages, the secondary naphtha formation rate declines with catalyst age, approaching a lower limit corresponding to the rate with no catalyst in the reactors.

◆ **Modelling C₁-C₃ Gas Yields**

The gas yields from Clovis Point and Black Thunder Wyoming coals followed the same correlation i.e. converted coal and second stage temperature; there was no discernable effect of catalyst age in the typical runs studied.

ECONOMIC STUDIES

Economic screening studies to gauge process and equipment improvements were conducted in the processing of bituminous and sub-bituminous coals using the Illinois and Wyoming coal conceptual Plant Design and 1988 Economics as a basis. Results are summarized below and discussed in further detail in Section VII of this report.

◆ **Sub-Bituminous Coal**

The economics of the CTSL™ processing of low rank coals was revised to incorporate new technologies (pressure vessels), up-to-date costs, new operating requirement information and recent financing concepts. Two plant sizes were investigated, a 2000 and 10,000 ton/day plant; the 2000 ton/day plant with partial DOE funding and the 10,000 ton/day facility financed fully by private equity.

◆ **Bituminous Coal**

Investment costs and operating requirements were updated to a 1991 level, using information derived from the Bechtel Study entitled "Direct Coal Liquefaction Baseline Design and System Analysis", under Contract No. DEAC2290PC89857. Bechtel's report designed off-site facilities in much greater detail than available to HRI in the earlier study.

The overall conclusions from these studies are:

- ◆ Larger diameter reactor available with current technology permit lower capital cost by reduction of the number of trains required.
- ◆ Steam reforming of natural gas is more cost effective than partial oxidation.
- ◆ An increase in sub-bituminous coal space velocity of 50% decreases product cost by ~\$2/bbl.
- ◆ Economics are quite sensitive to product price. A 10% increase in product price increases the rate of return 10% over the original.

RECOMMENDATIONS

Laboratory Scale Studies

The microautoclave apparatus has been shown to be a very valuable tool for coal screening, catalyst ranking, studying catalytic and thermal effects, effect of additives, solvent quality determinations and for kinetic interpretations. Further upgrading of this efficient and economic interpretive apparatus is recommended i.e.

- ◆ Lateral shaking rather than vertical. ⁽¹⁾
- ◆ More accurate gas collection and monitoring.
- ◆ Refrigerated condensation and collection of light ends.

(1) Cold modelling tests in previous contracts has shown lateral or horizontal mixing in the 20cc microautoclaves as much more effective than the vertical shaking at the frequencies currently used.

Laboratory testing on this scale should be encouraged, particularly for screening activities and kinetic studies.

Modelling Studies

- ◆ Kinetic interpretations presented in this report should be studied and updated as new data is generated from CTSL™ studies and becomes available from studies by others. For example, experiments are underway to determine the reactivity of various coals and resids and their components.
- ◆ Using kinetic models from this study, a CTSL™ process simulation model should be set up, to simulate the material and energy balances required for engineering design and economic studies.

Economic Studies

- ◆ Studies should be carried out that are consistent with DOE's Baseline Design.
- ◆ All basis and assumptions should be reviewed and be acceptable to DOE prior to performing evaluations.
- ◆ Contingencies should be assigned based on the level of design effort and contingencies.
- ◆ Screening studies should be based on hard data whenever practicable.

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SECTION I

LABORATORY SUPPORT - MICROAUTOCLAVE STUDIES (TASK 2)

The microautoclave tests described in this section included coal evaluations, start-up oil evaluations, catalyst tests, thermal pretreatment tests, carbon dioxide addition tests, and sulfur addition tests. Other microautoclave tests are described in the specific bench-run section to which they correspond. These tests included regenerated and rejuvenated catalyst evaluations and solvent quality tests for delayed coking liquid products. The microautoclave tests conducted in conjunction with the modelling effort are described in the "CTSL Modelling" section.

EQUIPMENT AND GENERAL PROCEDURES

All tests were conducted in the 20-cc shaken microautoclave with two side-by-side reactors, with designs similar to those used by others. After the reactors are charged with dried, ground coal, solvent, and catalyst that is suspended in a wire basket, they are threaded onto the shaker. Up to 2000 psig of hydrogen, nitrogen, or other gases are added through the $\frac{1}{8}$ -inch o.d. tubing that is welded into the reactor cap. The reactor is connected to the gas reservoir during the test so that the operating pressure is maintained at this level throughout the test. The assembly is lowered into a preheated, temperature-controlled sand bath controlled at the specified temperature, and shaken with approximately-1-inch vertical strokes at 460 strokes per minute. At the end of a test the reactors are quenched in a water bath. The entire system can be depressured into a gas sample bag when the gas products are to be analyzed.

All of the reactor contents are washed from the reactor using tetrahydrofuran (THF). The solids products are then recovered by filtration and appropriately analyzed. The liquid product is recovered by vacuum roto-evaporation removal of the THF from the filtered THF washings. The coal conversion is calculated by ash balance for total solids recovery. Residuum formation is based on the TGA simulated distillation and the quantity of liquid recovered after roto-evaporation of the THF filtrate.

The specific quantities of feed materials and catalyst and the specific conditions are listed for each of the studies in the descriptions below.

COAL EVALUATIONS

30 coal or treated-coal samples were evaluated in the microautoclave for their thermal and catalytic reactivity for liquefaction. The conditions for these tests were:

- 2 gms coal
- 8 gms solvent (HRI No. 5198 Wilsonville heavy dist.)
- 2 gms catalyst (HRI 5359P presulfided Shell S-317)
- 2000 psig hydrogen

Most of the evaluations were conducted at 800°F for 30 minutes, but additional severities were tested for some of the Black Thunder coal samples.

COAL RANKING

A series of thermal and catalytic microautoclave tests were carried out on 18 different coal samples to determine their relative reactivity and to identify coals that might perform well in larger scale liquefaction. *Table 1* ranks the coals according to coal and 975°F+ conversion. The coals tested were:

- Wyoming - Adaville Seam, Clovis Point, Black Thunder, Coal Creek, Rochelle Mine, and Belle Ayr Mine;
- Illinois No. 6 - Burning Star, BCR-Cleaned Burning Star, and Low Ash from Consolidation Coal Company;
- West Virginia - Elkhorn Mine No. 3 (Cleaned);
- Virginia - Dorchester Untreated and Microwaved;
- Montana - East and West Decker Mines;
- Ohio - Cleaned Ohio 5/6 seams;
- New Mexico - McKinley Mine

Analyses for most of these coals are listed in *Table 2*.

The Wyoming-Dakota sub-bituminous coals generally had catalytic coal conversions in the range of 86 to 92%. The Belle Ayr Mine sample was in this range with 89.7 W% maf coal conversion, but the "Bag House Dust" obtained in conjunction with its drying operation, containing more ash (11.2% compared to 7.5%), performed very poorly with only 74.4 W% maf coal conversion.

A sample of Dorchester, Va. coal and a microwaved sample of that coal prepared by AVCO Research Laboratory were evaluated. Their tests had indicated that

microwave treatment increased the solubilization in low temperature solvents. The untreated Dorchester coal, the elemental analysis of which corresponds to fairly high rank coal, gave 86.2% and 52.5% coal conversions in the catalytic and non-catalytic microautoclave tests, respectively. These results correspond most closely to those obtained with a West Virginia (Elkhorn) coal, and are the poorest of any high rank coal that has been tested. However, the AVCO microwave treated coal was extremely unreactive, with 29.7% and 22.6% conversion in our catalytic and non-catalytic microautoclave tests, respectively, by far the poorest performance obtained with any material tested. Proximate and ultimate analyses of the untreated and treated coal indicated appreciable degradation of the coal by the microwave treatment, indicating over 50% loss of the organic content, 50% lower hydrogen content, and 50% as much volatile matter. AVCO now considers that the microwave treatment used for this sample was too severe.

The coal conversions for McKinley Mine, New Mexico (HRI No. 5673) coal were fairly high, about in the range of Wyoming-Dakota sub-bituminous coals, but possibly several percent below those obtained with Burning Star Mine Illinois No. 6 bituminous coal. Residual oil yields with this coal showed the same pattern of yields - close to those with the sub-bituminous coals. Based on these results, the coal liquefaction performance of the McKinley Mine coal would likely be intermediate between that obtained with these two types of coal. A second shipment of the New Mexico coal (HRI No. 5709), which had been used in Co-Processing tests, was also evaluated as a candidate for CTSL tests. The coal conversion was 88.4% in the catalytic microautoclave test, 0.1% lower than obtained with the earlier shipment. The coal conversion was 75.3% in the non-catalytic microautoclave test, 6.6% lower than obtained with earlier shipment.

As well as ranking prospective liquefaction coals *Table 1* also compares Black Thunder coals dried to three different levels. The as-received Black Thunder coal ranked near the top, whereas the deeply dried coal (2.5 % H₂O) and the Bench Run composite coal feed (6.5 % H₂O) did not convert as well.

CLEANED ILLINOIS NO. 6 EVALUATIONS

Table 3 summarizes the results of microautoclave evaluations of Illinois No. 6 coals cleaned by several methods and the corresponding uncleaned coals. The cleaned oil-agglomerated Illinois coal (HRI No. 5716), containing 4.5 W% ash, supplied by Bechtel, and used in CTSL Bench Unit Run CC-6, gave a coal conversion of 93.7% in the catalytic microautoclave test, 1.5% lower than had been obtained in a heavy-media cleaned coal (HRI No. 5387) that been used in CTSL Bench Unit operations in 1988. The coal conversion in the non-catalytic test, 76.3%, was 5.0% lower than given by the heavy-media cleaned coal. The Run-of-Mine Illinois coal (HRI No. 5715) that Bechtel had used in their cleaning operation gave a catalytic test coal conversion 0.2% below that given by the oil-agglomerated coal, and a non-catalytic test conversion 11.9% higher than obtained with the oil-agglomerated coal.

The other cleaned coals included in *Table 3* were prepared by OTISCA Industries using their proprietary process. The samples included Micronized Cleaned Illinois No. 6 coal (HRI No. 5738) that was used as feed for CTSL Bench Unit 227-66 (CC-8), micronized Run-of-Mine coal (HRI 5739) that was also used in that run, the refuse from the cleaning operation (HRI No. 5761), a lower ash (1.3%) sample from preliminary tests (HRI No. 5732), and the raw coal (HRI No. 5762, not micronized but ground to -70 mesh at the HRI R & D Center).

Cleaned OTISCA coal (3.31 W% ash) and the micronized Run-of-Mine coal (10.57 W% ash) had very nearly the same coal conversions in the microautoclave catalytic test, around 93.4% of maf coal. However, in the thermal test, with no catalyst, the conversion for the Run-of-Mine coal was only 3% lower than in the catalytic test, while for the cleaned coal there was a considerably greater difference in conversions, around 8%. As discussed above, the Bechtel oil-agglomeration samples also exhibited this pattern, indicating that some catalytically effective components are contained in the mineral matter that is removed in the cleaning operations.

The refuse from OTISCA's cleaning operation (64.54 W% ash) had a comparatively low coal conversion, 81%, in catalytic microautoclave evaluations, and it had a relatively small 4.8% difference between the catalytic and thermal test results. These results indicate that the cleaning operation does remove a high proportion of the less reactive coal components, although this is not necessarily a very appreciable factor. The ash contents of the various streams involved in the cleaning indicate that the cleaned fraction amounts to about 88% of the coal feed, and contains about 95% of the organic content contained in the coal feed. The microautoclave results with the original coal and with the cleaning refuse indicate that the low reactivity component (essentially unreactive) removed corresponds to about 14-17% of the maf coal in the refuse, or about 0.65-0.75% of the original maf coal. Consequently, the cleaned portion should contain less inert coal in this proportion, so that coal conversions in comparable liquefaction operations would be about 0.7% higher with the cleaned coal than with the Run-of-Mine coal.

BLACK THUNDER MINE COAL EVALUATIONS

A number of microautoclave tests were performed to assure the quality of the Black Thunder Mine Coal used in the bench and PDU units during this program. *Table 4* shows the results.

The second shipment (HRI No. 5713), first used in CTSL Bench Unit Run CC-7, had a coal conversion of 89.8% in the catalytic microautoclave test, 1.9% higher than for the earlier shipment (HRI No. 5630). The 80.3% coal conversion in the non-catalytic test of the HRI 5713 shipment was 3.7% higher than for the earlier shipment. In addition, this HRI 5713 shipment was evaluated before it was again used, 10 months later, before Run CC-11. Catalytic coal conversion was now 3.2-4.7% lower than the earlier result, while non-catalytic coal conversion was 8%

lower than previously. However, these results were only marginally lower than the results with first shipment, HRI 5630, and a third shipment, HRI 5828. It was concluded that the stored sample of HRI 5713 Black Thunder coal was a satisfactory bench-scale feed.

As indicated in *Table 4*, the coal ground and dried by Empire Coke Co. for use in PDU Run 260-3, the HRI 5887 shipment, performed as well in the catalytic microautoclave tests as any of the coals used in the bench unit. The 91.4% coal conversion was the highest, and the 70.8% 975°F+ conversion was only 1.1% less than had been achieved previously.

Additional microautoclave tests were undertaken in conjunction with Bench Run 227-59(CC-3), where operating difficulties had been encountered during Period 2, causing as shutdown, and again during the restart. The coal in use at those times, Drums No. 23 and No. 24, were tested to determine if they were of unusual reactivity. The start-up oil for Run CC-3, HRI 5648, and relatively low temperatures were included in the tests to simulate the conditions in the first stage during the start-up period. *Table 5* shows the microautoclave conditions and results for this set of tests.

In *Table 5*, the results are also compared to those obtained on the coal feed to Run CC-1 and with the results using HRI 5198 solvent, which has been the reference oil for the current program of coal evaluations.

In summary, the Drum 23 feed of HRI 5630 Black Thunder coal gave a conversion in the microautoclave that was essentially the same as that obtained with the CC-1 feed. The Drum 24 feed of the coal was fairly reactive, but gave lower conversions in all of the four parallel tests by 1.7 to 4.5 W%.

The HRI 5648 Drum 6 solvent gave conversions about 3.5 W% higher than were obtained with the HRI 5198 solvent. This result corresponds to that obtained in the earlier solvent evaluations, which are discussed in the next section.

There was a considerable impact of temperature upon the conversions in these catalytic tests. The results, averaged for the two drums, were:

<u>Test Temp., °F</u>	<u>Coal Conversion W% maf Coal</u>
700	46.9
750	71.2
800	90.1

START-UP OIL EVALUATIONS

The solvent quality of all prospective start-up and makeup oils in this CTSL program were evaluated in the Microautoclave using Illinois No. 6 coal (HRI 5174) and Black Thunder Mine (HRI 5613) coal. The solvent quality evaluation is a thermal 30 minute test at 750°F under 2000 psig of nitrogen, using 2 grams of solvent per gram test coal.

Table 6 ranks these oils in the order of their solvent quality as determined by the microautoclave tests, and *Table 7* summarizes the available analyses. As indicated in *Table 7*, most of these oils came from the Wilsonville coal liquefaction facility. The start-up oils used in bench unit operations were HRI No. 5443, HRI No. 5757, HRI No. 5648, L-742, and HRI 5868. The HRI 5910 (from V-123) and HRI 5911 (from V-124A) were samples of distillate material available from Wilsonville, tested before the bulk shipment of HRI No. 5969 (from V-124) was obtained for the PDU start-up oil.

The tabulation of distillations and elemental analyses in *Table 7* is arranged in order of increasing conversions in the Illinois Coal solvent evaluation test. There is no apparent straight-forward relation of the solvent evaluation performance of these oils with the analytical data available. However, the very highest solvent performance was with the highest boiling range solvent, HRI 5648, and the poorest performance was with the lowest boiling range solvents, HRI 5969 and 227-25 S (a wash oil recovered after a CTSL run on Clovis Point Mine Coal). However, the other solvents having intermediate boiling points and intermediate solvent quality values did not have a straight-forward interrelation of these two parameters. While the more effective solvents tended to have lower hydrogen contents, this is more likely due to the different boiling ranges. The only solvent with a relatively low characterization factor, L-742, had a relatively high solvent quality in the Illinois Coal test, and the highest solvent quality according to the Black Thunder Coal evaluation.

Discussions of what factors influence the quality of solvent can be found in Conoco, Inc. (Consol) reports from 1980 to 1984 under contracts DE-AC05-79ET14503, DE-AC22-80PC30027 and latter contract DE-AC22-84PC70018.

CATALYST TESTS

Several alternative supported catalysts, catalyst presulfiding methods, iron catalyst additives, and bench-unit recovered catalysts were tested in the microautoclave. The conditions for the tests were 825°F, 2000 psig hydrogen, and 30 minutes with a coal-derived oil feed containing 28.4 W% residuum. The tests used a 1.00 catalyst/oil weight ratio, except where noted.

Catalyst Presulfiding Methods

The effectiveness of a possible alternative method of presulfiding catalysts before use in CTSL bench unit was evaluated using the microautoclave. The alternative method was the use of TNPS (di-tertiary nonyl polysulfide) as the sulfiding agent rather than DMDS (dimethyl disulfide). The TNPS would be preferred because of lower toxicity, handling and safety considerations. The presulfided Shell S-317 catalysts for these tests were prepared in a 200 cc fixed bed reactor. The procedure used 3.5% TNPS or 2.0% DMDS in L-721 Wilsonville distillate at a rate of 1.65 V/Hr/V, and involved a 3-hour hold at 500°F, followed by 8 hours bringing the temperature up to 700°F, and then a 2-hour hold at 700°F. Other catalyst samples were presulfided in the microautoclave with DMDS or TNPS in tetralin.

Table 8 includes the presulfiding comparisons for Shell S-317, and Figure 2 shows the differences graphically. The TNPS presulfided Shell S-317 catalyst was of apparently higher activity (41% residual oil conversion) than the DMDS presulfided catalyst (28% residual oil conversion). These conversions were higher than that obtained with the unpresulfided S-317 catalyst (22%). Also, the TNPS presulfiding resulted in higher activity than DMDS presulfiding, whether in gas oil carrier or tetralin carrier, for Shell S-317 catalyst.

The following table summarizes the analyses of the Shell S-317 catalysts that had been presulfided by the various techniques:

Catalyst Unit Carrier Oil	TNPS Presulf.		DMDS Presulf.	
	Fixed Bed	MicroA.	Fixed Bed	MicroA.
	Gas Oil	Tetralin	Gas Oil	Tetralin
Carbon, W%	6.44	2.03	7.20	2.50
Hydrogen, W%	0.81	0.78	1.07	0.83
Nitrogen, W%	0.24	0.02	0.27	0.01
Sulfur, W%	6.54	8.57	5.76	7.71
Ash, W%	81.05	82.12	82.25	84.11

The sulfur retention on the TNPS presulfided catalyst was higher than on the DMDS presulfided catalyst, corresponding to 10% greater sulfiding of the promoter metals. On the basis of these tests it was concluded the TNPS was a satisfactory alternative to DMDS and it was used for Bench Unit presulfiding starting with Run 227-62(CC-5).

Other presulfiding experiments were carried out in the microautoclave using DMDS or TNPS in tetralin mixtures in connection with the evaluation of alternative catalysts. The presulfiding was for two hours at 550°F, with 3.5 grams/gram catalyst of the mixture containing 17 W% sulfur. Such Tetralin/DMDS presulfiding was effective with sulfur retentions corresponding to 80-90% sulfide formation of the promoter metals. The carbon contamination of the DMDS/Tetralin presulfided catalysts was considerably less than on the gas oil/DMDS presulfided catalysts obtained using the fixed bed, with 1-2% carbon compared to 6-7%. The TNPS/tetralin presulfided catalyst had a higher sulfur retention than the DMDS/tetralin presulfided catalyst.

Tests of Alternative Supported Catalysts

The microautoclave test results for the three alternative supported catalysts are included in *Table 8*. The catalysts that were evaluated are listed below:

HRI 5359	Shell S-317 Nickel-Moly
HRI 5675	UOP RCM-1-121 Nickel-Moly, Macropores
HRI 5676	UOP RCM-1-122 Nickel-Moly, Std RCM-4 (Micropores)
HRI 5677	UOP RCM-1-123 Iron-Moly, Macropores

Table 8 the analytical data for the four catalysts. Another lot of the UOP RCM-4 catalyst was used in CTSL Bench Unit Run 227-37(I-17), in operations with Illinois No. 6 coal. The HRI 5677 lot of the Iron-moly catalyst was used in Run 227-58(CC-3) in operations with Black Thunder Mine coal. The HRI 5359 catalyst, or other lots of the Shell S-317 catalyst, was the catalyst for a number bench unit runs with Illinois and Black Thunder Mine coal. The HRI 5675 and HRI 5677 catalysts were of relatively low density with pore volumes per unit catalyst weight that were much higher than those of the other two catalysts.

The conditions for the tests were 825°F, 2000 psig hydrogen, and 30 minutes with a coal-derived oil feed containing 28.36 W% residuum. The tests used a 1.00 catalyst/oil weight ratio, except where noted.

Figure 1 summarizes the results of residual oil conversion tests for these four supported catalysts, which had not been presulfided, and also results for tests with presulfided HRI 5359 Shell S-317 catalyst.

The unpresulfided Shell S-317, the microporous nickel-moly, and the macroporous Iron-moly catalysts gave virtually equivalent performance. The macroporous, high pore volume, nickel-moly catalyst gave slightly poorer

performance, the degree of difference being greater than the difference in results for replicate tests with presulfided Shell S-317 catalyst.

The presulfided Shell S-317 catalyst (presulfided in a fixed bed by the technique used for CTSL bench unit catalysts) had considerably better performance than any of the unpresulfided catalysts.

The results for the presulfided catalysts given in *Table 8* indicate that the presulfided HRI 5677 Fe-Mo Macroporous catalyst, on an equal weight basis, was about as active as the Shell S-317 catalyst. The UOP microporous Ni-Mo catalyst had the highest activity of the four DMDS presulfided catalysts, while the UOP macroporous Ni-Mo catalyst was of the lowest activity.

A consideration in the use of these catalysts is that UOP macroporous catalysts are of considerably lower density than the Shell S-317, or the UOP microporous catalyst, with a bulk density of 0.38 gms/cc compared to 0.62 gms/cc. Consequently, a considerably lower weight of macroporous catalyst can be charged to the actual process reactors. Additional tests, also summarized in *Table 8*, with the UOP Fe-Mo macroporous catalyst were done using a lower proportion of catalyst corresponding the same volumetric catalyst-oil ratio as for the Shell S-317 catalyst.

These results using the lower proportion of Fe-Mo catalyst are ambiguous. With the presulfided catalyst with the lower proportion of catalyst (higher oil/catalyst ratio) did indicate the expected degree of lowered residual oil conversion, approximately proportional to the amount of catalyst. However, with unpresulfided Fe-Mo catalyst there was greater residual oil conversion with the lower proportion of catalyst than had been obtained with the higher proportion of catalyst.

These tests indicate that the iron-molybdenum promoted catalyst is at least virtually equivalent to the nickel-molybdenum promoted catalyst, but that the high pore volume support is probably inferior for possible process application because of the lower inventory of catalyst that can be charged to the reactors.

Tests of Iron Catalyst Additives

Four iron additives that were considered for use in CTSL Bench Unit Run 227-59/61(CC-4) were evaluated in the microautoclave for residual oil conversion activity. The additives tested were:

- HRI 5645 - Pyrrhotite (INCO)
- HRI 5664 - Iron Oxide (Southern Clean Fuels)
- HRI 5689 - Magnetic Pigment (Wright Industries)
- HRI 5693 - Pyrite (Pea Ridge Iron Ore Co.)

The additives were tested as received, and also with sufficient elemental sulfur to correspond to sulfiding of the iron in the additives. *Figure 3* summarizes the results of these tests. The as-received additives were all of some apparent catalytic effectiveness in converting CTSL residual oil, excepting the Southern Clean Fuels Iron Oxide where the residual oil content of the product was higher than that of the feed, but considerably less effective than the Shell S-317 catalyst. The addition of sulfur was minimally effective in improving residual oil conversion with the Magnetic Pigment, but resulted in poorer performance with the other three additives. The Iron Oxide additive gave exceptionally poor performance, with apparent formation of residual oil rather than any conversion. This unexpectedly poor result with the Iron Oxide additive was checked using a new resid-containing feed sample - in case the original feed material had deteriorated. However, the additional tests confirmed the regressive net formation of residual oil with this additive. Batch autoclave tests at Wilsonville, however, showed higher distillate yields (resid conversion) in the presence of this catalyst using DMDS/TNPS sulfiding agents.

Evaluation of Recovered CTSL Catalysts

In addition to the evaluation of the first and second stage catalysts from CTSL Run CC-12 (Rejuvenated Catalyst), which was discussed in the *Appendix B* of the Run CC-12 section of DE88818 Top-1⁽¹⁾, first and second stage catalysts from Runs CC-8 and CC-11 were similarly evaluated in the microautoclave. *Table 9* summarizes the results of these microautoclave tests with of the Run CC-8 and CC-11 catalysts. The microautoclave tests of the Run CC-12 catalysts had shown greater deactivation of the second stage catalyst, to 45% of activity of the rejuvenated catalyst charged to Run CC-12, than of the first stage catalyst, to 70% of charged catalyst activity.

CTSL Bench Unit Run CC-8 processed Illinois No. 6 Coal that had been cleaned by the Otisca Process to reduce the ash content to 3.5 W%. CTSL Bench Unit Run CC-11 processed Black Thunder Mine (Wyoming) coal. The catalyst for both runs was Shell S-317 catalyst, which was presulfided, using TNPS doped gas-oil at temperatures of 450-650°F, as part of the start-up operations of the run. During Run CC-11 H₂S was added, corresponding to 2 W% of the coal, so as to maintain the sulfided level of the catalyst. No H₂S was added during Run CC-8 because, with the higher sulfur content Illinois Coal, the H₂S formation during coal liquefaction was equivalent to this proportion.

The current microautoclave tests included a contemporary series of tests using Shell S-317 catalyst, HRI 5394P, which had been pre-sulfided somewhat similarly to the CTSL Bench Unit procedure, although in a small fixed bed. This series of tests was intended to supply a reference data base for "fresh" catalyst to use in comparison with the results for the recovered CTSL catalysts.

Referring to *Table 9*, all four of the recovered catalysts showed appreciable activity in converting the residual component in a recycle solvent obtained during

CTSL Bench Unit operations with Black Thunder Mine coal in Run CC-1. The residual oil conversion levels with the recovered catalysts were higher than obtained with half as much "fresh" catalyst, but lower, in three cases, than obtained with about the same amount of "fresh" catalyst. The first and second stage catalysts from Run CC-8 were of about the same catalyst effectiveness, 77-83% of that of "fresh" catalyst as these microautoclave tests have been correlated. In contrast, the first stage catalyst from Run CC-11 was considerably more effective than the second stage catalyst from that run. Actually, this first stage catalyst demonstrated an activity even higher than that of the "fresh" catalyst, while the second stage catalyst was only 71% as effective as the "fresh" catalyst.

The relative effectiveness of the four recovered catalyst that were tested corresponded to their carbon contents (noted in *Table 9*), with the least effective catalyst containing 18.8% carbon, and the most effective 10.0% carbon, and the catalysts of intermediate effectiveness having intermediate carbon contents. There were a pair of replicate tests with the "fresh" catalyst, Runs CM103 and CM105, which indicates the sensitivity of the microautoclave tests to the analytical results, where a difference of less than 1 W% in analyzed residual oil content corresponds to a difference of over 20% in indicated catalyst effectiveness. This is because the conversion pattern with increasing catalyst/oil ratio does not follow simple first-order kinetics. So that deeper residual conversions require disproportionate increases in catalyst effectiveness. The correlating equations indicated in *Table 9* correspond to a system with two residual oil components of differing reactivity, both following first-order kinetics.

Similarly, higher recovered first stage catalyst activity and lower recovered second stage catalyst activity had been demonstrated in an earlier series of microautoclave tests with recovered catalysts from Runs CC-1 and CC-2, which also processed Black Thunder Mine coal. The following tabulation summarizes the results of those tests, comparing the residual oil conversions for the various catalysts:

Run	Catalyst	Residuum Conversion, %
CM-01	DMDS Presulfided S-317	28
CM-02	" " "	28
CM-09	Second Stage Run CC-1	19
CM-37	First Stage Run CC-1	18
CM-40	First Stage Run CC-2	34

The poor performance of the Recovered First Stage Catalyst for Run CC-1 is possibly associated with the unusual pattern of first stage temperatures used in that run, with temperatures between 750 and 817°F, in contrast to the usual

practice of that temperature being between 750 and 775°F. The first stage temperature in Run CC-2 was 750°F throughout.

THERMAL PRETREATMENT OF COAL

The main purpose of thermal sub-bituminous coal pretreatment is to remove oxygen from the coal before the oxygen combines with hydrogen in the reactors. However, the pretreatment should not hinder the coal reactivity or the yield of quality products.

To determine pretreater conditions for such an operation in Bench Run CC-5, tests in the microautoclave were conducted attempting thermal pretreatment of the Black Thunder Mine coal for two hours at temperatures of 400°F, 500°F, and 600°F. Tests were done using the dry coal alone, and with 1.6 gm coal derived distillate solvent per gm coal.

Relatively small amount of carbon oxides were obtained, as shown in the following table summarizing carbon oxide yields as a percent of coal fed:

Test Temp., °F	Carbon Oxide Yield, % of Coal	
	No Solvent	With Solvent
400	0.16	0.99
500		0.90
600	0.51	1.64

A considerably greater impact of pretreatment temperature upon deoxygenation was indicated by elemental analyses and ash contents of the pretreatment products, as shown in the following table summarizing the ratio of oxygen content (by difference) to the ash content:

Test Temp., °F	Ratio of Oxygen to Ash	
	No Solvent	With Solvent
400	3.62	3.71
500	3.75	2.92
600	3.11	2.59

These analyses indicate up 30% removal of the oxygen in the higher temperature tests. However, TGA tests of the nominally dry coal do not indicate as great a change for these temperatures, as shown in the following table giving weight loss as a percent of charge:

Test Temp., °F	Weight Loss in TGA, W%		
	Minute	5 Hours	Difference
400	6.67	8.17	1.50
500	4.75	6.85	2.10
600	3.78	7.44	3.66

Figure 4 summarizes the results of further microautoclave tests which evaluated the reactivity of the product solids from the thermal pretreatment tests. These tests indicate no degradation of the coal by pretreatment at 500 and 600°F. In fact, there was some enhancement of the ultimate conversion beyond that obtained in similar tests with untreated coal.

IMPACT OF CO₂ UPON LIQUEFACTION

There were two microautoclaves using 10% CO₂ in hydrogen as the vapor phase environment rather than 100% hydrogen used in most tests. The tests used the HRI 5713 Shipment of Black Thunder coal, at 800°F and 2000 psig, for 30 minutes, with HRI 5198 Coal liquefaction distillate as solvent and 1 gram of Presulfided Shell S-317 Catalyst per gram of coal. The following results were obtained, compared to the recent test with 100% hydrogen atmosphere:

CO ₂ in Vapor, V%	0.0	0.0	10.8	10.8
Solvent/Coal, Gms/Gm	4.0	4.0	2.0	1.0
Coal Conversion, W%	85.1	86.6	90.9	89.9
Resid. Yield, W% of Conv. Coal	31.9	22.3	21.7	21.6
H ₂ O Recovery, W% of Conv. Coal			26	35
Gaseous Hydrocarbon, W% of Coal				5.4
CO, W% of Coal				0.85

Coal sample contained 6.4% water.

These results indicate no deleterious impact of the CO₂ upon conversion, or formation of residual oil, and a possible improvement in performance in these respects. The apparent water formation was considerably higher than can be ascribed to the derivation from coal alone. CO formation in the second test corresponded to only 1% of the coal reacted, which would discount the possibility of the water gas shift reaction of H₂ and CO₂, alone, accounting for the additional water formation. However, the light gas formation for this test, 5.4 W% of coal, was 2-3 times the amount expected on the basis of tests with no CO₂, indicating the possibility of a water gas shift-hydrocarbon synthesis reaction sequence.

EVALUATION OF CATALYST SULFIDE MAINTENANCE AGENTS

A series of microautoclave tests were conducted to evaluate candidate agents for maintaining the sulfide state of the catalyst in the PDU, specifically, TNPS (di-Tertiary Nonyl Polysulfide), DMDS (Dimethyl Disulfide), and elemental Sulfur.

A total of 16 tests were done at 825°F, 2000 psig hydrogen pressure, using Presulfided Shell S-317 catalyst, and a coal liquefaction distillate as carrier, with 1 weight of carrier per weight of catalyst. The sulfide maintenance agent was equivalent to 0.05 and 0.10 grams per gram of catalyst, at test times of 15 and 45 minutes. The following conclusion were drawn:

Sulfiding Effectiveness - Product catalysts from each test had a higher sulfur content than in the presulfided catalyst charged (which contained 6.54% sulfur, equivalent to 90% sulfiding to MoS_2 and NiS) by a factor of up to 1.2. The highest level of sulfur was obtained in the longer tests with the higher proportion of sulfiding agent with each agent. Although the very highest degree of sulfur addition was obtained in a DMDS test, all three agents had essentially the same performance in this respect.

Utilization of the Agents - Some unconverted sulfur remained with the solvent phase after the tests with the sulfiding agents. With TNPS this proportion was 13-16% of the sulfur in the agent, essentially the same level for all of the tests. With DMDS this proportion was 6-10% of the sulfur in the agent, unrelated to the test time, but perhaps at the lower percentage with the lower concentration of the agent. With elemental sulfur this proportion was 9-14% of the sulfur in the agent, with no relation to concentration of the agent, but perhaps lower for the long residence time tests.

Light Gas Yields - Light Gas yields with the TNPS and elemental sulfur agents were marginally higher than were obtained in background tests without any agent, e.g. in 45 minutes tests, methane yields were 0.5-0.7% of solvent when using the agents compared to 0.5% with no agent, and approximately 0.4-0.5% of solvent in all of the 15 minute tests. However, appreciably more methane was formed in the DMDS tests, with the increment of methane formation averaging 87% of the theoretical formation of methane from the decomposition of the DMDS, very close to apparent reaction, 92%, of the agent based on the retained sulfur contents.

Light Liquid formation - GC simulated distillation of the product liquid from a test with TNPS showed a very considerable enhancement of peaks in the nominal 225-250°F boiling range, particularly three peaks, corresponding to the expected range for C_9 isomers. The total of the enhanced peaks corresponded to 76% of the quantity to be expected if the TNPS were all converted to C_9 isomers, which is slightly below the degree of reaction of the TNPS, 85%, indicated by the sulfur retention in the solvent.

All three agents would be effective in maintaining sulfide levels, but would leave a small residue of unused material. DMDS would cause additional methane yield, about 0.5 times the amount of sulfur added. TNPS would produce additional naphtha boiling range product, about 1.7 times the amount of sulfur added.

TESTS WITH GAS OIL FRACTIONS

The filtered liquid from the second stage product (PFL) of CTSL Bench Unit Run 227-55(CC-1) Period 23A, using Black Thunder Mine coal, was fractionated by a D-1160 vacuum distillation into 600-700°F, 700-800°F, 800-900°F, and 900-975°F fractions. These fractions were then tested in the microautoclave non-catalytically and with the HRI 5359P presulfided Shell S-317 catalyst. The tests were at 2,000 psi H₂ pressure of 30 and 60 minutes duration at temperatures of 750 and 825°F. Gas samples were taken after these tests and the liquid products were analyzed by means of GC-simulated distillation to determine the relative reactivity of these fractions and the products that derive from their conversion.

The D-1160 distillation did not provide very closely fractionated product fractions, as is illustrated in *Figure 5* which compares the GC-simulated distillations of the feed and products from the microautoclave run which tested the 7-800°F D-1160 gas oil fraction. It will be noted that the feed material contained very significant proportions of oils boiling both below and above the nominal boiling range of the fraction. The following tabulation summarizes the boiling range distribution for each of the gas oil fractions used in these tests:

D-1160 Fract.	GC SimDist Analysis, W%					
	IBP-600	600-700	700-800	800-900	900-1000	1000°F*
600-700	36.9	44.7	16.5	1.8	0.1	
700-800	2.5	35.0	46.3	15.3	1.9	
800-900	0.2	4.6	35.1	45.1	15.0	
900-975	0.2	0.1	3.7	28.6	50.9	16.2

Table 10 summarizes the C₁-C₃ gas yields for the 30 minute tests at 825°F for both the catalytic and non-catalytic microautoclave tests. *Table 11* summarizes the apparent conversion to lower boiling products for each of the D-1160 gas oil fractions for 30 minute tests principally at 825°F, with one test at 750°F. *Table 12* summarizes the product distribution, that is, the selectivity to lower boiling components, for the tests with the various D-1160 gas oil components.

The conversion of various D-1160 gas oil fractions to lighter products ranged from 7.8 to 17.7% of the feed materials in the 30 minute tests at 825°F with 0.25 grams catalyst/gram oil (*Table 11*). The lowest proportion was for the lowest boiling range fraction, and the highest for the highest boiling range fraction. The

intermediate boiling range fractions had almost as great a degree of reaction as that of the highest boiling fraction. The average converted for the 700°F materials was about 15% of feed, corresponding to a first order rate constant of 0.3 grams/hour/gram, equivalent to a rate constant of about 20 lbs/ hour/ft³. However, not all of this conversion was to products boiling below 700°F (*see Table 12*), with 55-75% of the converted material having boiling points within 200°F of the IBP of the gas oil fraction. About 20% of the converted 800-900°F gas oil material boiled above 700°F, while 70% of the converted 900-975°F material boiled above 700°F.

The degree of gas oil conversion in the tests without catalyst was generally 0.6-0.7 times that in the tests with catalyst. The degree of conversion for the tests at 750°F were lower for the tests at 825°F, by factors of 0.6 in the test without catalyst and 0.3 in the catalytic test. Since the interpretation of the GC SimDist traces were very difficult, especially with the relatively small feed/product effect by the low degree of conversion obtained in the lower temperature tests, it is questionable whether there is an actual difference in temperature sensitivity for the non-catalytic and catalytic operations.

The principal results indicated by the gas analyses are summarized in *Figures 6, 7, 8, and 9*.

In *Figure 6* the gas yields at common conditions are compared for the four gas oil fractions, and for the unfractionated PFL, in tests with and without catalyst. There was appreciable formation of gas by all of the gas oil fractions. The lowest gas yield was with the 600-700°F fraction, and the highest yield with the 900-975°F fraction, by a factor of about 1.6. The other two gas oil fractions had intermediate gas yields. The yield of gas with the unfractionated PFL was in the same range as those obtained with the gas oil fractions. Consideration of the composition of the PFL indicates that the apparent contribution by the residual oil component was in the range of values obtained for the gas oil components, perhaps most closely matching the value indicated for the 900-975°F component. Gas yields without catalyst were consistently lower than with catalyst, by a ratio of 0.6 on the average. The gas yields with catalyst averaged 0.67 W% of oil for the these 30 minutes at 825°F, which corresponds to gas formation rate of 0.0134 grams/hr/gram of oil, approximately equivalent to 0.83 lbs/hr/ft³. This value is somewhat below the value obtained in the bench unit correlation of gas yields which indicated a reaction rate 1.24 lbs/hr/ft³ at 825°F for the formation of gas from secondary reaction of slurry phase components.

Figure 7 compares gas yields at 750 and 825°F for catalytic tests. There was a substantial impact of the change in temperature, by a factor of 3.1 for the 700-800°F MGO results presented. The gas yields presented for PFL tests a comparable impact of the change in temperature, although the data indicate some difficulties in determining methane at the low concentrations involved. The 3.1 factor in gas yields corresponds to an Arrhenius equation activation energy of 26 Kcal/mole.

Figure 8 compares gas yields at 750 and 825°F for non-catalytic tests. Here, too, there is a very considerable impact of temperature, perhaps even greater than indicated in the catalytic tests. However, the poor analytical definition, especially at the very low methane contents involved, makes the definition of the temperature sensitivity very uncertain.

Figure 9 summarizes data comparing the results at 30 and 60 minutes time, and with differing catalyst/oil ratios. While higher gas yields were obtained at 60 minutes time than at 30 minutes time, by a factor of about 1.5 for the most part, the yields were not exactly proportional to time. Increasing the oil charge from 2 grams to 8 grams, with a common value of 2 grams of catalyst, resulted in increased gas yield, but by a factor of only 1.4. While it is to be expected that gas yield would not be exactly proportional to the oil quantity, considering the differing proportions of catalytic and thermal (liquid phase) contributions involved, the thermal and catalytic gas formation rates noted above would project a somewhat greater impact of the amount of oil upon gas formation than was observed, with a projected ratio of about 2.5 for the two quantities of oil that were used.

MICROAUTOCLAVE TESTS USING MOLYVAN L MOLYBDENUM ADDITIVE

A program of 14 Microautoclave runs tested Molyvan L (R. T. Vanderbilt Co. lubricant additive containing 8.1 W% molybdenum) as a catalytic agent for coal liquefaction. This material has been used at Wilsonville as an additive and was reported to give improved results. We received a sample, HRI 6000, of the recovered catalyst from the Wilsonville operation, and our analyses indicated the possibility that some of the molybdenum in the Molyvan L had been retained by the extrudate catalyst (Shell S-324), although the scatter of the data left some uncertainty in this conclusion.

The Wilsonville recovered catalyst was also tested in the microautoclave for coal liquefaction residual oil conversion activity. These tests indicated high activity of the HRI 6000 sample, perhaps 80-85% of that of the fresh, presulfided catalyst, and considerably higher than the activities of recovered catalysts from some of our CTSL operations, which have been as low as 40% of fresh catalyst activity. However, the Wilsonville operation probably involved some replacement of the extrudate catalyst, and the high retained activity may have been due in part to this factor. These ambiguities suggested further experimental work in this area.

Analyses of Wilsonville Catalysts

The molybdenum contents of the charged and recovered catalysts for Wilsonville Run 262, in which a molybdenum additive (Molyvan L, R. T. Vanderbilt Co. lubricant additive containing 8.1 W% molybdenum) was used in addition to the

extrudate Shell (Criterion) 324 catalyst, were determined to determine the degree of molybdenum accumulation from the Molyvan L upon the extrudate catalyst.

The significance of the differences in the analyses is summarized in the following tabulation comparing the molybdenum contents on a volumetric basis (in effect assuming all contaminants in the recovered catalyst are in internal pores), to account for the diluting effect of the contaminants. The statistical analysis indicated a standard error for the molybdenum analysis of 0.44%, determined with 5 degrees of freedom, so that the 95% confidence range of a single analysis is +/- 1.1%.

Molybdenum, W% (Averged)	
Charged Cat. (4 Anal)	11.94
Recovered Cat. (3 Anal)	10.90
Bulk Density, Grams/cc	
Charge Catalyst	0.849
Recovered Catalyst	1.062
Particle Density, Grams/cc	
Charged Catalyst	1.334
Recovered Catalyst	1.567
Grams Molybdenum/cc Bulk	
Fresh, Average	0.1014
Recovered, Average	0.1158
Recovered/Fresh	1.14
t-Value	4.24
Confidence Level, %	99.2
Grams Molybdenum/cc Particle	
Fresh, Average	0.1594
Recovered, Average	0.1710
Recovered/Fresh	1.07
t-Value	2.24
Confidence Level, %	92.5

The molybdenum content on a bulk volume basis was 14% greater in the recovered catalyst than in the fresh catalyst. On a particle volume basis this difference was 7%. Conceptually, the more significant comparison is probably on the particle volume basis, since the bulk density would be affected by a change in packing factor, especially if the length of some of the extrudates were shortened during the liquefaction operations. If there was some "swelling" of the extrudate because of the accumulation of contaminants on the outside of the extrudate, the "true" molybdenum accumulations would be higher than estimated above.

Similar comparisons of the molybdenum contents of charged and recovered catalysts from CTSL Bench Unit operations had indicated molybdenum contents of recovered catalysts, on a catalyst volume basis, of 93 to 104% of that of fresh catalyst.

Tests with Wilsonville Catalyst

Table 13 summarizes the results of microautoclave evaluations of the charged and recovered catalysts for Wilsonville Run 262. These tests compared the performances of the catalysts in the conversion of the residual oil component of the filtered liquid product (PFL) from CTSL Run 227-55 Period 23. *Table 13* also includes similar comparisons of charged and recovered catalysts for CTSL Bench Unit which had used Shell S-317 Catalyst.

The recovered catalyst from Run 262 had a good activity for conversion of the residual oil, converting about one-half of this component in the 30 minute test. This conversion was higher than that obtained with the Shell S-324 catalyst, when that catalyst had not been presulfided, which resulted in about 20% conversion of the residual oil component. However, after the S-324 catalyst was presulfided with TNPS, it was far more active with almost 60% conversion of the residual oil component, a performance which was slightly superior to that of Shell S-317 catalyst after similar presulfiding. In simple first order kinetic terms the recovered Run 262 catalyst was about 85% as active as the presulfided S-324 Catalyst. As shown in *Table 13*, recovered catalysts from CTSL operations have been as low as 38% as active as the presulfided fresh catalyst charged to the CTSL operations, although some CTSL recovered first stage catalysts have retained high activity.

The elemental analyses of the oil products from these microautoclave tests indicated that the Presulfided S-324 catalyst gave slightly poorer hydrogenation than the Presulfided S-317 catalyst, while its denitrogenation activity was markedly higher. The recovered Run 262 catalyst was of considerably lower activity for hydrogenation and denitrogenation than the presulfided S-324 catalyst, by approximately a factor of two.

Results of Microautoclave Program Using Molyvan L

The addition of 1.25% Molyvan L on coal (equivalent to 1,000 ppm molybdenum) showed a slight increase upon coal conversion, most marked at conditions having low levels of conversion, that is, at low temperature or without extrudate catalyst. Molyvan L at this concentration, without extrudate catalyst, had an impact upon residual oil yield of the order of 10% of that extrudate catalyst. With extrudate catalyst, there was no definite impact of this amount of Molyvan L upon residual oil yield. Tests with 2 grams Molyvan L/gram coal were confounded by the apparent retention of the some of the Molyvan L upon filter cake product. However, there was virtually no impact of this higher level of Molyvan L addition upon residual oil yield. The product solids (coal ash and unconverted coal)

produced in Microautoclave tests in which there had been Molyvan L addition did not have any appreciable catalytic activity as consequence of any retained molybdenum. Extrudate catalyst recovered after Microautoclave tests in which there had been Molyvan L addition did not demonstrate any improvement in residual oil conversion activity. Actually, such recovered catalysts from the tests with the higher proportion of Molyvan L to coal showed relatively poor residual oil conversion activity. Molybdenum analyses of recovered extrudate catalysts from these tests indicate virtually no retention of the molybdenum from the Molyvan L.

Operating Conditions

The general conditions of these runs were the following:

- Solvent - HRI 5198 Wilsonville coal liquefaction
distillate, 4 grams/gram coal
- Coal - HRI 5887 Black Thunder Mine Coal
- Catalyst - 1 gram/gram coal
TNPS presulfided Shell S-317 extrudates, HRI 5359P2. Also,
L-758, recovered catalyst from Bench Unit CTSL operations with
Black Thunder Mine coal.
Also, thermal tests with no catalyst.
- Molyvan L - 1.25% Molyvan L on coal having a Molybdenum content
HRI 6046 equivalent to 1000 ppm of the coal (the proportion used at
Wilsonville). This amount of molybdenum is about 1% of the
molybdenum content of the extrudate catalyst used in these tests.
Also 2 grams Molyvan L/gram coal to study the impact of higher
proportions of Molyvan L.
- Pressure - 2,000 psig hydrogen
- Temp. - 750 and 800°F
- Time - 30 minutes

The results of the current program are summarized in *Table 14*.

Experiments with 1.25 W% Molyvan L on Coal

The following table summarizes the results of the tests with Molyvan L addition, corresponding to about 1.25 W% of the coal (1,000 ppm Mo on coal), compared to those with for tests where no Molyvan L was used. For comparison with results for operations where there had been no Molyvan L addition, this tabulation includes the results of earlier tests in 1991, with the HRI 5887 shipment at the same test conditions.

<u>Experiment</u>	<u>Molyvan L % of Coal</u>	<u>Extrudate gm/Gm Coal</u>	<u>Temp. °F</u>	<u>Conv. W% MAF</u>	<u>Resid Yield W% Conv. Coal</u>
CQ143	0.00	0.00	800	75.6	46.2
CE59	0.00	0.00	800	78.4	44.9
CE50	1.34 ⁺	0.00	800	81.0	42.0
CQ144	0.00	1.00	800	91.4	22.6
CE47	0.00	1.00	800	91.7	25.7
CE46	1.26	1.00	800	92.1	24.2
CQ145	0.00	0.00	750	57.8	54.5
CQ146	0.00	1.00	750	74.0	25.2
CE49	0.00	1.00	750	71.8	30.2
CE48	1.22	1.00	750	76.8	32.2

* Coal evaluation series in 1991

+ 1.25 W% = 1,000 ppm Mo on coal, 1.34 W% = 1,100 ppm

In all three sets of comparisons, the highest conversion was obtained in the experiments where Molyvan L was added. This difference was relatively narrow for the highest severity operation at the highest conversion levels with extrudate catalyst. At lower temperature, or where there was no extrudate catalyst, the impact of Molyvan L addition was greater, by an average of 4% at a conversion level of 73-77% (this difference for the data cited has statistical confidence level of 94.8%, a standard error of 1.5% in the conversion values). This 4% increase in conversion with the addition of 1.34% Molyvan L (1100 ppm Mo) was considerably less than the 15% increase in coal conversion obtained with the use of extrudate catalyst.

There was a mixed impact of Molyvan L addition upon apparent residual oil yields. At 800°F without extrudate catalyst the addition of 1.34% Molyvan L lowered apparent residual oil yield by 3-4% of converted coal, again a much smaller impact than that of the extrudate catalyst where the decrease was about 21% of converted coal. At 800°F, in tests with extrudate catalyst, the addition of Molyvan L resulted in a residual oil yield intermediate between the results obtained in the two tests with extrudate catalyst alone. At 750°F, in tests with extrudate catalyst, the addition of Molyvan L resulted in a residual oil yield higher than those obtained with extrudate catalyst alone. The apparent impact of Molyvan L, at this level, upon residual oil yield is of the order of the apparent experimental error, certainly a minor fraction of that of the extrudate catalyst.

Tests with 200% Molyvan L on Coal

Experiments were carried out using 2 grams Molyvan L per gram coal and the presulfided S-317 Catalyst (HRI 5359P), Run CE54, and also recovered catalyst from Bench Unit CTSL operations with Black Thunder Mine Coal (L-758), Run

CE55. The intent of these experiments was study the effect of equivalent amounts of Molybdenum in the Molyvan L used, 0.32 Grams, and in the extrudate charges, 0.19 grams. These tests, and those of the reference runs without the Molyvan L additive, were done at 800°F. The following table summarizes the results of this set of tests:

<u>Experiment</u>	<u>Molyvan L % of Coal</u>	<u>Extrudate gm/Gm Coal</u>	<u>Ash. Recov</u>	<u>Conv. W% MAF</u>	<u>Resid Yield W% Conv. Coal</u>
CE47	0	1.00	124.7	91.7	21.8
CE 54	200	1.00	279.8	58.2	21.8
CE59	0	0.00	102.7	78.4	44.9
CE58	0	1.00	99.5	76.3	27.2
CE55	200	1.00	305.5	52.5	26.0

HRI 5359P2 presulfided Shell S-317 Catalyst

** L-758 recovered catalyst from Bench Unit Operations with Black Thunder Mine Coal.

There was a very high ash recovery for both runs, 280% of the coal ash in Run CE54, and 305% of the coal ash in Run CE55. The ash quantity in excess of coal ash corresponded to 7.1 W% of the Molyvan L used in Run CE54, and 8.1 W% of the Molyvan L used in Run CE55. These values are 70-80% of the equivalent amount of Mo_2O_3 that would be formed in combustion of the Molyvan L, 10.1% of the Molyvan L. However, the actual molybdenum contents of the recovered ashes were considerably lower than this proportion, with only 13% of the molybdenum in the Molyvan L found in the recovered ash for Run CE54, and 16% found there for the Run CE55 product. The "missing" molybdenum did not appear to be in the THF soluble product, since the ash content (by TGA analysis) of that product for the two runs was low, actually 0.00% for Run CE54, and a value correspond to 1% of the Mo content of the Molyvan L for Run CE55.

Another anomaly for these tests is the high proportion of THF insoluble organic material remaining after these tests, 41.8% of maf coal for Run CE54, and 47.5% of maf coal for Run CE55. These values correspond to nominal coal conversions of 58.2% and 52.5% for the two runs, respectively, which are about 22% lower conversions than obtained in the tests without catalyst or Molyvan L, and about 37% lower than obtained in the tests with extrudate catalyst.

These results indicate that a major part, but not all, of the Molyvan L is decomposed, since the amount of "excess" THF insoluble material corresponds to about 21 W% of the organic content of the Molyvan L. It could be evidence of retrograde reaction.

The residual oil content of the THF soluble product corresponded to 22 W% of coal for Run CE54, and 27 W% for Run CE55. These values are very close to the values obtained in experiments without Molyvan L additive, indicating that the addition of the massive amounts of Molyvan L was ineffective in reducing residual yield. The organic complex associated with Molyvan L tested at Wilsonville was found to cause problems during solubility and filtration operations in the laboratory at 1,000 ppm mf coal levels. Using 200% Molyvan L on coal basis could affect analytical results⁽⁹⁾.

Test with Recovered CTSL Catalyst without Molyvan L

The results of Run CE58, using L-758 catalyst (recovered from CTSL bench unit operations) and no Molyvan L, are unexpected, in that the recovered catalyst gave a coal conversions in the range of the those obtained in thermal tests without catalyst, although the residual oil yield was more nearly that obtained in tests with the Presulfided HRI 5359P2 catalyst. The residual oil result of Run CE58 was consistent with that of an earlier test, CE33, with the L-758 catalyst where the activity for conversion of the residual oil component of CTSL product PFL was about half of that of fresh catalyst. The very poor coal conversion result of Run CE58 is unexpected since in the Bench Unit CTSL runs the coal conversion does not change appreciably in the course operations, while there is well defined increase in residual oil yields reflecting declining catalyst activity for residual oil conversion. There have been no other microautoclave tests with recovered CTSL catalyst with coal where the activity for coal conversion would be evaluated.

Experiments with Product Solids from Molyvan L Tests

Molybdenum Accumulation on Coal Ash

After Run CE52, which tested the catalytic activity of the solids recovered after Runs CE46 and CE48 in which 1.25 W% (on coal) Molyvan L had been added, the ash in the filtered product solids were analyzed for molybdenum and nickel contents with the following results:

Molybdenum, W%	2.99
Nickel, W%	0.63

Nominally, these analyzes indicate the retention of 18 mg of molybdenum in the product solids of the two earlier runs, which is considerably higher than the molybdenum content of the Molyvan L that had been added, 4 mg. Evidently, extrudate catalyst had accumulated in these product solids, a point that is supported by presence of nickel therein, in a ratio, 1:4.7 to molybdenum, very similar to that of the extrudate catalyst, 1:5.3. A second point supporting this inference, is that ash recoveries in the microautoclave runs from which the solids charged to Run CE52 was obtained were above 100% (112% in Run CE46 and 148% in Run CE48), indicating that some broken extrudate catalyst was in the

solids product. Assuming the excess ash to be extrudate catalyst, the expected analysis of the final Run CE52 ash would be:

Molybdenum, W%	1.96
Nickel, W%	0.38

or about two-thirds the respective analyzed values.

This interpretation indicates the possibility that some of the molybdenum accumulation was derived from the Molyvan L, one-third or 6 mg nominally. However, since these calculated molybdenum and nickel contents deviate from the observed values by the same proportion, such a conclusion is uncertain.

Test CE52 tested the activity of a blend of the filter cakes from these two microautoclave runs with the fresh coal/solvent mixture for prospective catalytic activity, with the following results. The comparison includes a test using the product solids from a Bench Unit CTSI operation with Black Thunder Mine coal, Run 227-71 Period 11, in which the coal conversion level was 94.0% of maf coal:

<u>Experiment</u>	<u>Catalyst</u>	<u>Ash in Cat. Extrudate</u> <u>gm/gm coal</u>	<u>Ash.</u> <u>Recov</u>	<u>Conv.</u> <u>W% MAE</u>	<u>Resid Yield</u> <u>W% Conv. Coal</u>
CE59	No	-	102.7	78.4	44.9
CE52	CE4648 Sol.	0.179	102.6	82.0*	44.7
CE53	227-71 PFS	0.322	93.8	70.3**	48.8

* W% of organic content in fresh coal and solid "catalyst".
85.8% of organic in fresh coal, if organics in "catalyst" were converted to reach 95% of original coal to Tests CE46 and CE48.

** W% of organic content of the fresh coal.
60% of organics in fresh coal plus 227-72 PFS solids charged.

This performance of both product solids cannot be considered significantly different from the thermal performance of Run CE59.

Experiments with Catalysts Recovered after Tests using Molyvan L

The extrudate catalysts that were recovered after Runs CE46, CE48, CE54 and CE55, in which Molyvan L had been used along with extrudate catalysts, were tested again in Runs CE51, CE56, and CE57 to see if the Molyvan L addition had resulted in any enhanced catalytic activity because of molybdenum retention by the extrudates, with the following results:

<u>Experiment</u>	<u>"Catalyst"</u>	<u>Ash in Cat.</u> <u>gm/gm Coal</u>	<u>Ash.</u> <u>Recov</u>	<u>Conv.</u> <u>W% MAF</u>	<u>Resin Yield</u> <u>W% Conv. Coal</u>
CQ144	HRI 5359P2 [*]	1.00	96.1	91.4	22.6
CE47	HRI 5359P2 [*]	1.00	124.7	91.7	25.7
CE51	CE4648 Recv.	1.00	120.5	88.2	23.4
CE56	CE54 Recv.	0.96	147.1	91.2	30.3
CE58	L-758 ^{**}	1.00	99.5	76.3	27.2
CE57	CE4648 Sol.	0.96	137.5	87.5	40.9

^{*} HRI 5359P2 was the catalyst charged to Runs CE46, CE48, (both with .0125 grams Molyvan L/gm catalyst) and CE54 (with 2.00 grams Molyvan L/gm catalyst).

^{**} L-758 was the catalyst charged to Run CE55 (with 2.00 grams Molyvan L/gm catalyst).

The Run CE51 test of the blend of the Run CE46 and CE48 recovered catalysts (where the Molyvan L addition was 1.25% of the extrudate catalyst used) gave a slightly lower residual oil yield than the reference Run CE47 test, a difference that is probably less than the experimental uncertainty. Both tests with recovered catalyst where 2 grams Molyvan L per gram of catalyst had been used (CE56 and CE57) gave residual oil yields higher than in the reference tests without Molyvan L. There is no clear indication of enhanced catalytic performance for residual oil conversion because of molybdenum retention on the catalysts.

The analyses of the catalyst recovered after the various Microautoclave runs were the following:

Runs Charging HRI 5359P2 Catalyst

Run	Molyvan L gm/gm Catalyst	Recovered Catalyst Analysis		
		Mo, W%	Ni, W%	C, W%
HRI 535P2		(9.4)	(1.8)	6.44
CE47	0.0000	9.26	1.82	8.55
CE46	0.0126	9.65	1.78	7.72
CE48	0.0122	9.23	1.78	9.26
CE51	0.0124 [*]	9.65	1.83	10.06
CE56	2.00 ^{***}	8.76	1.54	8.56

Runs Charging L-758 Catalyst

Run	Molyvan L gm/gm Catalyst	Recovered Catalyst Analysis		
		Mo, W%	Ni, W%	C, W%
L-758		7.78	1.69	17.25
CE58	0.000	8.17	1.42	16.46
CE57	2.00 ^{***}	7.94	1.50	15.01

- ^{*} In prior use in Runs CE46 and CE48
- ^{**} In prior use in Run CE54
- ^{***} In prior use in Run CE55

In Tests CE46 and CE48 the possible retention of molybdenum on the extrudate catalyst was 0.1 W% of the catalyst, which is probably not significant after considering the scatter of these analyses. The analyses of the Run CE56 and CE57 catalysts, where 2.0 grams Molyvan L per gram of extrudate catalyst (having a molybdenum content equivalent to 16 W% of the extrudate catalyst) had been used, do not indicate any accumulation of molybdenum.

EVALUATION OF FeOOH-IMPREGNATED COAL

Feed coal, Black Thunder coal, to the Bench Run CC-15 was impregnated with iron catalyst precursor (hydrated iron oxide) using an incipient wetness technique developed by the Pittsburgh Energy Technology Center. The activity of several samples, two laboratory prepared and seven from the bulk iron treated coal for Run CC-15, were compared with that of the untreated coals.

Table 15 summarizes the ash and iron content of the iron treated and untreated coals. The iron content of the untreated Black Thunder coal is 1,380 and 2,000 for HRI-5828 and 5887, respectively. Both the laboratory samples (HRI-5991A and 5991B) and the bulk sample both were prepared using HRI-5828. However, the laboratory samples contain 2,500 ppm of iron, while that of the bulk samples are in the range of 5,600 to 6,980 ppm. The fine coal sample recovered (by filtration) from the decanted liquid was also tested. The "decanted" sample is significantly higher in ash content (12.3 W% mf coal) compared with the other treated coal samples (6.0 to 6.40 W%).

The microautoclave tests were conducted at 800°F for 30 minutes under 2,000 psig of hydrogen over-pressure with or without supported catalyst. Except for the initial Tests YY01 and 02, dimethyl disulfide was added. The solvent (HRI-6002) is a Wilsonville distillate obtained prior to PDU Run 260-03.

Two sets of tests were performed to evaluate the impact of finely dispersed iron under thermal (no supported catalyst) and catalytic conditions. The coal/solvent ratio for these tests was also different: $\frac{1}{4}$ for all catalytic tests and $\frac{1}{2}$ for most of the thermal tests. The thermal tests were designed to maximize the effect of the iron catalyst precursor. Results are presented in *Table 16*.

At a low coal/solvent of $\frac{1}{2}$ without any support catalyst (thermal test), coal conversion of the iron treated coal (L-780) is about 3.7 to 9.3 W% higher than the untreated coal (HRI-5828). The lower value is corresponding to the first batch of iron treated coal (L-780A) prepared using the bulk preparation procedure at HRI. As the preparation technique became more refined in the latter batches (L-780B and other dated samples), the activity of the coal also increased an average value of 81.55 W% from that of L-780A (75.97 W%). However, the iron catalyst has no significant impact on resid conversion.

The "decanted solid" seems to be more active, 7.2 W% higher in coal conversion but 4.0 W% lower in resid yield reflecting a higher concentration of iron. Also, in Test YY17 the iron catalyst was initially activated at 527°F for 15 minutes prior to the coal liquefaction. Pretreatment seems to improve coal conversion by 3 W% but resulted in a 4.2 W% increase in resid production.

By doubling the solvent to coal ratio from 2/1 to 4/1 and in the presence of supported catalyst the effect of dispersed catalyst becomes insignificant. The coal conversion is 88.67 and 87.83 W% for the untreated (HRI-5887) and iron

treated coal (HRI-5991 and HRI-6050), respectively. Similar comment can be made to the resid yield. Under this condition, with plenty of solvent and in the presence of effective hydrogenation catalyst, the catalytic effect of iron is less dominant.

RANKING OF COALS BY MICROAUTOCLAVE RESULTS

Ranked by Coal Conversion in Thermal Tests

RANK	RUN NUMBER	COAL FEED	THF CONV	975 F+ CONV
1	cq25	5599-Adaville Seam	89.18	46.27
2	cq7	5472-Ohio Cl.	84.93	46.9
3	cq10	5011-Clovis Pt.	84.89	50.6
4	cq23	5613-B1 Thund	84.59	51.96
5	cq51	5638-East Decker	82.85	42.77
6	cq79	5673-New Mexico	81.91	32.42
7	cq8	5387-Il1 BCR Cl	81.25	39.9
8	cq31	5612-Coal Creek	80.77	51.40
9	cq9	5174-Il1 B. S.	79.93	38.52
10	cq33	5616-Rochelle Mine	79.80	63.13
11	cq53	5639-West Decker	79.77	42.51
12	cq45	5630-B1 Thund Dry	79.56	59.57
13	cq43	5630-B1 Thund Feed	76.61	44.26
14	cq87	5709-New Mexico	75.31	56.96
15	cq75	5690-1 Bel Ayr Unoil	74.29	43.38
16	cq27	5606-Il1 Low Ash	69.68	30.89
17	cq55	5661-Elkhorn 1.3F	64.10 !	20.84 !
18	cq77	5690-2 Bel Ayr Dust	57.83	36.56

Ranked by 975 F Conversion In Thermal Tests
(975 F+ Analytical Method Changed for CQ89 and Later)

1	cq33	5616-Rochelle Mine	79.80	63.13
2	cq45	5630-B1 Thund Dry	79.56	59.57
3	cq87	5709-New Mexico	75.31	56.96
4	cq23	5613-B1 Thund	84.59	51.96
5	cq31	5612-Coal Creek	80.77	51.40
6	cq10	5011-Clovis Pt.	84.89	50.6
7	cq7	5472-Ohio Cl.	84.93	46.9
8	cq25	5599-Adaville Seam	89.18	46.27
9	cq43	5630-B1 Thund Feed	76.61	44.26
10	cq75	5690-1 Bel Ayr Unoil	74.29	43.38
11	cq51	5638-East Decker	82.85	42.77
12	cq53	5639-West Decker	79.77	42.51
13	cq8	5387-Il1 BCR Cl	81.25	39.9
14	cq9	5174-Il1 B. S.	79.93	38.52
15	cq77	5690-2 Bel Ayr Dust	57.83	36.56
16	cq79	5673-New Mexico	81.91	32.42
17	cq27	5606-Il1 Low Ash	69.68	30.89
18	cq55	5661-Elkhorn 1.3F	64.10 !	20.84 !

! based on maf product without ash balance

TABLE 1

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RANKING OF COALS BY MICROAUTOCLAVE RESULTS

Ranked by Coal Conversion in Catalytic Tests

RANK	RUN NUMBER	COAL FEED	THF CONV	975 F+ CONV
1	cq18	5387-Ill BCR Cl	95.28	60.76
2	cq24	5613-B1 Thund	94.64	75.22
3	cq28	5606-Ill Low Ash	94.13	60.80
4	cq26	5599 Adaville Seam	93.94	69.48
5	cq12	5011-Clovis Pt.	92.93	75.76
6	cq17	5472-Ohio Cl.	92.39	55.32
7	cq11a	5174-Ill B. S.	91.01	70.95
8	cq54	5639-West Decker	90.53	71.64
9	cq46	5630-B1 Thund Dry	89.80	75.62
10	cq76	5690-1 Bel Ayr Unoil	89.70	72.45
11	cq52	5638-East Decker	89.62	70.72
12	cq88	5709-New Mexico	88.51	69.49
13	cq80	5673 New Mexico	88.35	66.52
14	cq34	5616-Rochelle Mine	88.27	72.99
15	cq44	5630-B1 Thund Feed	87.94	72.86
16	cq32	5612-Coal Creek	87.77	71.41
17	cq56	5661-Elkhorn 1.3F	86.50	47.94
18	cq89	5726-Dorchester	86.18	37.90
19	cq78	5690-2 Bel Ayr Dust	74.41	55.66
20	cq90	5727-Dorch. Micro	29.70	20.83

Ranked by 975 F Conversion In Catalytic Tests
(975 F+ Analytical Method Changed for CQ89 and Later)

1	cq12	5011-Clovis Pt.	92.93	75.76
2	cq46	5630-B1 Thund Dry	89.80	75.62
3	cq24	5613-B1 Thund	94.64	75.22
4	cq34	5616-Rochelle Mine	88.27	72.99
5	cq44	5630-B1 Thund Feed	87.94	72.86
6	cq76	5690-1 Bel Ayr Unoil	89.70	72.45
7	cq54	5639-West Decker	90.53	71.64
8	cq32	5612-Coal Creek	87.77	71.41
9	cq11a	5174-Ill B. S.	91.01	70.95
10	cq52	5638-East Decker	89.62	70.72
11	cq88	5709-New Mexico	88.51	69.49
12	cq26	5599 Adaville Seam	93.94	69.48
13	cq80	5673 New Mexico	88.35	66.52
14	cq28	5606-Ill Low Ash	94.13	60.80
15	cq18	5387-Ill BCR Cl	95.28	60.76
16	cq17	5472-Ohio Cl.	92.39	55.32
17	cq78	5690-2 Bel Ayr Dust	74.41	55.66
18	cq56	5661-Elkhorn 1.3F	86.50	47.94
19	cq89	5726-Dorchester	86.18	37.90
20	cq90	5727-Dorch Microwave	29.70	20.83

TABLE 2

Page 1 of 3

ANALYSES FOR COALS USED IN MICROAUTOCLAVE EVALUATIONS

HRI Identific.	5011	5174	5387	5472	5599	5606
COAL SOURCE						
State	Wyoming	Illinois	Illinois	Ohio	Wyoming	Illinois
Mine	Clovis Pt	Burning St	Burning St.		Kemmerer	
Company	Kerr-Mcgee	Consolid.	Consolid.	Cravat	Pitt.& Midw.	Consolid.
Seam	Wyodak	No. 6	No. 6	5/6 Seams	Adaville	No. 6
Treatment	As-Rec'd	As-Rec'd	Float	Float	As Rec'd	As Rec'd
MINED COAL						
Moisture	31.5	12.32				
Vol. Mat.	31	31				
Fixed Carbon	31.2					
Ash	6.3	11				
Btu/lb	8100	11094				
HRI SAMPLE						
Moisture, W%					10.3	
V. M. W% MAF	50.3		42.6	43.4	45.1	39.2
F. C. W% MAF	49.7		57.4	56.6	54.9	60.8
Anal. (Dry)						
Carbon	64.34	69.98	75.74	77.50	72.12	75.81
Hydrogen	4.41	4.62	4.66	4.96	4.81	4.79
Sulfur	1.14	3.40	2.79	2.08	1.06	1.18
Nitrogen	0.92	1.36	1.48	1.58	1.13	1.77
Ash	9.49	10.34	5.35	3.78	3.19	6.02
Chlorine					0.02	0.41
Total	80.30	89.70	90.02	89.90	82.33	89.98
Btu/lb (Dry Basis)	11408		12899	14001	12720	13460
Btu/lb (maf)	12604		13628	14551	13139	14322
Sulf. In Ash	8.42				7.44	1.07
SO3-free Ash	7.49				2.60	5.86
Forms of Sulfur						
Pyritic					0.13	0.46
Sulfate					0.02	0.07
Organic					0.76	0.53

TABLE 2

Page 2 of 3

ANALYSES FOR COALS USED IN MICROAUTOCLAVE EVALUATIONS

HRI Identific.	5612	5613	5616	5630F	56300	5638
COAL SOURCE						
State	Wyoming	Wyoming	Wyoming	Wyoming	Wyoming	Montana
Mine	Coal Creek	Black Thund.	Rochelle	Black Thund.	Black Thund.	East Decker
Company	Thund. Basin	Thund. Basin	Rochelle	Thund. Basin	Thund. Basin	Decker Coal
Seam	Wyod. Ander	Wyod. Ander	Roland	Wyod. Ander	Wyod. Ander	Anderson
Treatment	As Rec'd	As Rec'd	As-Rec'd	Dried - 6.3%	Dried - 2.5%	As Rec'd
MINED COAL						
Moisture	30	27	26	27	27	23.8
Vol. Mat.	30.7	32.2	32	32.2	32.2	32
Fixed Carbon	32.4	34.9	37	34.9	34.9	40
Ash	5.6	5	5	5	5	4.2
Btu/lb	8390	8890	8800	8890	8890	9500
HRI SAMPLE						
Moisture, W%						20.5
V. M. W% MAF	46.8	47.7	43.8	44.1		42.1
F. C. W% MAF	53.2	52.3	56.2	55.9		57.9
Anal. (Dry)						
Carbon	68.60	70.50	68.51	67.70		71.54
Hydrogen	4.45	4.47	4.19	4.54		4.51
Sulfur	0.46	0.46	0.42	0.48		0.41
Nitrogen	1.21	0.98	1.04	1.05		1.36
Ash	7.35	6.55	6.34	7.27		5.31
Chlorine	0.13	0.03	0.04	0.04		0.04
Total	82.20	82.99	80.54	81.08		83.17
Btu/lb (Dry)	11751	12048	11289	11797		12282
Btu/lb (maf)	12683	12892	12053	12721		12971
Sulf. in Ash	6.11	7.56	4.40	6.35		5.46
SO3-free Ash	6.23	5.31	5.64	6.12		4.59
Forms of Sulfur						
Pyritic	0.05		0.03			0.06
Sulfate	0.01		0.01			0.05
Organic	0.41		0.37			0.28

TABLE 2

Page 3 of 3

ANALYSES FOR COALS USED IN MICROAUTOCLAVE EVALUATIONS

HRI Identific.	5639	5661	5673	5690-1	5690-2
COAL SOURCE					
State	Montana	West Va.	New Mexico	Wyoming	Wyoming
Mine	West Decker		McKinley	Belle Ayr	Belle Ayr
Company	Decker Coal	Consolid.	R & M Coal	Amax	Amax
Seam	Anderson	Elkh. No.3			
Treatment	As Rec'd	1.3 Float	As Rec'd	Dried	Bag House Dust
MINED COAL					
Moisture	23.8				
Vol. Mat.	32				
Fixed Carbon	40				
Ash	4.2				
Btu/lb	9500				
HRI SAMPLE					
Moisture, W%	19.90	1.95	7.28	12.42	
V. M. W% MAF	41.4	38.3	45.9	47.2	
F. C. W% MAF	58.6	61.7	54.1	52.8	
Anal. (Dry)					
Carbon	71.30	80.93	70.37	65.84	
Hydrogen	4.57	5.16	5.05	4.59	
Sulfur	0.41	1.68	0.55	0.73	
Nitrogen	1.23	0.71	1.29	1.34	
Ash	5.13	1.68	10.72	7.55	11.24
Chlorine	0.03	0.33	0.02	0.04	
Total	82.67	90.49	88.00	80.09	
Btu/lb (Dry Basis)	12057	14348	12058	12095	
Btu/lb (maf)	12709	14593	13106	13082	
Sulf. In Ash	6.74	3.97	1.97		
SO ₃ -free Ash	4.27	1.51			
Forms of Sulfur					
Pyritic	0.10		0.02	0.09	
Sulfate	0.02		0.01	0.01	
Organic	0.28		0.43	0.50	

CLEANED ILLINOIS NO. 6 COALS RANKED BY MICROAUTOCLAVE RESULTS

Ranked by Coal Conversion in Thermal Tests

RANK	RUN NUMBER	COAL FEED	THF CONV	975 F+ CONV
1	cq97	5739-Ot. ROM Ill 6	89.98	52.73 (Micronized)
2	cq85	5715-Ill Run-of-Mine	88.22	52.18
3	cq95	5783-Ot. Cl. Ill 6	85.71	60.53 (3.3 % Ash)
4	cq8	5387-Ill BCR Cl	81.25	39.9
5	cq93	5732-Ot. Cl. Ill 6	80.03	62.15 (1.3 % Ash)
6	cq9	5174-Ill B. S.	79.93	38.52
7	cq101	5761-Ot. Ill 6 Ref	76.39	51.64 (64.54 % Ash)
8	cq83	5716-Ill Agglomerate	76.32	43.19
9	cq103	5762-Ot. Raw Ill 6	74.19	46.61
10	cq109	5762-Ot. Raw Ill 6	67.05	(10/90 test)
11	cq27	5606-Ill Low Ash	69.68	30.89

Ranked by 975 F Conversion In Thermal Tests
(975 F+ Analytical Method Changed for CQ89 and Later)

1	cq93	5732-Ot. Cl. Ill 6	80.03	62.15 (1.3 % Ash)
2	cq95	5783-Ot. Cl. Ill 6	85.71	60.53 (3.3 % Ash)
3	cq97	5739-Ot. ROM Ill 6	89.98	52.73 (Micronized)
4	cq85	5715_Ill Run-of-Mine	88.22	52.18
5	cq101	5761-Ot. Ill 6 Ref	76.39	51.64 (64.54 % Ash)
6	cq103	5762-Ot. Raw Ill 6	74.19	46.61
7	cq83	5716-Ill Agglomerate	76.32	43.19
8	cq8	5387-Ill BCR Cl	81.25	39.9
9	cq9	5174-Ill B. S.	79.93	38.52
10	cq27	5606-Ill Low Ash	69.68	30.89

CLEANED ILLINOIS NO. 6 COALS RANKED BY MICROAUTOCLAVE RESULTS

Ranked by Coal Conversion in Catalytic Tests

RANK	RUN NUMBER	COAL FEED	THF CONV	975 F+ CONV
1	cq18	5387-Ill BCR Cl	95.28	60.76
2	cq94	5732-Ot. Cl. Ill 6	94.65	67.35 (1.3% Ash)
3	cq28	5606-Ill Low Ash	94.13	60.80
4	cq84	5716-Ill Agglomerate	93.70	74.16
5	cq85	5715-Ill Run-of-Mine	93.45	73.70
6	cq96	5738-Ot. Cl. Ill 6	93.36	61.42 (3.3% Ash)
7	cq98	5739-Ot. ROM Ill 6	93.29	64.65 (Micronized)
8	cq104	5762-Ot. Raw Ill 6	93.16	61.97
	cq110	5762-Ot. Raw Ill 6	92.11	60.67 (10/90 Test)
9	cq11A	5174-Ill B. S.	91.01	70.95
10	cq102	5761-Ot. Ill Refuse	81.14	73.82 (64.54% Ash)

Ranked by 975 F Conversion In Catalytic Tests
(975 F+ Analytical Method Changed for CQ89 and Later)

1	cq84	5716-Ill Agglomerate	93.70	74.16
2	cq102	5761-Ot. Ill Refuse	81.14	73.82 (64.54% Ash)
3	cq85	5716-Ill Run-of-Mine	93.45	73.70
4	cq11A	5174-Ill B. S.	91.01	70.95
5	cq94	5732-Ot. Cl. Ill 6	94.65	67.35 (1.3% Ash)
6	cq98	5739-Ot. ROM Ill 6	93.29	64.65 (Micronized)
7	cq104	5762-Ot. Raw Ill 6	93.16	61.97
	cq110	5762-Ot. Raw Ill 6	92.11	60.67 (10/90 Test)
8	cq96	5738-Ot. Cl. Ill 6	93.36	61.42 (3.3% Ash)
9	cq28	5606-Ill Low Ash	94.13	60.80
10	cq18	5387-Ill BCR Cl	95.28	60.76

TABLE 4

**MICROAUTOCLAVE TEST RESULTS WITH
BLACK THUNDER MINE COAL**

Shipment HRI No. -----	Test Date -----	Coal Conversion, W% maf -----		975 F+ Conversion, W% maf -----	
		Thermal -----	Catalytic -----	Thermal -----	Catalytic -----
5630	1/89	76.6	87.9	44.3	72.9
5713	1/90	80.3	89.8	45.4	66.4
5713	11/90		85.1		58.0
5713 (6.38% H ₂ O)	11/90	72.1	86.6	51.1	67.2
5828	11/90		84.2		63.9
5887	5/91	75.7	91.4	40.7	70.8

HRI No. 5630 = original shipment used in Runs CC-1 through CC-5
HRI No. 5713 = second shipment used in Runs CC-7, CC-11, and CC-12
HRI No. 5828 = third shipment used in Run CC-13
HRI No. 5887 = original sample ground and dried by Empire Coal Co.
before preparing the remaining coal for PDU Run 260-3

TABLE 5

MICROAUTOCLAVE EVALUATION OF FEED MATERIALS FOR RUN 227-59

All Tests: 2000 psig, hydrogen, 30 Minutes
 -RI 5359P Catalyst, 4/1 Solvent/Coal

RUN NUMBER	COAL FEED	SOLVENT TESTED	TEMP F	THE CONV	ASH BALANCE	MATERIAL BALANCE
cg44	5630- 227-55 Feed	-RI 5198	800	87.94	125.03	93.63
CQ61	5630-Drum 23	-RI 5198	800.	87.73	100.83	93.59
CQ62	5630-Drum 24	-RI 5198	800.	85.73	96.60	97.83
CQ63	5630-Drum 23	5648 Drum 6	800.	90.89	96.53	91.59
CQ64	5630-Drum 24	5648 Drum 6	800.	89.29	96.38	87.98
CQ65	5630-Drum 23	5648 Drum 6	700.	47.78	111.37	97.16
CQ66	5630-Drum 24	5648 Drum 6	700.	46.03	106.67	97.59
CQ67	5630-Drum 23	5648 Drum 6	750.	73.48	112.71	98.68
CQ68	5630-Drum 24	5648 Drum 6	750.	68.91	95.94	87.26

TABLE 6

RANKING OF SOLVENTS IN MICROAUTOCLAVE EVALUATIONS

30 minute tests at 750 F, 2 grams solvent/gram test coal

Tests with HRI-5174 Illinois No. 6 Coal

Solvent	Run	Coal Conversion, %
HRI 5910	CQ151	70.2
HRI-5648	CQ74	70.1
L-742	CQ72A	67.4
HRI 5911	CQ153	65.8
HRI-5757	CQ100	61.9
L-721	CQ37	60.8
L-721	CQ135 (4/91)	61.6
HRI 5868	CQ131 (4/91)	59.3
HRI-4907	CQ35	58.0
HRI-5443	CQ47, (CQ39)	57.8, (69.4)
HRI 5969	CQ155	55.6
227-25 S	CQ41, CQ48	53.4, 55.3

Tests with HRI-5613 Black Thunder Mine Coal

Solvent	Run	Coal Conversion, %
L-742	CQ71A	65.9
HRI-4907	CQ36	65.4
L-721	CQ38	63.7
HRI-5648	CQ73	61.5
HRI-5757	CQ99	58.8
HRI 5868	CQ132 (4/91)	57.0
HRI-5443	CQ40, CQ49	54.8, 57.4
HRI 5910	CQ151	53.8
227-25 S	CQ42, CQ50	53.0, 47.2
HRI 5969	CQ156	52.0
HRI 5911	CQ154	51.7

TABLE 7

ANALYSES OF SOLVENTS USED IN MICROAUTOCLAVE SOLVENT EVALUATION TESTS

HRI Number	227-25 S	5969	5443	4907	5868	L-721	5757	L-742	5648
Wilsonville Ident.		V-124	V-160	H-Coal***		V-1076	V-1074	V-1074	Run 257
Gravity, API	15.9	15.3	10.2	15.1	7.2	13.1	8.2	6.2	5.9
Distillation, F									
1BP	451	411	205	496	466	492	700	485	735
5 V%	500	492		522	656	539	721	547	776
10 V%	510	512	585	530	736	583	734	586	798
20 V%	527	551	656	539	771	623	745	630	810
30 V%	536	583	697	548	786	646	755	695	830
40 V%	550	606	721	560	805	665	772	717	842
50 V%	572	633	750	575	819	682	790	753	858
60 V%	594	650	778	592	838	699	805	780	876
70 V%	623	663	812	620		715	827	816	888
80 V%	666	693	850			731	850	854	902
90 V%	727	751	925			754	881	887	930
E. P.	884	871	975	650	850	800	945	975	1008
Recovery, V%	98	97	98	79	66			98	98
Residue, W%	2.4	1.0							1
Volume Average B. P.	594	628	754	(594)	(819)	666	797	747	854
Watson Character. Factor	10.55	10.62	10.61	(10.51)	(10.64)	10.63	10.64	10.3	10.64
Carbon, %		87.66	88.63	88.62	86.51	89.63*	89.68	88.49	90.14
Hydrogen, W%		10.61	10.12	10.12	9.56	10.93*	10.17	9.22	9.85
Sulfur, W%		0.09	0.04		0.47	0.02*	0.03	0.05	0.06
Nitrogen, W%		0.36	0.25	0.34	0.26	0.28*	0.27	0.76	0.37
Solvent Quality**									
Illinois No. 6 Coal	54.4	55.6	57.8	58.0	59.3	61.2	61.9	67.4	70.1
Black Thunder Coal	50.1	52.0	56.1	65.4	57.0	63.7	58.8	65.9	61.5

* HRI 5542 (Wilsonville V-1076) topped to prepare L-721, 16.9 API, 614 VABP, 10.68 Watson K

** Thermal Conversion at 750 F, 30 Minutes, 2/1 solvent/coal

*** Catlettsberg Product Received through Lummus Co.

TABLE 8

MICROAUTOCLAVE TESTS TO EVALUATE
ALTERNATIVE CATALYSTS
AND PRESULFIDING METHODS

Catalyst -----	Catal/Oil -----		Resid conversion -----		Presulfiding -----
	Gm/Gm -----	cc/Gm -----	Unpresulf. -----	Presulf. -----	
Shell S-317	0.25	0.25	13		DMDS/gas oil
Shell S-317	1.00	1.61	22	28	DMDS/gas oil
Shell S-317	1.00	1.61	22	41	TNPS/gas oil
Shell S-317	1.00	1.61	22	45	DMDS/tetralin
Shell S-317	1.00	1.61	22	54	TNPS/tetralin
5675 Ni-Mo Macro	1.00	2.63	18	29	DMDS/tetralin
5676 Ni-Mo Micro	1.00	(1.61)	21	52	DMDS/tetralin
5677 Fe-Mo Macro	1.00	2.63	21	46,47	DMDS/tetralin
5677 Fe-Mo Macro	0.60	1.59	26	30	DMDS/tetralin

CATALYST ANALYSES

HRI NO.	5359	5675	5676	5677
Source	Shell	UOP	UOP	UOP
Identification	S-317	RCM	RCM	RCM
		1-121	1-122	1-123
Shape	Extrud.	Bead	Bead	Bead
Fe, Wt				2.38
Ni, Wt	2.86	1.69	1.70	
Mo, Wt	10.76	9.54	9.36	9.35
Bulk Density, Gm/cc	0.64	0.38		0.38
Pore Volume, cc/gm	0.68		0.71	1.31
Crush Strength, Lb/mm	1.78	2.68	6.76	1.76

TABLE 9

MICROAUTOCLAVE TESTS WITH RECOVERED CATALYSTS FROM CTSL OPERATIONS

825°F, 2,000 psig H₂, 30 Minutes with CTSL Recycle Solvent (PFL)

CTSL Run	CC-8	CC-8	CC-11	CC-11	--- Presulfided Shell S-317 Catalyst ---			
Stage	First	Second	First	Second				
Coal Feed	Illinois No. 6		Black Thunder					
Cat. Age, Lb Coal/Lb	560	560	748	748				
<u>Catalyst Analysis</u>								
Carbon, W%	12.56	13.61	10.04	18.82		5.81		
Sulfur, W%	6.32	6.02	6.34	5.48		5.24		
Metal Contam., W%	0.97	1.12	2.35	2.45				
Molybdenum, W%	7.46	7.39	8.25	7.78		9.49		
Microautoclave Run	CM99	CM100	CM101	CM102	CM103	CM105	CM104	CM106
<u>Catalyst/Oil</u>								
As Charged	1.00	1.00	1.00	1.00	1.00	1.00	0.50	0.25
Equivalent	0.79	0.78	0.87	0.82	1.00	1.00	0.50	0.25
Product Residuum, W%	20.73	20.68	18.39	20.94	18.61	19.58	21.39	24.64
<u>Relative Catalyst</u>								
Activity	0.81	0.83	1.39	0.74	1.14	0.86	(1.00)	(1.00)
Activity	0.77	0.79	1.21	0.71	1.00	0.79	(1.00)	(1.00)

Relative contaminant-free catalyst, based on molybdenum content relative to that of presulfided catalyst.

TGA analysis, CTSL feed to tests contained 29.87 W% residuum (Run CC-1, Period 23 PFL).

Presulfided Catalyst correlated as $C = Co \cdot (0.70 \cdot \text{Exp}(-0.1165 \cdot (\text{Cat/Oil}) + 0.30 \cdot \text{Exp}(-2.996 \cdot \text{Cat/Oil}))$ - Fits avg. of CM103, CM105Presulfided Catalyst correlated as $C = Co \cdot (0.70 \cdot \text{Exp}(-0.1462 \cdot (\text{Cat/Oil}) + 0.30 \cdot \text{Exp}(-2.813 \cdot \text{Cat/Oil}))$ - Fits. CM103 only

TABLE 9B

MICROAUTOCLAVE TESTS WITH VARIOUS SULFIDING AGENTS

Conditions - 825 F, 2000 psig hydrogen

2.0 grams HRI 5198 Coal Liquefaction Distillate Product (440-900 F BP)

2.0 Grams HRI 5359P, Presulfided Shell S-317 Extrudate Catalyst

Run	-----	Agent	-----	Time	Sulfur on Sulf. In Oil Prod. CH4 225-250 F			
Type		Grams	S, Grams	Minutes	Cat. W% Prod., Grams	Grams	Prod. Gms *	
Charge Cat.					6.54			
CS-01	None			45	6.66	0.003	0.010	0.013
CS-02	TNPS	0.27	0.10	45	7.03	0.016	0.009	0.108
CS-03	DMDS	0.15	0.10	45	7.19	0.006	0.051	
CS-04	Sulfur	0.10	0.10	45	7.06	0.010	0.013	
CS-05	TNPS	0.54	0.20	45	7.78	0.028	0.013	
CS-06	DMDS	0.29	0.20	45	7.96	0.018	0.105	0.029
CS-07	Sulfur	0.20	0.20	45	7.66	0.019	0.014	
CS-08	TNPS	0.27	0.10	45	7.68	0.015	0.017	
CS-09	None			15	5.97	0.005	0.004	
CS-10	TNPS	0.27	0.10	15	7.09	0.015	0.006	
CS-11	DMDS	0.15	0.10	15	7.22	0.005	0.047	
CS-12	Sulfur	0.10	0.10	15	6.69	0.014	0.005	
CS-13	TNPS	0.54	0.20	15	6.99	0.026	0.005	
CS-14	DMDS	0.29	0.20	15	7.18	0.020	0.077	
CS-15	Sulfur	0.20	0.20	15	7.20	0.024	0.007	
CS-16	DMDS	0.15	0.10	15	7.30	0.012	0.044	

* GC sim-dist of oil recovered after run

TNPS - di-Tertiary Nonyl Polysulfide

DMDS - DiMethyl disulfide

Sulfagent.tab

TABLE 10

GAS YIELDS AND SELECTIVITIES

Microautoclave Tests with 227-55-23A PFL Distillate Fractions
825 F, 30 Minutes

D-1160 Cut	Catalyst/Oil	C1-C3 Gas Yields, W%	Converted Feed, W%*	Selectivity To Gas
600-700 F	0.00	0.24	4.6	0.052
	0.25	0.52	7.8	0.067
700-800 F	0.00	0.40	9.6	0.042
	0.25	0.70	15.9	0.044
800-900 F	0.00	0.42	2.4	0.175
	0.25	0.62	12.9	0.048
900-975 F	0.00	0.54	12.7	0.043
	0.25	0.84	14.3	0.059
Total PFL	0.25	0.67		
	1.00	1.86		

* Increase in concentration of components below nominal IBP
of fraction.

TABLE 11

MICROAUTOCLAVE REACTION OF D-1160 DISTILLATE FRACTIONS

30 Minute Tests

Feed	Test Temp. F	Product Cut	---Conc. Ratio, Prod./Feed---	
Catalyst/Oil, gm/gm			0.0	0.25
D-1160 600-700 F	825	600 F+	0.954	0.912
D-1160 700-800 F	825	700 F+	0.904	0.841
	750	700 F+	0.940	0.952
D-1160 800-900 F	825	750 F+	0.976	0.879
		800 F+		0.871
D-1160 900-975 F	825	850 F+	0.873	0.823
		900 F+	0.754	0.857
Distrates.tab				

TABLE 12

SELECTIVITIES OF DISTILLATE FRACTIONS REACTIONS

D-1160 Fractions Fed, Microautoclave - 30 Minute Tests
GC Simulated Distillations of Feed and Products

Feed	Test Temp. F	Test	Reacted Fraction	-----Selectivity, Fraction of Converted Materials-----					
				400 F-	400-500 F	500-550 F	550-600 F	600-650 F	650-700 F
D-1160 600-700 F	825	Thermal	600 F+	0.262	0.222	0.436	0.080		
		Catalytic	600 F+	0.315	0.378	0.261	0.046		
D-1160 700-800 F	825	Thermal	700 F+	0.108	0.156	0.303	0.199	0.205	0.089
		Catalytic	700 F+	0.098	0.168	0.257	0.196	0.148	0.132

Feed	Test Temp. F	Test	Reacted Fraction	-----Selectivity, Fraction of Converted Materials-----						
				400 F-	400-500 F	500-600 F	600-700 F	700-750 F	750-800 F	800-850 F
D-1160 800-900 F	825	Thermal	750 F+	0.066	0.107	0.257	0.358	0.211		
		Catalytic	800 F+	0.105	0.140	0.218	0.338	0.065	0.134	
D-1160 900-975 F	825	Thermal	850 F+	0.002	0.066	0.127	0.139	-----0.260-----		0.406
		Catalytic	850 F+	0.004	0.041	0.082	0.154	-----0.460-----		0.260

TABLE 13

MICROAUTOCLAVE TESTS ON CATALYSTS FROM WILSONVILLE

Tests at 825 F, 2,000 Psig For 30 Minutes with PFL Product From Run 227-55 Period 23

Autoclave Run		CE43	CE44	CE45	CE36	CM37	CM09	CM40
Catalyst		Wilsonville Recovered Run 262	Fresh S-324	Presulfided *. S-324	Shell S-317	HRI Run 55 1st Stage	HRI Run 55 2nd Stage	HRI Run 57 1st Stage
Catalyst/Oil Ratios								
Grams/Gram		1.56	1.33	1.42	1.00	1.00	1.00	1.00
cc (particle)/Gram		1.00	1.00	1.00	1.00	0.72	0.68	0.75
Product Oil Analyses (Feed)								
Carbon		88.86	89.43	85.06	88.15			
Hydrogen	8.53	8.68	8.43	8.99	9.10			
Nitrogen	0.57	0.22	0.33	0.07	0.20			
Sulfur	0.04	0.06	0.03	0.09	0.14			
Residuum (TGA)	30.2	14.9	24.0	13.0	14.1	23.33	23.04	18.76
Ln(Co/C)		0.71	0.23	0.84	0.76	0.21	0.21	0.66
Relative Activity **		0.93	0.30	1.11	1.00	0.38	0.41	1.16
Catalyst Analyses								
Charged Catalyst								
Carbon, W%		4.56		1.85	1.83	15.57	18.90	8.69
Hydrogen, W%		0.79		0.69	0.58	0.75	0.99	0.90
Nitrogen, W%		1.21		0.00	0.06	0.28	0.17	0.20
Sulfur, W%		6.76		8.72	7.68	5.59	5.42	5.90
Molybdenum, W%		10.6	11.9			8.47	8.26	9.72
Particle Dens., g/cc		1.57	1.33					
Mo/cc, gms/cc		0.166	0.158					
Recovered Catalyst								
Carbon, W%		4.95	2.88	7.83				
Hydrogen, W%		0.56	0.38	0.86				
Nitrogen, W%		0.58	0.19	0.27				
Sulfur, W%		6.77	0.36	8.03				
Ash (TGA), W%		82.8	91.4	81.0				
Total		95.7	95.2	98.0				

* Presulfided in microautoclave using 4 grams/gram 30% TNPS in Tetralin at 500 F.

** Ln(Co/C) divided by 0.76 divided by cc catalyst/gram oil.

TABLE 14

MICROAUTOCLAVE TESTS WITH MOLYVAN ADDITIVE

RUN NUMBER	CAT- ALYST	THF CONV	975 F+ CONV	ASH BALANCE	MATERIAL BALANCE	RECOVERY BALANCE	COAL FEED	SOLVENT TESTED	TEMP F	TIME MIN	OIL /COAL	GAS	MOLYVAN /COAL
CE46	5359P2	92.08	69.77	111.93	94.03	87.03	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.0126
CE47	5359P2	91.73	68.11	124.69	92.43	86.83	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.00
CE48	5359P2	76.83	52.10	148.33	96.43	91.94	5887 BlTh	HRI 5198	750.	30.	4.0	H2	0.0122
CE49	5359P2	71.84	49.96	148.41	95.24	92.05	5887 BlTh	HRI 5198	750.	30.	4.0	H2	0.00
CE50	No	81.05	46.99	100.27	90.82	85.56	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.0134
CE51	CE4648	88.18	67.54	120.47	98.17	88.07	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.00
CE52	SO4648	82.0*	44.7 a	102.7	97.15	91.43	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.00
CE53	SOL227	60.0*	37.3 a	93.8	94.92	91.78	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.00
CE54	5359P2	58.16	34.45	279.77	93.07	73.46	5887 BlTh	HRI 5198	800.	30.	4.0	H2	2.00
CE55	L-758	52.49	24.38	305.45	91.43	108.02	5887 BlTh	HRI 5198	800.	30.	4.0	H2	1.99
CE56	CE54	91.17	63.56	147.08	91.86	83.88	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.00
CE57	CE55	87.52	51.64	137.48	97.32	90.83	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.00
CE58	L-758	76.31	47.33	99.50	92.16	85.60	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.00
CE59	No	78.43	43.19	102.70	90.00	83.99	5887 BlTh	HRI 5198	800.	30.	4.0	H2	0.00

* W% of organic mater in coal and "catalyst" (product solids from CE46 and CE48, or from Run 227-71 Period 11)

a Resid Yield, W% of converted coal

Material Balance - Weight of product liquids and solids remaining in Autoclave as a percentage of liquids and solids charged (as determined by weighing the microautoclave before and after the test at atmospheric condition).

Recovery Balance - Weight of recovered liquids and solids washed from Autoclave as a percentage of liquids and solids charged.

TABLE 15

**ANALYSIS OF FEOOH-IMPREGNATED BLACK THUNDER COAL
Ash and Iron Contents**

	Ash Content mf W%	S in Ash W% Ash	Iron Content mf W% Coal
<u>Untreated Coal</u>			
HRI-5828	7.03	7.13	0.200
HRI-5887	6.82	6.70	0.138
<u>Iron Treated Coal</u>			
HRI-5991A	6.86	3.56	0.244
HRI-5991B	6.84	3.89	0.266
HRI-6050*	6.22	4.85	0.507
L-780A	6.07	6.36	0.698
L-780A (washed)	6.06	4.57	0.567
L-780B	6.24	6.17	0.614
L-780 (decanted)	12.27	2.49	n/a
L-780 9/26	6.11	5.13	0.560
L-780 9/28	6.40	5.60	0.560
L-780 9/29	6.31	5.49	0.560
L-780 10/8	6.00	4.81	0.560

* Coal sample supplied by PETC.

TABLE 16

**MICROAUTOCLAVE TESTS TO EVALUATE
FEOOH-IMPREGNATED BLACK THUNDER COAL
800° F, 30 min., 2000 psig H₂
Solvent: HRI-6002 Catalyst: Shell 317**

<u>Test No.</u>	<u>Coal</u>	<u>DMS</u> g/2g coal	<u>Mode</u>	<u>Coal Conv.</u> W% coal	<u>Resid Yield</u> W% coal
COAL/SOLVENT RATIO = 1/4					
Untreated Coal					
YY02*	HRI-5887	---	Catalytic	92.69	24.10
YY02A	HRI-5887	0.10	Catalytic	82.63	20.20
YY04	HRI-5887	0.10	Catalytic	90.90	22.50
YY06	HRI-5887	0.11	Catalytic	88.47	19.00
YY08	HRI-5887	0.09	Thermal	82.58	36.00
Iron Treated Coal					
YY01	HRI-5991A	---	Catalyst	90.8 0	22.80
YY1A	HRI-5991A	0.12	Catalytic	87.25	23.20
YY03	HRI-5991B	0.10	Catalytic	86.56	21.00
YY05	HRI-6050	0.12	Catalytic	87.51	19.00
YY07	HRI-6050	0.09	Thermal	83.66	37.26
YY14	L-780A	0.11	Catalyst	90.00	18.40
YY13	L-780A	0.11	Thermal	79.65	31.20
COAL/SOLVENT RATIO = 1/2					
Untreated Coal					
YY10	HRI-5828	0.15	Thermal	69.91	33.90
YY12	HRI-5828	0.14	Thermal	72.84	38.90
YY18**	HRI-5828	0.15	Thermal	73.00	33.00
YY24	HRI-5828	0.15	Thermal	73.20	17.62
Iron Treated Coal					
YY09	L-780A	0.15	Thermal	74.65	32.90
YY15	L-780A	0.16	Thermal	75.84	36.90
YY16	L-780A(Washed)+	0.15	Thermal	77.42	32.10
YY11	L-780B	0.16	Thermal	80.43	32.60
YY17**	L-780A	0.15	Thermal	79.00	38.10
YY19	L-780 9/26	0.15	Thermal	82.76	36.34
YY21	L-780 9/28	0.15	Thermal	80.88	37.91
YY20	L-780 9/29	0.15	Thermal	83.27	37.22
YY23	L-780 10/8	0.15	Thermal	80.39	24.15
YY22	Decanted Solid	0.15	Thermal	88.55	29.92

+ Washed sample (to removal loosely attached nitrogen compounds from the impregnation procedure.

* Temperature at 825° F

** Temperature staging: 15 min. @ 527° F
followed by 30 min. @ 800° F

FIGURE 1

TEST OF DMDS AND TNPS PRESULFIDED CATALYST

S-317 Cat. - 227-55-23A PFL, 825 F

FIGURE 2

CATALYST ACTIVITY FOR RESID CONVERSION

Microautoclave - 227-55-23A PFL - 825°F

MICROAUTO. EVAL. OF IRON ADDITIVES

2275523A PFL, 1/1 oil/cat, 825 F, 30 Min

FIGURE 3

CONVERTIBILITY OF THERMALLY TREATED COAL

Conversion Tests – 30 Minutes at 800 F

FIGURE 4

GC SIM-DIST CM04 FEED AND PRODUCT

7-800°F Feed - 825°F, 30 Min., Catalyst

FIGURE 5

GAS YIELD – RUN 227–55–23A PFL FRACTIONS

Microautoclave – 30 Minutes – 825 F

FIGURE 6

GAS YIELD – EFFECT OF TEST TEMPERATURE

Microautoclave – 30 Minutes – Catalytic

FIGURE 7

GAS YIELD – EFFECT OF TEST TEMPERATURE

Microautoclave – 30 Min. – No Catalyst

FIGURE 8

GAS YIELD – EFFECT OF TIME AND CHARGE

Microautoclave – 825 F – 227-55-23A PFL

FIGURE 9

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SECTION II

CORRELATION OF ILLINOIS COAL YIELDS

Correlations were based on first order kinetics, with respect to weight fraction concentration in the slurry phase in the respective first and second stage reactors. Slurry phase flows for both stages were based on the slurry flow from the hot separator, which was generally between 600 and 650°F.

Coal Conversion

The maf coal was characterized as consisting of three species of different reactivity one of which was considered virtually unreactive at the usual process conditions. The values of these parameters and first order rate constants for Mine-washed Illinois No. 6 Coal (Burning Star Mine No. 2) containing 10-12 W% ash were as follows:

Coal Distribution	
High Reactivity	90.5 W%
Low Reactivity	6.0 W%
Unreactive	3.5 W%
Rate Constants at 750°F	
Lbs/hr/ft ³ Reactor	
Low Reactivity Constituent	11.95
High Reactivity Constituent	1,790
Activation Energy, Kcal/mole	
Both Constituents	53.8

There was no strong evidence of appreciable changes in coal conversion during CTSL Bench Unit operations over the usual range of catalyst deactivation which was indicated by changes in liquid product distribution, hydrogen content, and nitrogen content. However, in Microautoclave tests lower conversions were obtained in tests with no catalyst using solvent that was produced from coal liquefaction operations. In such tests at 800°F, the non-catalytic and catalytic test conversions were 90.0 and 93.3 W% of converted coal, which would correspond to non-catalytic rate constants about 0.05 as great as the catalytic rate constants (although such an interpretation is critically affected by very small changes in the experimental conversions and the correlating parameters).

975°F Residual Oil Yields

Residual oil yields were correlated as resulting from a portion of the primary reaction of the coal less secondary reaction of the residual oil following first

order kinetics. The yield of residual oil increased as runs continued, which reflected an effect of catalyst deactivation, either as 1) a direct impact upon the specific activity of the catalyst upon the cracking reaction or as 2) an indirect impact upon a hydrogenation/hydrogen transfer mechanism which promotes the cracking activity of the residual oil. The second mechanism would involve a hydrogenation of a hydrogen donor species, a hydrogen transfer reaction to the residual oil, and finally the cracking reaction of the residual oil itself, requiring far more correlating parameters than could be derived from the amount of Bench Unit Data available, and still would represent a complex resulting in a cracking rate related to catalyst age. A useful correlation was obtained using the first alternative as a correlation of the reaction rate constants against temperature and catalyst age.

Primary Residual Oil Yield W% of Converted Coal	60.5
Reaction Rate Constant, Lbs/hr/ft ³ Reactor Fresh Catalyst At 750°F	11.6
Activation Energy Kcal/gm mole	32.0
Catalyst Deactivation D in Deactivation equation*	
First Stage, 750°F	~0.0
Second Stage, 825°F	0.00195

$$* K = K_o \exp(-D * \text{Age})$$

D - Deactivation factor, lbs cat/lb coal with catalyst age
(Age) in lbs coal/lb catalyst

The use of no deactivation factor in the first stage reflects a pattern where the scatter in apparent first stage rate constants was such that it obscured any definitive trend with catalyst age. Subsequent microautoclave tests of catalysts recovered from the first and second stages confirmed the lower degree of deactivation of the first stage catalyst, but did indicate some deactivation of the first stage catalyst. A typical result was recovery of a first stage catalyst (after operations at 750°F) with an activity for residual oil conversion about 70% of that of fresh presulfided catalyst, while that of the second stage recovered catalyst (after operations at 800°F) was 45% as active as fresh catalyst. These evaluations correspond to a catalyst deactivation factor at 750°F about 1/3 that at 825°F.

C₁-C₃ Gas Yields

The C₁-C₃ gas yields were correlated as deriving in part from the primary reaction of the coal, and the balance as secondary formation from the constituents of the slurry phase in the reactor. The final correlating parameters were the following:

Primary C ₁ -C ₃ Formation W% of Converted Coal	4.06
Secondary Slurry Phase Reaction Rate at 825°F, Lbs/hr/ft ³ Reactor	1.004
Activation Energy, Kcal/gm mole	57

These parameters reflect little impact either of catalyst deactivation upon gas yield, or of slurry phase composition. The gas yields in an operation with no catalyst in the one of the two stages corresponded to the correlated results for operations with catalyst in both stages. As correlated, no allowance was made for solids content of the slurry phase, which was about 10-15 W% and the correlation could be modified to a slurry phase liquid components by increasing the secondary rate constant by a factor of 1.15. Microautoclave tests with the liquid phase product from the second stage and its gas oil components, indicated a gas formation rate of the whole liquid about the same as the average of those of the gas oil components, indicating the gas formation from the residual oil was at the same rate as from the gas oil components. In these microautoclave tests the gas formation rate was about 0.7 W% of the oil for 30 minutes tests at 825°F with 0.25 grams catalyst/gram oil, corresponding to a gas formation rate of 0.9 lbs/hr/ft³ liquid, slightly below the above rate correlated from the bench unit results. In such microautoclave tests without catalyst the gas formation was about 0.6 times the rate obtained with the catalyst.

C₄-390°F Naphtha Yields

The formation of naphtha was correlated by means of reaction model similar that above for the formation of C₁-C₃ gases, in which there is some formation from the reaction of the coal and secondary formation from the reaction of the slurry phase components. There was an apparent decline in naphtha yields as the catalyst deactivated apparently more severe with higher second stage temperature. These were lower naphtha yields for the operations where there was no catalyst in the second stage reactor.

The final values of the correlating parameters for the naphtha formation rate were the following;

Primary formation, W% of coal converted	8.4
Secondary formation	
Rate at 825°F, Lbs/hr/ft ³ reactor	
Thermal Contribution	1.20
Fresh Catalyst	2.88
Activation Energy, Kcal/gram mole	51
Catalyst Rate Deactivation, D	
Deactivation factor at 825°F	0.052
Temperature Dependence	
Activation Energy, Kcal/gram mole	39

$$K = K_o \exp(-D * \text{Age})$$

- K - Catalytic Rate Constant at Age
- K_o - Rate Constant for fresh catalyst
- D - Deactivation factor at temperature
- Age - Catalyst Age, Days of coal operations

In the microautoclave tests described above in the correlation the gas formation rates, in tests with 600-900 boiling point gas oil fractions, the naphtha yield was 1.4-2.5 W% of the oil for 30 minutes tests at 825°F with 0.25 grams catalyst/gram oil, corresponding to formation rates of 1.8-3.2 lbs/hr/ft³ liquid, with the highest formation rate for the tests with the lowest boiling gas oil fractions. Such tests with 900-975°F gas oil indicated virtually no naphtha formation. The microautoclave tests results are in the general range of the bench unit reaction rate to naphtha, but the rates are somewhat below the bench unit correlated rate. The GC simulated distillation method used in analysis of the microautoclave products was relatively crude and more reliable results would be obtained with the improved analytical methods now available. The microautoclave results indicate that a more complex model for correlating naphtha yields should be considered, which considers the detailed composition of the reactor slurry and probable higher rates of naphtha formation from the lower boiling liquid phase components. The "catalyst deactivation" factor in the above correlation may principally reflect the displacement of lower boiling gas oil components by higher boiling oils, having lower selectivity for naphtha formation, as the catalyst deactivates.

390-975°F Gas Oil Yields

Direct correlation of the yields of the gas oil fractions was not attempted, so that yields are estimated as the balance of the reacted coal less the correlated gas, naphtha, residual oil, and by-products yields, after appropriate elemental balances. The microautoclave tests on the gas oil fractions indicate a complex pattern, with the principal products of each fraction being gas oils of slightly lower boiling point with 55-75% of the converted material with boiling points within 200°F of the IBP of the fraction.

A correlation of the yield of 650-975°F gas oils was attempted assuming that this fraction was the sole product of residual oil conversion, which indicated effects of temperature and catalyst age (dependent on operating temperatures), giving the following correlating parameters:

Reaction Rate Constant	
Lbs/Hr/Ft ³ Reactor	
Fresh Catalyst at 825°F	12.4
Activation Energy, Kcal/g-mole	40
Deactivation Factor, D	
At 825°F	0.032
Activation Energy, Kcal/g-mole	47

$$K = K_o \exp(-D * \text{Age})$$

- K - Catalytic Rate Constant at Age
- K_o - Rate Constant for fresh catalyst
- D - Deactivation factor at temperature
- Age - Catalyst Age, Days of coal operations

Microautoclave tests on 100°F boiling range gas oil constituents of the bench unit product liquids, indicated an average reaction rate constant for the 650-975°F fractions at 825°F to products boiling below 650°F of 11 lbs/hr/ft³ liquid, not appreciably different from the above value correlated from the bench unit results. However, the microautoclave tests indicated a more complex pattern conversion of the gas oil components, with 20-30% of the reaction products having boiling points with 100°F of the IBP of the fraction, and 50-70% within 200°F of that temperature. The microautoclave tests indicated the constituents boiling below 650°F had a reaction rate about half of the that of the higher boiling fractions.

The correlated bench unit rate constant for the 650-975°F fraction was used in an estimate of the potential for complete elimination of the heavier gas oil components by adjusting the recycle oil composition. This projection was in

reasonable agreement with the experimental results in the "extinction" mode operation of Run 227-47(1-27).

By-Product Yields

Water and Carbon Oxides

The average yields of water and the carbon oxides, for Illinois Coal Operations, were the following as a percentage of the amount of converted coal:

Water	12.0
CO	0.1
CO ₂	0.3

Water yields were scattered, +/- 1 of the average yield, and there was no evident trend with catalyst age, within this range.

These average yields correspond to a total oxygen content of 10.9 W% of converted coal, slightly below the nominal oxygen content (by difference) of the feed coal to the bench unit runs, 11.0 W% of maf coal.

In the bench unit run with no catalyst in the second stage the water yields averaged about 1.5 W% lower than the above yield, and the CO₂ yield 0.2 W% higher, and the oxygen elimination to these products that was lower by 1.3 W% of converted coal. Nominal oxygen contents (again by difference) of the liquid products for the run with no catalyst in the second stage averaged about 0.7 W% lower than for operations with catalyst in that stage, supporting the apparent effect of catalyst upon oxygen conversion to water and carbon oxides.

Ammonia Yields

Calculate Ammonia yields (by nitrogen balance calculations) averaged 1.6 W% of converted coal, corresponding to nitrogen elimination of 1.3 W% of converted coal. The nitrogen elimination compares to the nitrogen content of the feed coal, 1.5 W% of maf coal, corresponding to the nitrogen retained in the liquefied components of 0.2 W% of the converted material. The nitrogen retained in the liquified products was affected by catalyst age, at about 0.15 W% of converted with relatively fresh catalyst and 0.25 W% of converted material after 20 days of coal operations.

Hydrogen Sulfide Yields

Calculated hydrogen sulfide yields averaged 2.6 W% of dry coal fed (equivalent to 2.5 W% sulfur), compared to the total sulfur content of the feed coal of 3.5 W%, of which 1.5 W% was pyritic sulfur. The hydrogen sulfide yield was then correlated as consisting of sulfur derived as follows:

0.98 times the organic sulfur in the reacted coal
0.5 times the pyritic sulfur in the feed coal.

Hydrogen Consumption and Hydrogen Contents

Hydrogen consumption can be calculated by an appropriate elemental balance using the hydrogen content of the feed coal and the hydrogen content of the broad product fractions for which correlations have been developed, with Age in days of coal operations.

$$\begin{array}{l} \text{C}_4\text{-390}^\circ\text{F Naphtha} \\ \text{W\% H}_2 = 14.49 - 0.023 * \text{Age} \end{array}$$

$$\begin{array}{l} \text{400-650}^\circ\text{F Gas Oil} \\ \text{W\% H}_2 = 11.92 - 0.046 * \text{Age} \end{array}$$

$$\begin{array}{l} \text{650-975}^\circ\text{F Gas Oil} \\ \text{W\% H}_2 = 10.46 - 0.056 * \text{Age} \end{array}$$

$$\begin{array}{l} \text{975}^\circ\text{F}^+ \text{Residuum} \\ \text{W\% H}_2 = 7.67 - 0.050 * \text{Age} \end{array}$$

The hydrogen content of the unreacted maf coal can be taken as the same as the hydrogen content of the maf feed coal.

The average distribution of light gases was in this proportion

$$\begin{array}{l} \text{C}_1 - 0.30 \\ \text{C}_2 - 0.35 \\ \text{C}_3 - 0.35 \end{array}$$

About 95% of the C₂ and C₃ products were saturated hydrocarbons. With this distribution the hydrogen content of the C₁-C₃ product then becomes 20.8 W%.

CORRELATION OF CLOVIS POINT MINE WYOMING COAL YIELDS

Correlations were based on first order kinetics, with respect to weight fraction concentration in the slurry phase in the respective first and second stage reactors. Slurry phase flows for both stages were based on the slurry flow from the hot separator, which was generally between 600 and 650°F.

Coal Conversion

The maf coal was characterized as consisting of two species of different reactivity. (This correlation which was done before those for the Illinois and Black Thunder Mine coal, did not consider the possibility of a third unreactive component, since there was no additional microautoclave testing of the product solids from the Clovis Point coal which indicated a limit to possible convertability of the other coals). The values of these parameters and first order rate constants for Clovis Point Mine coal were the following:

Coal Distribution	
High Reactivity	60 W%
Low Reactivity	40 W%
Unreactive	0 W%

Rate Constants at 750°F	
Lbs/hr/ft ³ Reactor	
Low Reactivity Constituent	18.5
High Reactivity Constituent	1050

Activation Energy, Kcal/mole	
Both Constituents	38.5

These parameters correlated the observed first stage and overall two stage conversions ranging from 32 to 92.5 W% of maf coal, within 1 W% for the overall conversion. If projected conversions are above this range, consideration should be given to modification of the correlation to incorporate the presence of an unreactive component, about 3 W% of maf coal as for the Black Thunder Mine Coal with appropriate adjustments of the proportion and rate constant for the low reactivity component.

975°F Residual Oil Yields

Residual oil yields were correlated as resulting from a portion of the primary reaction of the coal less secondary reaction of the residual oil following first order kinetics. The yield of residual oil increased as runs continued, which reflected an effect of catalyst deactivation, either as 1) a direct impact upon the

specific activity of the catalyst upon the cracking reaction or as 2) an indirect impact upon a hydrogenation/hydrogen transfer mechanism which promotes the cracking activity of the residual oil. The second mechanism would involve a hydrogenation of a hydrogen donor species, a hydrogen transfer reaction to the residual oil, and finally the cracking reaction of the residual oil itself, requiring far more correlating parameters than could be derived from the amount of Bench Unit Data available, and still would represent a complex resulting in a cracking rate related to catalyst age. A useful correlation was obtained using the first alternative as a correlation of the reaction rate constants against temperature and catalyst age.

Primary Residual Oil Yield	
W% of Converted Coal	100
Reaction Rate Constant,	
Lbs/hr/ft ³ Reactor	
Fresh Catalyst At 750°F	49
Activation Energy	
Kcal/gm mole	32
Catalyst Deactivation	
D in Deactivation equation*	
First Stage, 750°F	0.0077
Second Stage, 825°F	0.0365

$$* K = K_o \exp(-D * \text{Age})$$

D - Deactivation factor, with catalyst age (Age) in days of coal operations.

Correlation of later bench unit and microautoclave experiments with Illinois and Black Thunder Mine coals indicate the primary formation of residuum would be of the order of 60% of the converted coal.

C₁-C₃ Gas Yields

The C₁-C₃ gas yields were correlated as deriving in part from the primary reaction of the coal, and the balance as secondary formation from the constituents of the slurry phase in the reactor. The final correlating parameters were the following:

Primary C ₁ -C ₃ Formation W% of Converted Coal	3.8
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Secondary Slurry Phase Reaction Rate at 825°F, Lbs/hr/ft ³ Reactor	1.15
Activation Energy, Kcal/gm mole	57

These parameters reflect little impact either of catalyst deactivation upon gas yield, or of slurry phase composition. These correlating factors resulted in estimated gas yields for the five bench unit runs used in the correlation with a standard error of 1.1 W% of dry coal fed. However, the results of only three of those runs corresponded fairly closely to the correlated values. In the other two runs the apparent secondary rate constants were 2/3 and 4/3 the value given above. There was no apparent difference in other operating parameters could be associated with these deviations.

C₄-390°F Naphtha Yields

The formation of naphtha was correlated by means of reaction model similar that above for the formation of C₁-C₃ gases, in which there is some formation from the reaction of the coal and secondary formation from the reaction of the slurry phase components. There was an apparent decline in naphtha yields as the catalyst deactivated apparently more severe with higher second stage temperature, and lower naphtha yields for the operations where there was no catalyst in the second stage reactor.

The final values of the correlating parameters for the naphtha formation rate were the following;

Primary formation, W% of coal converted	12.3
Secondary formation Rate at 825°F, Lbs/hr/ft ³ reactor Fresh Catalyst	2.41
Activation Energy, Kcal/gram mole	57
Catalyst Rate Deactivation, D Deactivation factor	0.0109

$$K = K_o * (1 - D * \text{Age})$$

K - Catalytic Rate Constant at Age
 K_o - Rate Constant for fresh catalyst
 D - Deactivation factor
 Age - Catalyst Age, Days of coal operations

390-975°F Gas Oil Yields

Direct correlation of the yields of the gas oil fractions was not attempted, so that yields are estimated as the balance of the reacted coal less the correlated gas, naphtha, residual oil, and by-products yields, after appropriate elemental balances. The kinetics of the reaction of these gas oil components was summarized in the correlation of the yields of these constituents for the operations with Illinois No. 6 coal.

By-Product Yields

Water and Carbon Oxides

The average yields of water and the carbon oxides, for Clovis Point Mine coal Operations, were the following as a percentage of the amount of converted coal:

Water	20.8
CO	0.5
CO ₂	1.2

Water yields were scattered, +/- 2% of the average yield excepting in a single low severity operation giving 74.6% coal conversion where the water yield was higher by 4.5 W% of converted coal. There was no evident trend with catalyst age, within this range.

These average yields correspond to a total oxygen content of 19.6% W% of converted coal, about 90% of the nominal oxygen content (by difference) of the feed coal to the bench unit runs, 21.5 W% of maf coal.

The carbon oxides yields were very scattered from run to run, with an average of yield of CO₂ of 2.0% of converted coal in one run, and an average yield of 0.5% in another run. This variation could not be related to any of the operating variables, and is considered principally a result of analytical problems with this gas component.

Ammonia Yields

Calculated Ammonia yields (by forced nitrogen balance, when such analyses were available) averaged 1.03 W% of converted coal, corresponding to nitrogen elimination of 0.85 W% of converted coal. The nitrogen elimination compares to the nitrogen content of the feed coal, 1.0 W% of maf coal, corresponding to the nitrogen retained in the liquefied components of 0.15 W% of the converted material. The nitrogen retained in the liquefied products was affected by catalyst age, at about 0.05 W% of converted coal with relatively fresh catalyst and 0.25 W% of converted material after 20 days of coal operations.

Hydrogen Sulfide Yields

Calculated hydrogen sulfide yields averaged 0.84 W% of dry coal fed (equivalent to 0.80 W% sulfur), compared to the total sulfur content of the feed coal of 1.1 W%, of which 0.36 W% was pyritic sulfur. The hydrogen sulfide yield was then correlated as consisting of sulfur derived as follows:

0.94 times the organic sulfur in the reacted Coal
0.5 times the pyritic sulfur in the feed coal.

Hydrogen Consumption and Hydrogen Contents

Hydrogen consumption can be calculated by an appropriate elemental balance using the hydrogen content of the feed coal and the hydrogen content of the broad product fractions for which correlations have been developed, with age in days of coal operations.

$$\begin{array}{l} \text{C}_4\text{-390}^\circ\text{F Naphtha} \\ \text{W\% H}_2 = 14.2 - 0.023 * \text{Age} \end{array}$$

$$\begin{array}{l} \text{400-650}^\circ\text{F Gas Oil} \\ \text{W\% H}_2 = 11.2 - 0.046 * \text{Age} \end{array}$$

$$\begin{array}{l} \text{650-975}^\circ\text{F Gas Oil} \\ \text{W\% H}_2 = 10.8 - 0.039 * \text{Age} \end{array}$$

$$\begin{array}{l} \text{975}^\circ\text{F}^+ \text{Residuum} \\ \text{W\% H}_2 = 8.56 - 0.080 * \text{Age} \end{array}$$

The hydrogen content of the unreacted maf coal can be taken as the same as the hydrogen content of the maf feed coal.

The average distribution of light gases was in this proportion

$$\begin{array}{rcl} \text{C}_1 & - & 0.40 \\ \text{C}_2 & - & 0.30 \\ \text{C}_3 & - & 0.30 \end{array}$$

About 95% of the C₂ and C₃ products were saturated hydrocarbons. With this distribution the hydrogen content of the C₁-C₃ product then becomes 21.2 W%.

CORRELATION OF BLACK THUNDER MINE WYOMING COAL YIELDS

Correlations were based on first order kinetics, with respect to weight fraction concentration in the slurry phase in the respective first and second stage reactors. Slurry phase flows for both stages were based on the slurry flow from the hot separator, which was generally between 600 and 650°F.

Coal Conversion

The maf coal was characterized as consisting of three species of different reactivity, one of which was essentially unreactive in the range of the operating conditions that were used. Microautoclave testing of the Black Thunder Mine coal and of the product solids from the Bench Unit operation on this coal indicated a presence of species of different reactivity and a limit to possible convertability of the other coals. The values of these parameters and first order rate constants developed from the Bench Unit results and subsequent microautoclave tests with Black Thunder Mine coal were the following:

Coal Distribution	
High Reactivity	55 W%
Low Reactivity	42 W%
Unreactive	3 W%
Rate Constants at 750°F	
Lbs/hr/ft ³ Reactor	
Low Reactivity Constituent	17.1
High Reactivity Constituent	1000
Activation Energy, Kcal/mole	
Both Constituents	38.5

These parameters correlated the observed overall two stage conversions, ranging from 86 to 92.3 W% of maf coal, with a standard error of 0.5%. First stage coal conversions with a range of 65 to 87.7% were correlated with a standard error of 1.9%.

In Microautoclave tests with the product solids from Bench Unit operations with Black Thunder coal, consisting of materials remaining after 87.6 to 92.6% of the original coal, the further conversion appeared to be limited to about 95.5% of the original maf coal fed to the Bench Unit operation. The results of Microautoclave tests with fresh Black Thunder coal (using 4 grams of coal liquefaction derived gas oil and 1 gram of catalyst per gram of coal) supported a model similar to that used to correlate the Bench Unit results, although the values of correlating parameters were somewhat different, as follows:

Coal Distribution	
High Reactivity	59.5 W%
Low Reactivity	34.5 W%
Unreactive	5.6 W%

Rate Constants at 750°F	
Minutes ⁻¹	
Low Reactivity Constituent	0.024
High Reactivity Constituent	0.275

Activation Energy, Kcal/mole	
Both Constituents	41.7

The distribution of three coal species and the activation energy are reasonably in agreement with values correlated from the bench unit results. However, these apparent rate constants correspond approximately to rate constants at 750°F of 90 lbs/hr/ft³ and 1030 lbs/hr/ft³ for the low reactivity and high reactivity components, respectively (the form used in correlating the bench unit data), which indicates a rate constant for low reactivity component about five times that of the bench unit correlation. These results do not correlate with maceral analysis. Some of the macerals classified as inertinite are found to be convertible.

975°F Residual Oil Yields

Residual oil yields in the first and second stages were correlated as resulting from a portion of the primary reaction of the coal less secondary reaction of the residual oil in the slurry phase following first order kinetics. The yield of residual oil increased as runs continued, which interpreted as a direct effect of catalyst deactivation for the secondary reaction.

Primary Residual Oil Yield	
W% of Converted Coal	43
Reaction Rate Constant,	
Lbs/Hr/Ft ³ Reactor	
Fresh Catalyst At 750°F	33.3
Activation Energy	
Kcal/gm mole	6
Catalyst Deactivation	
D in Deactivation equation*	
First Stage, 750-817°F	0.0485
Second Stage, 766-825°F	0.0485

$$* K = K_o \exp(-D * \text{Age})$$

D - Deactivation factor, with catalyst age (AGE) in days of coal operations.

The above parameters fitted the first stage, second stage, and net process residual oil yields for Run 227-55 (CC-1), ranging from net formation of about 15 W% of dry coal (in the first stage) to a net reaction of 11% of dry coal (in the second stage) with a standard error of 0.3 W%. However, the above correlating parameters differ markedly from those obtained in the correlation of Illinois No. 6 coals particularly in three aspects: 1) the proportion of primary formation from the reacted coal is much lower than the 60-100% used in the other correlations; 2) the activation energy is much lower than the value of 32 Kcal/mole used in the other correlations; and 3) the rate of deactivation of the first and second stage catalysts are equal rather than a lower rate of deactivation for the first stage catalyst in other correlations (this pattern is possibly associated with the first stage/second stage temperature patterns of Run 227-55 (CC-1) where some of the operations had first stage temperatures that were higher than contemporary second stage temperatures, while in the other operations the first stage temperatures were consistently lower than the second stage temperatures).

Subsequent Microautoclave experiments with Black Thunder coal, the liquid products from its bench unit operations, and the recovered catalysts indicated correlating parameter corresponding more closely to those of the correlations with the other coals. These experiments indicated that first stage catalyst after 13 days operations at 750°F was 70% as active as the charged presulfided catalyst, while the second stage catalyst (after operation at 800°F) was 45% as activate for residual oil conversion. These results correspond to deactivation factors in the above equation of 0.027 and 0.061 at the respective temperatures.

However, the reaction model indicated from the Microautoclave tests was more complex than that used to correlate the bench unit results.

The residual oil formation in Microautoclave experiments with Black Thunder mine coal could not be fit by a single species first order model for the secondary reaction of residual oil formed from the reacted coal. It was necessary assume two species of residual oil again of different reactivities. With the limited data used it was not considered that the proportions of these residual oil species could be independently determined. For the purposes of correlation it was assumed that the more reactive residual oil species was solely derived from the more reactive coal species, with a like relation for the low reactivity species, and that the primary formation of the two residual oil species were the same proportions of the amount of reaction of the respective coal species. The final correlating parameters were the following:

Primary Residual Oil formation	- 57.3% of coal conver.
Rate Constants at 800°F	
Catalytic, High React. Residuum	- 0.0829 min ⁻¹
Non Catal., High React. Residuum	- 0.0101 min ⁻¹
Low Resid Rate/High Resid Rate	- 0.0417
Activation Energy, Kcal/mole	
Catalytic Data	- 18
Non-Catalytic Data	- 41

C₁-C₃ Gas Yields

The C₁-C₃ gas yields were correlated as deriving in part from the primary reaction of the coal, and the balance as secondary formation from the constituents of the slurry phase in the reactor. The final correlating parameters were the following:

Primary C ₁ -C ₃ Formation	
W% of Converted Coal	2.8
Secondary Slurry Phase Reaction	
Rate at 750°F, Lbs/hr/Ft ³ Reactor	0.236
Activation Energy, Kcal/gm mole	38

As correlated, no allowance was made for solids content of the slurry phase, which was about 10-15 W%, and the correlation could be modified to a slurry phase liquid components by increasing the secondary rate constant by a factor of 1.15.

Microautoclave tests with the liquid phase product from the second stage during the bench unit operations with Black Thunder coal and its gas oil components, had a gas formation rate of the whole liquid (including about 30% residual oil) about the same as the average of the gas formation rates of the gas oil components, indicating the gas formation from the residual oil was at the same rate as from the gas oil components. In these microautoclave tests the gas formation rate was about 0.7 W% of the oil for 30 minutes tests at 825°F with 0.25 grams catalyst/gram oil, corresponding to a gas formation rate of 0.9 lbs/hr/ft³ liquid, slightly below the above rate correlated from the bench unit results. In similar microautoclave tests without catalyst the gas formation was about 0.6 times the rate obtained with the catalyst.

C₄-390°F Naphtha Yields

The formation of naphtha was correlated by means of reaction model similar that above for the formation of C₁-C₃ gases, in which there is some formation from the reaction of the coal and secondary formation from the reaction of the slurry phase components. There was an apparent decline in naphtha yields as the catalyst deactivated apparently more severe with higher second stage temperature, and lower naphtha yields for the operations where there was no catalyst in the second stage reactor.

The final values of the correlating parameters for the naphtha formation rate were the following;

Primary formation, W% of coal converted	7.5
Secondary formation	
Rate at 750°F, Lbs/hr/ft ³ reactor	0.62
Activation Energy, Kcal/gram mole	36
Deactivation Factor (D), 1/day	0.013

These parameters correlated overall naphtha yields, ranging from 14.3 to 22.7 W% of dry coal fed, with a standard error of 1.1 W%. There was no apparent effect of catalyst age.

In Microautoclave tests using product liquid from bench unit operations with Black Thunder Mine coal described above in the correlation the gas formation rates, the tests with 600-900 boiling point gas oil fractions had the naphtha yields of 1.4-2.5 W% of the oil for 30 minutes tests at 825°F with 0.25 grams catalyst/gram oil. These yields correspond to naphtha formation rates of 1.8-3.2 lbs/hr/ft³ liquid, with the highest formation rate for the tests with the lowest boiling gas oil fractions. There naphtha formation rates are in the range of the correlated bench unit rate given above. Microautoclave tests with 900-975°F gas oil indicated virtually no naphtha formation. The microautoclave tests results are in the general range of the bench unit reaction rate to naphtha, but the rates are somewhat below the bench unit correlated rate. The GC simulated distillation method used in analysis of the microautoclave products was relatively crude and more reliable results would be obtained with the improved analytical methods now available. The microautoclave results indicate that a more complex model for correlating naphtha yields should be considered, which considers the detailed composition of the reactor slurry and probable higher rates of naphtha formation from the lower boiling liquid phase components.

390-975°F Gas Oil Yields

Direct correlation of the yields in the Bench Unit operations of the gas oil fractions was not attempted, so that yields are estimated as the balance of the

reacted coal less the correlated gas, naphtha, residual oil, and by-products yields, after appropriate elemental balances. The microautoclave tests on the gas oil fractions indicate a complex pattern, with the principal products of each fraction being gas oils of slightly lower boiling point with 55-75% of the converted material with boiling points within 200°F of the ibp of the fraction.

By-Product Yields

Water and Carbon Oxides

The average yields of water and the carbon oxides, for Illinois Coal Operations, were the following as a percentage of the amount of converted coal:

Water	21.8
CO	0.4
CO ₂	0.6

Water yields were scattered, +/- 2 of the average yield, and there was no evident trend with catalyst age within this range.

These average yields correspond to a total oxygen content of 20.1 W% of converted coal, slightly below the nominal oxygen content (by difference) of the feed coal to the bench unit runs, 21.1 W% of maf coal.

Ammonia Yields

Calculate Ammonia yields (by nitrogen balance calculations) averaged 1.10 W% of converted coal, corresponding to nitrogen elimination of 0.90 W% of converted coal. The nitrogen elimination compares to the nitrogen content of the feed coal, 1.1 W% of maf coal, corresponding to the nitrogen retained in the liquefied components of 0.20 W% of the converted material. The nitrogen retained in the liquified products was affected by catalyst age, at about 0.15 W% of converted material with relatively fresh catalyst and 0.3 W% of converted material after 20 days of coal operations.

Hydrogen Sulfide Yields

Calculated hydrogen sulfide yields averaged 0.35 W% of dry coal fed (equivalent to 0.33 W% sulfur), compared to the total sulfur content of the feed coal of 0.48 W%, of which 0.11 W% was pyritic sulfur. The hydrogen sulfide yield was then correlated as consisting of sulfur derived as follows:

0.95 times the organic sulfur in the reacted Coal
0.5 times the pyritic sulfur in the feed coal.

Hydrogen Consumption and Hydrogen Contents

Hydrogen consumption can be calculated by an appropriate elemental balance using the hydrogen content of the feed coal and the hydrogen content of the broad product fractions for which correlations have been developed, with Age in days of coal operations.

$$\begin{array}{l} \text{C}_4\text{-390}^\circ\text{F Naphtha} \\ \text{W\% H}_2 \quad = 14.23 \end{array}$$

$$\begin{array}{l} \text{400-650}^\circ\text{F Gas Oil} \\ \text{W\% H}_2 \quad = 12.09 - 0.038 * \text{Age} \end{array}$$

$$\begin{array}{l} \text{650-975}^\circ\text{F Gas Oil} \\ \text{W\% H}_2 \quad = 10.84 - 0.060 * \text{Age} \end{array}$$

$$\begin{array}{l} \text{975}^\circ\text{F}^+ \text{Residuum} \\ \text{W\% H}_2 \quad = 8.78 - 0.113 * \text{Age} \end{array}$$

The hydrogen content of the unreacted maf coal can be taken as the same as the hydrogen content of the maf feed coal.

The average distribution of light gases was in this proportion

$$\begin{array}{l} \text{C}_1 \quad - \quad 0.39 \\ \text{C}_2 \quad - \quad 0.28 \\ \text{C}_3 \quad - \quad 0.33 \end{array}$$

About 98% of the C_2 and C_3 products were saturated hydrocarbons. With this distribution the $\text{C}_1\text{-C}_3$ product contained 21.3 W% hydrogen.

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SECTION III COAL CONVERSION CORRELATIONS

Correlation of Coal Conversion - Illinois No. 6 Coal

Coal conversion in the individual stages of the two stage operation has been modelled by characterizing the raw coal in three fractions of high, low, and no reactivity, following first order CSTR kinetics. The resulting distribution and kinetic parameters, applying to both stages, give a reasonably close correspondence (0.12% standard deviation of the overall conversions) to the effects of changes in first and second stage temperatures and residence times, for the characteristic operations recycling 650°F+ solvent containing 20-40% residual oil. The few operations with all vacuum distillate solvent recycle had experimental conversions somewhat below those projected using this model.

The best fit for overall conversion has been obtained with the following values for the correlating parameters (*Figure 1*).

Coal Distribution	
High Reactivity	0.905
Low Reactivity	0.060
Unreactive	0.035
Rate Constants at 750°F	
Lbs/hr/ft ³ *	
Low Reactivity Constituent	11.95
High Reactivity Constituent	1,790
Activation Energy, Kcal/mole	
Both Constituents	53.8

* For weight fraction of component in slurry phase.

For the data of Runs 227-30 (I-12) and 227-32 (I-13), involving first stage temperatures of 725 to 775°F, and second stage temperatures of 800 to 825°F, the overall two stage conversions are projected with a nominal standard deviation of 0.13 W%, reflecting 96.5% reduction in variance (*Figure 2*). These parameters project first stage coal conversions with a nominal standard deviation of 1.6 W%, representing 74.6% reduction in variance (*Figure 3*). The projected effects of stage temperatures and residence times (slurry rates) upon overall two stage coal conversions correspond closely to the experimental trends (*Figure 4*).

When these parameters are extrapolated to an operation of Run 227-18 (I-8) with a first stage temperature of 650°F, the projected first stage conversion was 28.8% compared to an experimental value of 42.5%, with a projected overall conversion of 93.4% compared to an experimental value of 90.7%. Two considerations might be involved in these discrepancies. First, there is probably yet another coal component, effectively of extremely high reactivity, such as is evident in simple solvency tests at very low temperatures. A value of 15 W% for this hyperactive component would resolve the discrepancy between these projected and experimental first stage conversions. Second, this operation used vacuum distillate as solvent recycle in contrast to the solvent containing residual oil used in the other operations cited, which might have contributed to the low overall experimental conversion. However, other operations in Run 227-18 (I-8) which used filtered liquid recycle had experimental overall coal conversions that were 1.5% lower than the values projected using the model, 92.7% against 94.2%.

FIGURE 1

FIGURE 2

FIGURE 3

PARITY PLOT FOR CORRELATION
OF FIRST STAGE COAL CONVERSION

- Run 227-18(1-8)
- Run 227-30(1-12)
- Run 227-32(1-13)
- ▲ Run 227-33(1-14)

FIGURE 4

COMPARISON OF EXPERIMENTAL AND
CORRELATED TWO STAGE COAL CONVERSIONS

Curves Based On Correlation Model For
Indicated First and Second Stage Temperatures

Characterization of Reactive Coal Components by Means of Petrographic and Reflectance Analyses

Samples of the oil-agglomeration cleaned (containing 4.6 W% ash) and Illinois No. 6 coal received from the mine (containing 15.2 W% ash) used in Run 227-63 (CC-6), and the solids products from the run, were submitted to Penn State for petrographic and reflectance determinations.

Table 1 is the interpretation of these analyses, in terms of apparent degree of reaction in the Run 227-63 (CC-6) operations of the five reflectance cohorts which were reported by Penn State. They present an interesting pattern in that the low reflectance materials, corresponding to vitrinite, were highly converted (98.0-99.6%). The intermediate reflectance materials, more or less liptinite and semi-inertinite, were appreciably converted (80-92.5%), and highest reflectance materials, corresponding in quantity to inertinite, were converted to a degree, about 60%.

The pattern of the change in conversion of the various 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:

- A) Cohorts up to 1.0% reflectance (vitrinite) are virtually completely convertible;
- B) Cohorts between 1.0 to 2.5% reflectance (liptinite and semi-inertinite) are converted to a degree, which is effected by reaction severity. The increase in conversions of these cohorts with increased reaction severity corresponds closely to first order kinetics, assuming that the cohorts are completely convertible;
- C) Cohorts above 2.5% reflectance (inertinite), while reactive to a degree, contains a component which is apparently unaffected by process severity and is essentially unreactive, amounting to about 2.0% of the cleaned coal and 2.6% of the run-of-mine coal. This proportion of unreactive coal is closed to the values, 3-4%, indicated by correlation of the coal conversion data from CTSL™ operations on Illinois No. 6 coal.

TABLE 1
PETROGRAPHIC AND REFLECTANCE ANALYSES
RUN 227-63 (CC-6)

Coal Feeds and Product Solids

Coal Feed	Coal Feeds		Product Solids		
	HRI 5715 Rec'd from Mine	HRI 5716 Cleaned	Period 4 Cleaned	Period 9 Cleaned	Period 12 Rec'd from 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

Correlation of Coal Conversion Clovis Point Mine Wyoming Coal

In *Figure 5* the data for first stage conversion for Run 227-22 are plotted against first stage slurry rate (in effect the inverse of residence time) and first stage temperature. Considering the data at 750°F, it is evident that no simple functionality will rationalize the relatively low range of coal conversions obtained, when over 90% of the coal can be converted at sufficiently high severity, as reflected by the conversion levels attained in the second stage.

A simple first order reaction model assuming uniformly reactive coal could not fit the moderate range of first stage conversion over a range of four fold in residence time and allow for the high conversions obtained through two stages of operation.

A more involved model, retaining first order kinetics, assuming two reactive species, one termed high reactivity coal and the other low reactivity coal, was fitted to the coal conversion data. For evaluation of this model, it was assumed that the two species had the same temperature dependence in terms of the activation energy of the Arrhenius equation. The evaluation of the model required adjustment of the proportion of the two species (which were assumed to total 100% of the coal), the specific rate constants for each of the species, and the activation energy. An approximate least squares fit of the first and second stage conversion data was made by using a matrix of the values of these four parameters.

A reasonable fit to the data was obtained with the following values for the correlating parameters:

High Reactivity Coal	- 60% of maf coal
Low Reactivity Coal	- 40% of maf coal
High Reactivity Rate	- 1050 lbs/hr/ft ³ @ 750°F
Low Reactivity Rate	- 18.5 lbs/hr/ft ³ @ 750°F
Activation Energy	- 38.5 Kcal/mole

With these parameters, the square root of the mean square error of the projected first stage conversions was 3.3 %, and that of the projected second stage conversions was 1.1%.

Figure 5 compares the projected conversions using these correlating parameters with the experimental conversions for the first stage, as related to slurry rate and first stage temperature. *Figure 6* gives a similar comparison for the two stage conversions, as related to slurry rate and the two stage temperatures. The projections reasonably correspond to the experimental effects of the individual stage temperatures, and of the slurry rate (residence time).

WYOMING CLOVIS POINT COAL

FIGURE 5

First Stage Conversion - Run 227-22

Vs

Product Slurry Rate and First Stage Temperature

Curves are Correlated Relations, Based on 60% High Reactivity and 40% Low Reactivity Components. At Indicated Temperature

WYOMING CLOVIS POINT COAL
Two Stage Conversion - Run 227-22
Vs
Product Slurry Rate and Stage Temperature

Curves are Correlated Relations, Based on 60% High Reactivity and 40% Low Reactivity Components. At Indicated First Stage Temperature First Stage Slurry Rate Taken to be 5% Greater Than Second Stage Rate

Correlation of Coal Conversion - Black Thunder Mine Coal

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

<u>227-55(CC-1) Condition</u>	<u>Black Thunder 277-55(CC-1) Coal Conversion</u>	<u>Clovis Point Projected Conv.</u>
1	87.2	90.5
2	91.1,91.4	94.9
3	92.3,91.4	94.7
4	92.4,92.3	95.4
5	92.0,91.8	94.9
6	88.6,87.3	91.7
Average	90.4	93.7

In kinetic terms the difference in performance corresponds to reaction rate constants for the Black Thunder coal that were 66.3% of those for the Clovis Point coal.

Modified correlating parameters were developed for the first and second stage conversions during Run 227-55(CC-1), with reference to the previous work on Clovis Point Mine (Wyoming) coal and Illinois coals and microautoclave tests, which assumed the presence of the third coal species in the feed coal that was essentially unreactive at the usual liquefaction conditions. The following tabulation summarizes the results of this correlation:

	<u>Black Thunder</u>	<u>Clovis Point</u>
Coal Distribution, W%		
High Reactivity	55	60
Low Reactivity	42	40
Unreactive	3	0

Kinetic Parameters

Low Reactivity Constant

Lbs/hr/ft ³ @ 750°F	17.1	18.5
Act. Energy, Kcal/mole	38.5	38.5
High Rate/Low Rate	56.7	56.7

Figure 7 is a parity plot comparing the experimental two stage conversions for Black Thunder coal with the values project using the above kinetic parameters. The projections were made by means of a reaction system model with input of the coal feed rate, stage temperatures, recycle flows of PFL and TSB (containing recycle solids), the atmospheric overhead removal in generating to TSB, and the vapor flow from the second stage (to fix the slurry flow). The parity plot indicates very good correspondence of experimental and project values over the range of the bulk of the data which were used in developing the correlation and a reasonable extrapolation to the more extreme conditions represented by the early data of the run, where the solids concentrations had not reached the higher equilibrated levels reached later in the run. The standard error of the correlated two stage conversions was 0.5%.

Figure 8 is parity plot comparing the experimental and projected first stage conversions. The scatter from the parity line is slightly greater than for the two stage conversions, but still does represent a good correspondence over the full range of conversions obtained. The standard error of the correlated first stage conversions was 1.9%. The variation in first stage conversion was principally affected by changes in first stage temperature, so that the correspondence of experimental and projected effects indicates that the value of activation energy is close to the best fit.

In Run 227-57 (CC-2) the first stage reactor volume was twice that of the second stage in contrast to the equal volumes in all other bench unit operations. The pattern of first stage conversions in this run, and in comparable operations of Run 227-55(CC-1), corresponds fairly closely to that projected by the coal conversion model developed from the results of the earlier run, as follows:

	<u>Proj. Conv.</u>	<u>Experi. Conv.</u>
Run 227-57(CC-2)		
Condition 1	75.8	76.4
Condition 2	71.9	72.3
Condition 3	66.7	68.3
Run 227-55(CC-1)		
Condition 1	68.1	65.4
Condition 2	68.8	68.9
Condition 6	64.4	66.3

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

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

	<u>Proj. Conv.</u>	<u>Experi. Conv.</u>
Run 227-57(CC-2)		
Condition 1	89.5	88.4
Condition 2	90.6	89.4
Condition 3	87.8	85.7
Run 227-55(CC-1)		
Condition 1	86.8	87.2
Condition 2	91.5	91.4
Condition 6	88.5	87.3

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

Microautoclave tests on solids products from CTSL™ operations on Black Thunder Mine coal

While adequate correlations of the CTSL™ bench unit coal conversions have been obtained by this model, the definition of the unreactive portion represents some extrapolation of the experimental results. Partially converted materials derived from the CTSL™ operations and fresh coal were tested in the microautoclave to obtain additional insight into the definition of the convertibility of the coal.

Table 2 summarizes the results of microautoclave tests on filter cake products from the CTSL™ operations using the Black Thunder Mine coal. *Table 3* summarizes the results of similar tests on the fresh coal and on solids samples obtained from the first stage during the CTSL™ operations, these samples being of a lower degree of conversion than the filter cake product. The L-721 solvent

used in most of these tests is a heavy distillate produced at the Wilsonville Coal Liquefaction facility processing Illinois No. 6 coal.

In *Table 2*, in tests at 825°F, a solids feed that had been 92.6% converted in the CTSL™ operation was increased to 94.5% converted material in a 30 minute test, and to 95.1% converted material in a 60 minute test. A solids feed that had been 87.6% converted in the CTSL™ operation was increased to 93.1% converted in a 30 minute test, and to 94.3% converted in a 60 minute test. This pattern of incremental conversions indicates a practical limit of convertibility of about 95.5% of the original coal, assuming first order kinetics apply and only a single reactive species remained in solids that were tested.

A microautoclave test using 227-55-23A PFL as solvent in place of the L-721 solvent increased the converted material by about 0.3% more than had been obtained with the L-721 solvent. While this nominally indicates about 50% greater reaction rate with the PFL it is uncertain whether this is a significant difference, analytically and operationally. A test for 60 minutes at 750°F increased the conversion level by a slightly greater degree than obtained in a 30 minute test at 825°F, which difference corresponds to an activation energy of about 16 kcal/mole.

In *Table 3*, in 30 minute catalytic tests at 825°F, fresh coal was converted to a degree, to 92.4% converted material, almost as great as was obtained with the partially converted materials discussed above. This factor indicates that the fresh coal contains a species that is of considerably higher reactivity than the principal reactive species remaining in the partially converted materials discussed above. A similar test without catalyst resulted in an appreciably lower degree of conversion, to 75.9% converted material. A 60 minute catalytic test with fresh coal at 750°F resulted in a degree of conversion, 85.2%, appreciably less than obtained in the 825°F test.

Tests with solids from the CTSL™ first stage, having a degree of conversion up to 25% lower than that of the second stage product solids discussed above, resulted in a final degree of conversion within 0.4% of that obtained with the second stage product solids. This pattern suggests that the higher proportion of unconverted material in the first stage sample is principally of the high reactivity species.

Microautoclave Kinetic Test Matrix with Black Thunder Mine Coal

The results for a kinetic Microautoclave test matrix with the HRI 5887 Black Thunder mine coal are summarized below. These tests were at 2,000 psi H₂ pressure, using 4 grams of HRI 5198 coal liquefaction product heavy distillate per gram of coal, and presulfided Shell S-317 catalyst.

<u>Temp., °F</u>	<u>Time, Min.</u>	<u>Cat/Coal</u>	<u>Conv., % of MAF Coal</u>	<u>Residual Oil % of Conv. Coal</u>
750	30	0	57.8	54.5
800	30	0	75.6	46.2
800	60	0	84.5	39.9
825	30	0	82.9	41.1
750	30	1	74.0	25.2
800	30	1	91.4	22.6
800	60	1	94.1	18.1
825	30	1	93.3	20.0

These results follow a definite kinetic pattern with increased coal conversion and decreased residual oil formation with increased reaction severity (test temperature or test time) and in the tests with catalyst. However, a simple first order model involving single reactive species will not fit the results.

The coal conversion data for both the catalytic and non-catalytic tests would not fit a first order kinetic model assuming a single reactive species. For such a model, the catalytic data indicated a reactive component amounting to 94.2% of maf coal, compared to 86.1% indicated by the non-catalytic data.

The data were fit more closely assuming two reactive species of different reactivity along with an unreactive species, giving a reasonable fit for both the catalytic and non-catalytic data. The final correlating parameters were the following:

Coal Composition	
High Reactivity	59.5%
Low Reactivity	34.8%
Unreactive	5.6%

Reaction Rates

High Reactivity @ 800°F	0.951 Min ⁻¹
Low React./High React.	0.0869
Non-Cat Rate/Cat Rate	0.251
Activation Energy	42 Kcal/mole

The following tabulation compares the experimental and correlated coal conversions:

Temp., °F	Time, Min.	Cat/Coal	Conversion, % of Maf Coal	
			Experimental	Correlated
750	30	0	57.8	57.8
800	30	0	75.6	75.6
800	60	0	84.5	84.4
825	30	0	82.9	83.0
750	30	1	74.0	77.4
800	30	1	91.4	91.5
800	60	1	94.1	94.1
825	30	1	93.3	94.0

The characterization of the proportion of the three coal species, as well as the activation energy, is close to that obtained from correlation of bench-scale conversion results. However, the relative reactivities of the two reactive components, here by a factor of 11.5, is much lower than the value in the bench unit correlation, a factor of 55.

FIGURE 7

PARITY PLOT FOR CORRELATED CONVERSIONS

Overall Conversion — Run CC-1, Black Thunder Coal

PARITY PLOT FOR CORRELATED CONVERSIONS

First Stage Conversion – Run CC-1, Black Thunder Coal

TABLE 2

RESULTS OF MICROAUTOCLAVE PROGRAM TO MODEL COAL CONVERSION

Testing Product Solids from Black Thunder Coal in Run 227-55

Microautoclave Run	5	25	27	6	26	31
Feed	----- 227-55-6 ----- Filt. Cake*			----- 227-55-16 ----- Filt. Cake*		
Microautoclave Cond.						
Temperature, F	825	825	750	825	825	825
Time, Minutes	30	60	60	30	60	30
Pressure, psig	2000	2000	2000	2000	2000	2000
Gas	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂
Feed, grams	2.001	2.002	2.002	2.002	2.001	2.001
Catalyst HRI	5359P	5359P	5359P	5359P	5359P	5359P
Grams	2.01	2.00	2.02	2.00	2.01	2.01
Solvent	L-721	L-721	L-721	L-721	L-721	23A PFL
Grams	8.00	8.00	8.02	8.02	8.04	8.04
Loss from Autoclave, Grams	0.81	0.37	0.28	1.28	0.43	0.59
Recovered Solids*, Grams	1.2657	1.2610	1.3760	1.4067	1.6192	1.5284
W% of Feed	63.28	62.98	68.73	70.35	80.92	76.41
Recovered Solvent, Grams	8.67	8.75	9.25	7.48	8.11	7.62
THF content, W% (TGA Anal)	18.15	6.81	9.32	10.9	2.95	0.64
Residual Oil, W% (TGA)	2.10	2.12	1.93	2.94	1.39	31.11
Solids plus THF Free Oil, gms	8.36	9.41	9.76	8.07	9.49	9.10
Loss from charge, grams	1.64	0.59	0.24	1.93	0.51	0.90
Feed Analysis						
Ash, W%	-----	36.13	-----	-----	49.03	-----
Carbon, W%		48.97			38.65	
Hydrogen, W%		2.68			1.97	
Nitrogen, W%		0.81			0.47	
Sulfur, W%		0.91			1.24	
Sulfur in Ash, W%		2.27			2.13	
SO ₃ -Free Ash, W%		34.08			46.42	
Product Solids Analysis*						
Ash, W%	51.02	55.97	51.84	56.79	59.90	58.31
Carbon, W%		31.78	36.01		30.87	30.82
Hydrogen, W%		1.73	1.99		1.67	1.58
Nitrogen, W%		0.40	0.55		0.35	0.36
Sulfur, W%		1.68	1.41		1.60	1.60
SO ₃ -Free Ash, W%**	48.12	52.89	48.99	53.76	56.60	55.10
Ash Balance, W%	89.34	97.57	98.80	81.39	98.85	90.79
Degree of Conversion,						
Percent Of Original maf Coal						
Microautoclave Feed	-----	87.63	-----	-----	92.62	-----
Microautoclave Product	93.11	94.30	93.34	94.50	95.10	94.78
Residual Oil recovered, grams	0.182	0.185	0.178	0.220	0.113	
Percent of Coal Converted	31.1	26.0	29.0	80.4	31.2	

* THF Washed

L-721 - Wilsonville Heavy Distillate

** Products taken to have 2.2 W% sulfur in ash.

23A PFL - Recycle Solvent Run 227-55 Period 23A

*** Excess ash taken to be catalyst with 82.25% ash and 17.75% organics.

Modlconv.tab

Testing Black Thunder Mine Coal and First Stage Solids from Run 227-55

Microautoclave Run	7	8	28	29	30	32
Feed	-----HRI 5630----- Black Thunder Coal			-----First Stage Solids----- Pd 7A Pd 17A Pd 17A		
Microautoclave Cond.						
Temperature, F	825	825	750	825	825	825
Time, Minutes	30	30	60	30	30	30
Pressure, psig	2000	2000	2000	2000	2000	2000
Gas	H ₂	H ₂	H ₂	H ₂	H ₂	H ₂
Feed, grams	2.001	2.001	2.001	2.001	2.001	2.001
Catalyst HRI	-----	5359P	5359P	5359P	5359P	5359P
Grams	0	2.00	2.02	0	2.00	2.02
Solvent	L-721	L-721	L-721	L-721	L-721	23A PFL
Grams	8.00	8.00	8.02	8.00	8.00	8.02
Loss from Autoclave, Grams	0.67	1.02	0.39	1.26	0.18	1.20
Recovered Solids*, Grams	0.6132	0.2927	0.5002	0.6531	0.9032	1.2429
W% of Feed	30.66	14.63	25.00	32.65	45.16	62.14
Recovered Solvent, Grams	8.87	8.81	8.90	8.56	9.20	7.46
THF content, W% (TGA Anal)	9.6	17.0	2.97	5.38	5.76	1.45
Residual Oil, W% (TGA)	7.72	2.26	4.33	5.93	8.89	28.93
Solids plus THF Free Oil, gms	8.63	7.60	9.13	8.75	9.57	8.59
Loss from charge, grams	1.37	2.40	0.87	1.25	0.43	1.41
Feed Analysis						
Ash, W%	-----	7.15	-----	16.79	38.79	38.79
Carbon, W%		67.70		65.48	47.39	47.39
Hydrogen, W%		4.54		4.04	2.48	2.48
Nitrogen, W%		1.05		1.27	0.75	0.75
Sulfur, W%		0.48		0.56	1.12	1.12
Sulfur in Ash, W%		6.35		2.81	2.59	2.59
SO ₃ -Free Ash, W%		6.01		15.61	36.27	36.27
Product Solids Analysis*						
Ash, W%	26.34	52.17	43.04	52.62	58.33	56.45
Carbon, W%			45.05	37.78	32.66	33.31
Hydrogen, W%			2.80	1.48	1.48	1.65
Nitrogen, W%			0.97	0.47	0.47	0.44
Sulfur, W%			2.00	1.68	1.68	1.76
SO ₃ -Free Ash, W%**	24.89	49.30	40.67	49.73	55.12	53.34
Ash Balance, W%	126.98	120.01***	167.93***	104.33	68.56	91.34
Degree of Conversion, Percent Of Original maf Coal						
Microautoclave Feed	0.00	0.00	0.00	65.43	88.76	88.76
Microautoclave Product	75.87	92.38	85.18	93.53	94.79	94.41
Residual Oil recovered, grams	0.684	0.199	0.385	0.508	0.818	
Percent of Coal Converted	45.1	11.3	19.3	36.1	108.1	

* THF Washed

L-721 - Wilsonville Heavy Distillate

** Products taken to have 2.2 W% sulfur in ash.

23A PFL - Recycle Solvent Run 227-55 Period 23A

*** Excess ash taken to be catalyst with 82.25% ash and 17.75% organics.

Modlconv.tab

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SECTION IV MODELLING OF THE FORMATION AND CONVERSION OF RESIDUAL OILS

Residual Oil Modelling

The overall two-stage yield of residual oil was modelled on the basis of the performance of the separate stages, which had been estimated using the analyses of first-stage samples which were obtained for equilibrated CTSL™ operations.

Residual Oil Yields - Illinois No. 6 Coal

A preliminary modelling effort was made assuming the residual oil in the operating system consisted of a single species of uniform composition and reactive properties. While such a simple model developed insights into the pattern of reactions involved, it did appear to have some short-comings most notably in rationalizing the performance of an operation in which there was no catalyst in the second stage. The correlations were developed using the data of Run 227-30 (I-12) (with first stage temperatures of 750°F, and second stage temperatures of 825°F) and Run 227-32 (I-13) (with first stage temperatures of 725-775°F, and second stage temperatures of 810-816°F). In both runs first and second stage performance was evaluated using the analyses of first stage slurry samples.

These samples indicated net formation of residual oil in the first stage between 15 and 32% of dry coal fed, and net residual oil conversion in the second stage between 3 and 26 W% of dry coal.

The patterns follow a general model in which the residual oil is formed as a portion of the primary liquefaction of the coal, and subsequently undergoes secondary reaction to lighter products. Some degree of this secondary reaction occurs apparently in both stages, but there is net formation of residual oil in the first stage because of the high proportion of primary coal conversion and primary residual oil formation in that stage, and there is net reaction of residual oil in the second stage because of the low proportion of primary coal conversion in that stage.

The results of Run 227-30 (I-12) were interpreted on the basis of a kinetic model assuming that residual oil formation was a fixed proportion of the products of the primary conversion of coal, and reacted to lighter products following first order CSTR kinetics. The following is the basic equation for the model considering the parameters for an individual stage:

$$\text{Netres} * F = Q * F * \text{Conv} - K * \text{Concres}$$

Netres	- Net Residuum Formation, W% of Dry Coal Fed
F	- Dry Coal Feed Rate to Operation, Lbs/Hr/Ft ³
Q	- Primary Residuum Formation Weight Fraction of Converted Coal
Conv	- Coal Conversion in Stage, W% of Dry Coal Fed
K	- Reaction Rate Constant, Lbs/Hr/Ft ³
Concres	- Concentration of Residuum, W% of Slurry Leaving Stage

This equation can be transformed to the following form:

$$\text{Netres/Conv} = Q - K * \text{Concres}/(F * \text{Conv})$$

This latter equation indicates that a plot of Netres/Conv against Concres/(F * Conv) should be linear with an intercept on the Y-axis corresponding to Q, the proportion of residuum formed from the primary reaction of coal, and a slope corresponding to the reaction rate constant (assuming, of course, that there is no catalyst deactivation so that there is a fixed reaction rate constant for the data considered).

Figure 1 summarizes the residual oil formation in the first stage for the operations of Run 227-30 (I-12) in terms of the latter equation. The indicated proportion of primary residuum formation is 60.5% of the converted coal, and the rate constant for secondary residual conversion is 13.6 Lbs/Hr/Ft³, calculated by least squares fitting the data.

Figure 2 plots against catalyst age the apparent reaction rate constant for the secondary reaction of residuum in the first stage, taking the primary formation as 60.5% of the coal converted in the stage. There is little indication in this figure of catalyst deactivation in the first stage with respect to this reaction, although the limited data do not entirely eliminate the possibility of some deactivation.

A similar analysis of the second-stage data to determine the formation of residuum from the primary conversion of coal is not practical for two reasons. Firstly, the amount of coal reaction in the second stage was very low so that the residuum deriving from the coal reaction was only a minor fraction of the net change in residuum quantity in that stage. Secondly, there was indication of considerable catalyst deactivation in the second stage, negating the critical requirement of a fixed reaction rate constant. Accordingly, the second stage results respecting residual oil formation were interpreted by assuming that the formation of residuum from the coal reaction in this stage was the same as indicated by the first stage results, 60.5% of coal converted, and using this quantity in calculating the reaction rate constant for secondary reaction of residuum in the stage.

Figure 2 includes the resulting reaction rate constants for secondary reaction of residuum in the second stage plotted against catalyst age. This plot indicates substantial catalyst deactivation in the course of operations. The correlating line in the figure is at least squares fit of a logarithmic decline of the rate constants and indicates an 85% decline in the rate constant between a catalyst age of 200 lbs coal/lb catalyst and a catalyst age of 1,200 lbs coal/lb catalyst (31 days of coal operations).

For Run 227-32 (I-13), Figure 3 summarizes the secondary residuum reaction rate constants, using the 60.5 W% factor for primary formation from coal, for the two stages as related to catalyst age and the second stage temperatures involved. The rate constants in the second stage follow a fairly regular downward trend with increasing catalyst age, with an indicated increase when the second stage temperature was increased from 800 to 816°F. For the first stage, there is no indication of deactivation for this reaction, with generally higher rate constants indicated at a higher second-stage temperature.

The final correlation, with parameters selected to fit to the average yields for the first stage, second stage, and the two stages, was developed by applying the parameters in a material balance/kinetic model program calculating first stage, second stage, and overall yields with input of the first- and second-stage temperatures, coal feed rate, solvent/recycle rate, and atmospheric distillate removal from the recycle solvent. The correlating parameters were first-stage rate constant at 750°F, activation energy for temperature dependence to fit the rate constants for both stages, and a deactivation factor (D) against catalyst age (A) for the second stage rate constant, by an equation of the form:

$$K = K_o \exp(-D * A)$$

The developed values of these parameters using 60.5% primary parameters of residuum, which follow the curves shown in Figures 2 and 3, were the following:

Rate Constant, Lbs/Hr/Ft ³ at 750°F	11.6
Activation Energy, Kcal/Mole	32.0
Deactivation Factor (D), Lb Catalyst/Lb Coal (Second Stage at 800-835°F)	0.0019

The results of Run 227-33 (I-14), where there was catalyst only in the first stage, give some support to the patterns of residual oil reactions correlated above. Without catalyst in the second stage overall residual oil yields were 2-4 W% of dry coal higher than those at comparable conditions where there was catalyst in the second stage. The apparent rate constants for the secondary reaction of residual oil in the second stage were generally lower than when there was catalyst in the second, as shown in the following tabulation:

Run	I-14	I-12	I-14	I-13	I-14	I-13
Condition	1	1	2	3	3	6
Second Stage Catalyst	None	1A	None	1C	None	1C
First Stage, °F	751	750	776	776	775	776
Second Stage, °F	824	825	800	800	840	816
Catalyst Age, Lb/Coal/Lb	303	363	407	492	536	775

Rate Constants,
Lbs/Hr/Ft³

First Stage	9.3	15.2	17.1	16.7	16.7	18.1
Second Stage	22.9 (16.8)*	29.8	4.8	9.4	9.1	15.8

* Second stage rate constant assuming first stage rate constant of 15.2 to estimate residual oil concentration in the feed to the second stage.

For Run I-14 in Conditions 2 and 3 the apparent second stage rate constants were lower than obtained with highly deactivated catalysts, and the first stage rate constants are about the same as obtained in Run I-13. However, for Condition 1 of Run I-14 the apparent second stage rate constant was relatively high, in the range calculated for moderately deactivated catalyst, even after adjustment for a possible error in the interstage residual oil analysis.

FIGURE 1

CORRELATION OF FIRST-STAGE RESIDUAL OIL FORMATION

RUN 227-30(I-12)

Yields Assuming First Stage Vapors Equals Second Stage Vapors
First Order Kinetics Model for Secondary Reaction of Residuum

FIGURE 2

APPARENT FIRST- AND SECOND-STAGE SECONDARY RESIDUUM REACTION RATES

RUN 227-30(1-12)

Yields Assuming First Stage Vapors Equals Second Stage Vapors

First Order Kinetics Model
Primary Formation of Residuum - 60.5% of Converted Coal
(Based on First-Stage Correlation)

FIGURE 3

APPARENT FIRST- AND SECOND-STAGE RESIDUUM REACTION RATES

RUN 227-32(I-13)

Assumed Primary Formation - 60.5% of Converted Coal

Kinetic Correlation of Residual Oil Yields for Clovis Point Coal Operations

The kinetic correlation of the residual oil yields for CTSTM operations using Clovis Point Mine coal was developed using the apparent first and second stage performances based on the analyses of samples of the first stage slurries in four runs, 227-22, 227-25, 227-26 and 227-27. Sampling and analytical techniques were being developed at this time, which may be the principal reason for the considerable scatter of the results which is evident in these correlations.

In all cases, there was net residual oil formation in the first stage, and net residual oil consumption in the second stage. However, there were indications of some actual secondary reaction of residual oil in this first stage, since the net formation in that stage was appreciably lower for operations at long residence times than for operation at short residence times in that stage. For example, in the operation shortest residence time (Run 227-22 Period 2) net first stage residual oil formation was 62% of the coal converted in that stage, and in the operation at long residence time (Run 227-27, Period 17) this formation was 14% of the coal converted in the stage.

In general terms the changes in residual oil yields for the two stages correspond to a model of a major portion of the conversion of coal being to residual oil, followed by secondary reaction to lighter products. However, definition of the this proportion of primary formation could not be made with any precision. *Figure 4* correlates the apparent first stage formation of residual oil in Run 227-22 against a reaction severity parameter, which should be directed at zero reaction severity to a value equal to the proportion of primary residual oil produced in the primary reaction of the coal. A least square fit of the data at 750°F first stage temperature is shown in the figure, and correlating curves for the other temperatures (650-775°F) assuming an activation energy of 19.5 Kcal/mole using the intercept value for the data at 750°F. The best fit indicated an intercept corresponding to formation of residuum of 81% of converted coal, and a second reaction rate for the residuum of 39 lbs/hr/ft³. The correlation is poor, with only 54% statistical confidence level, and an a-priori assumption of 100% primary formation does not result in a significantly poorer correlation than obtained using 81% primary formation. The value of 100% primary formation was used in further interpretation of the experimental data.

The values of apparent residual oil secondary reaction rate constants for both first and second stage operations are correlated against catalyst age in *Figures 5 through 8*.

In *Figure 5*, for first stage operations of the four runs at 750°F with catalyst age taken as hours of coal operations, there is no definite trend with increasing catalyst age. The least squares fit indicated in the figure shows a small downward trend with increasing catalyst (about 20% deactivation over 700 hours

of coal operations, but as indicated by the 95% confidence range shown the figure, this trend is not significantly different from zero, and there is a 2.5% probability of a deactivation as great as 60% over 700 hours of coal operations. The considerable scatter in *Figure 5* is largely in the Run 227-22 and Run 227-25 data. The results of Runs 227-26 and 227-27 are more regular, as shown in *Figure 6* but even here the confidence range of the deactivation trend is about the same as noted in *Figure 5*.

Figure 7 summarizes the second stage secondary reaction rate constant for the four runs (again taking the primary formation as 100% of converted coal) against catalyst age. While the data scatter considerably, there is a definite downward trend with increasing catalyst age. There may have been significant differences between the result for the four runs, with higher rates of deactivation for Runs 227-26 and 227-27 than for Runs 227-22 and 227-25. *Figure 8* summarizes the second rate constants for Runs 227-26 and 227-27, alone.

Figure 7 includes the least squares fit through the pooled data of the second stage rate constants for the four runs summarized by an equation of the form:

$$K = K_o * \exp (-D * \text{Age})$$

- K - Rate Constant, lb/hr/ft³
- K_o - Nominal Fresh Catalyst Rate Constant
- D - Deactivation Factor
- Age - Catalyst Age, Hours of Coal Operations

For the pooled data, K_o has a value of 115, and D a value of 0.001524, and the indicated regression against catalyst age is statistically significant with a confidence level of 99.70%.

Treating the runs separately, with a common value of the deactivation factor, gives an improved fit, with 99.75% confidence level for the indicated differences in the performance of the runs. Also, considering that the deactivation may have been different for the four runs gives a further improvement in the fit, with 95.7% confidence level for the consideration of differing deactivation factors, the following tabulation summarizes the correlating equations for the various cases:

Case	Ko	D
Pooled Data	115.0	0.001524
<u>Common Deactivation</u>		
Run 227-22	171.6	0.001894
Run 227-25	143.0	0.001894
Run 227-26	81.9	0.001894
Run 227-27	86.1	0.001894
<u>Differing Deactivation</u>		
Run 227-22	153.2	0.001562
Run 227-25	108.0	0.001192
Run 227-26	144.0	0.004270
Run 227-27	140.2	0.003623

Actually, the apparent differences in performance are between the results of Run 227-22 pooled with Run 227-25, and Run 227-26 pooled with run 227-27. That is, statistical analysis indicates only an 83.3% confidence level for the apparent difference between the Run 227-22 and Run 227-25 results (with only 37.2% confidence level for the deactivation slopes for these two runs); similarly, there is a 51.2% confidence level for the difference in performance of Runs 227-26 and 227-27, and 36.1% confidence level for the difference in deactivation slopes for these two runs.

Again, the second stage performance in these terms was more regular for Run 227-26 and 227-27 than for the other runs. *Figure 8* summarizes the second stage apparent residual oil reaction rate constant against catalyst age for Runs 227-26 and 227-27.

The indicated rates of deactivation for the two stages correspond to a substantially greater deactivation for the second stage. The least squares fit for the pooled data indicated a second stage deactivation factor 4.8 times that of the first stage. For the Run 27-26 data this ratio was 5.9 times, and for the run 227-27 data this ratio was 5.5 times. Statistical analysis indicates a 97.4% confidence level in the difference in two stage deactivation factors of run 227-26, and a 93.4% confidence level for the data of Run 227-27.

In summary, for apparent residual oil conversion activity, there was no definite deactivation in the first stage for this function, but a more certain indication of deactivation in the second stage.

The rate constant, and deactivation factors used to project the yields for the various operations of Run 227-22 and 227-25. These calculations required the

stage temperatures, coal feed rate, slurry rates from the two stages, the amount of residual oil recycled and the proportion of coal reacted in the two stages. *Figure 9* is a parity plot of the projected residual oil formations in each of the two stages against experimental formation. The relative performance of the two stages is fairly well reflected by the projections. However, considering the results for each of the two stages separately, the projected changes in residual oil yield over the range of severity involved appears to be somewhat less than was indicated by the experimental data.

CORRELATION FOR SECONDARY RESIDUUM REACTION PARAMETERS

Run 227-22 - First Stage Operations

Least Squares Fit for 750°F Operations
Other Temperatures Related on Basis of 19.5 Kcal Activation Energy

APPARENT FIRST STAGE REACTION RATE CONSTANT FOR RESIDUAL OIL CONVERSION

FIGURE 5

Primary Residuum - 100% of Converted Coal
First Stage Temperature - 740-750°F

○ Run 227-22

◇ Run 227-26

● Run 227-25

□ Run 227-27

APPARENT FIRST STAGE RESIDUAL OIL REACTION RATE CONSTANTS

FIGURE 6

Runs 227-26 and 227-27

○ Run 227-26

● Run 227-27

APPARENT SECOND STAGE REACTION RATE CONSTANT FOR RESIDUAL OIL CONVERSION

FIGURE 7

Primary Residuum - 100% of Converted Coal

APPARENT SECOND STAGE RESIDUAL OIL REACTION RATE CONSTANTS

FIGURE 8

Runs 227-26 and 227-27

○ Run 227-26

● Run 227-27

PARITY PLOT FOR CORRELATED RESIDUAL OIL YIELDS FIRST and SECOND STAGE - RUNS 227-22 and 227-25

Data for Operations with Oven Dried Coal

○ Run 227-22 First Stage	● Run 227-22 Second Stage
□ Run 227-25 First Stage	■ Run 227-25 Second Stage

Calc. Bases: Primary Residuum - 100% of Converted Coal
 Residuum Rate Constant at 750°F - 71.95 Lbs/Hr/Ft³
 Activation Energy for Rate Equation - 19.51 Kcal
 Deactivation Factor at 750°F - 0.000743 per Hour
 Activation Energy for Deactivation Factor - 22.17 Kcal

Residual Oil Formation - Black Thunder Mine Coal

Kinetic Correlation of Residual Oil Formation

The kinetic correlation of the residual oil formation from two-stage liquefaction of Black Thunder Mine coal was based on the analysis of first and second stage slurry samples collected in Run 227-55 and 227-57.

The formation of 975°F residual oil in each of the stages have a general pattern of a moderate formation in the first stage, and net reaction in the second stage. For the Condition 2 through 6 operations of Run 227-55 (CC-1) the residual oil formation in the first stage ranged from 7.3 to 13.9 W% of dry coal feed. There was a considerably higher formation, 23.5 W% indicated for the Condition 1 operations, but there were other anomalies in the Condition 1 sample, particularly the sulfur contents, and this result has been discounted in the interpretation of these data.

The net yield of residual oil in the second stage ranged from -10.9% of dry coal to -2.8 W% (excepting the Condition 1 result). This pattern of first stage/second stage residual oil formation and reaction corresponds to a model where the primary reaction of the coal forms some residual oil, which under goes a secondary reaction to lighter products. The net formation of residual oil in the first stage reflects the relatively high proportion of coal reacting in that stage, with consequent residual oil formation greater than the amount of secondary reaction. The net reaction of residual oil in the second stage reflects the lower proportion of coal reacted in that stage. There is apparently a significant amount of secondary reaction of the residual oil even at relatively low reactor temperatures, notably the performance of the second stage in the Condition 4 operation with that stage at 767°F, with the greatest net consumption of residual oil for the reliable experimental results.

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

$$K_1 = F * (C_1 * S - R_1) / C_{res1}$$

$$K_2 = F * (C_2 * S - R_2) / C_{res2}$$

$$K_2/K_1 = \text{Exp}(\Delta E * (T_2 - T_1) / (T_1 + 460) / (T_2 + 460) / 1.987)$$

$$K_1, K_2 = \text{First and second stage reaction rate constants}$$

F	=	Dry Coal Feed rate
C1, C2	=	First and second stage coal reacted, W% of dry coal
R1, R2	=	First and second stage residual oil formation, W% of dry coal
S	=	Selectivity of residual oil formation from coal reaction, Weight fraction
Cres1, Cres2	=	First and second stage residual concentration, W% of slurry phase

By assuming the activation energy (ΔE) a value of the selectivity, S, could be calculated for each of the experimental conditions. *Figure 10* summarizes the relation of calculated selectivity against assumed activation energy for each of the Condition 2 through 6 data sets. The Condition 2, 3, 4, and 5 data sets show a confluence at an activation energy, of 6 Kcal/mole and a selectivity of 0.43 lbs residuum/lb coal reacted. The Condition 6 relation deviates considerably from those of the other data sets, but this data set is considered less reliable than the others because of the use of make-up oil during the Condition 6 operation and the possibility of insufficient equilibration time.

These values of activation energy and primary formation of residuum were used to calculate apparent reaction rate constants for the secondary reaction of residuum for each stage for each of the Condition 2 through 6 data sets. These rate constants, adjusted to 750°F using the 6 Kcal/mole activation energy, are plotted against catalyst age (Days of coal operations) in *Figure 11*. For the Condition 2 through interval of the run (10 to 19 days), there was a smooth downward progression of these rate constants, with close correspondence for the two stages of the temperature adjusted rate constants. The second stage rate constant for the Condition 6 operation (22 days) continues this trend, but the first stage rate constant for this final operation deviates considerably from the trend. For better correspondence of the Condition 6 results a lower value for the primary formation of residual oil and a higher activation energy would be required, but this would increase the scatter for the Condition 2 through 5 correlation.

In *Figure 11* the curve of adjusted rate constant against age corresponds to the equation:

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

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

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

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

K750 - First order rate constant at 750°F,
Lbs/Hr/Ft³, based on weight fraction
resid in slurry

K_t - Rate constant at Temperature T,
T - Temperature, °F

This rate constant equation was used with a reactor model in conjunction with the appropriate operating condition parameters to project residual oil yields for the first stage, second stage, and the combined stages for the final five Conditions, and the combined stage yield for Condition 1. *Figure 12* is a parity plot of the projected yields against the experimental yields. The projected combined stage yields have a good parity correspondence to the experimental values for all six results compared. For the most part the first and second stage yields also have good projected/experimental correspondence. The outlying first stage/second stage points in *Figure 12* are the Condition 6 results.

The values of the above correlating parameters differ considerably from those obtained by similar analyses for the Clovis Point coal, where the primary formation of residuum was taken to be 80-100% of converted coal (indicated by a plot of residuum yield in the first stage against a severity function involving residual oil concentration and the amount of coal reacted) and the activation energy was 19.5 Kcal/mole (based upon the impact first stage temperature changes between 650°F and 775°F). To better define the values of these parameters, tests were conducted in a microautoclave using the products obtained during bench unit Run 227-57 (CC-2).

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

increasing space velocity during Run 227-57(CC-2), although it is probable even after this consideration some catalyst deactivation is indicated.

SELECTIVITY OF COAL TO RESIDUUM VS ACTIVATION ENERGY – RUN 227-55

FIGURE 10

RESIDUUM REACTION RATE CONSTANTS

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

FIGURE 11

PARITY PLOT FOR RESIDUUM YIELDS

Run 227-55 - Proj. Using Kin. Model

FIGURE 12

Residual Oil Yields in Microautoclave Tests With Black Thunder Mine Coal

The results for a kinetic Microautoclave test matrix with the HRI 5887 Black Thunder Mine coal, which have been discussed above in the correlation of coal conversions, are summarized below. These tests were at 2,000 psi H₂ pressure, using 4 grams of HRI 5198 coal liquefaction product heavy distillate per gram of coal, and presulfided Shell S-317 catalyst.

Temp., °F	Time, Min.	Cat/Coal	Conv., % of MAF Coal	Residual Oil % of Conv. Coal
750	30	0	57.8	54.5
800	30	0	75.6	46.2
800	60	0	84.5	39.9
825	30	0	82.9	41.1
750	30	1	74.0	25.2
800	30	1	91.4	22.6
800	60	1	94.1	18.1
825	30	1	93.3	20.0

The coal conversion results were correlated, following first order kinetics, with the following correlating parameters were the following:

Coal Composition

High Reactivity	59.5%
Low Reactivity	34.8%
Unreactive	5.6%

Reaction Rates

High Reactivity @ 800°F	0.951 Min ⁻¹
Low React./High React.	0.0869
Non-Cat Rate/Cat Rate	0.251
Activation Energy	42 Kcal/mole

The residual oil formation in these Microautoclave tests also could not be fit by a single species first order model for the secondary reaction of the residual oil formed as proportion of the reacted coal. It was necessary assume two species of residual oil again of different reactivities. With the limited data used it was not considered that the proportions of these residual oil species could be independently determined. For the correlation it was assumed that the more reactive residual oil species was solely derived from the more reactive coal species, and a like relation for the low reactivities species, and that the primary

formation of the two residual oil species were the same proportions of the amount of reaction of the respective coal species.

The kinetic equation for series reaction of coal to residual oil to lighter products was of the form:

$$Cr/Cco = kc * [Exp(-kc*t) - Exp(-kr*t)] / (kr - kc)$$

Cr/Cco - Ratio of residual oil yield to initial coal quantity

kc - Rate constant for coal reaction

kr - Rate Constant for secondary residual oil reaction

t - test time

For the two reactive component model this equation was proportionately applied to each of the two high/low reactivity coal/residual oil regimes.

The final correlating parameters were the following:

Primary Residual Oil formation: 57.3% of coal conver.

Rate Constants at 800 F

Catalytic, High React. Residuum: 0.0829 min⁻¹

Non Catal., High React. Residuum: 0.0101 min⁻¹

Low Resid Rate/High Resid Rate: 0.0417

Activation Energy

Catalytic Data: 18.1 Kcal/mole

Non-Catalytic Data: 41.1 Kcal/mole

The following tabulation compares the experimental and correlated residual oil yields:

Temp., °F	Time, Min.	Cat/Coal	Resid Oil, % of Coal Conv.	
			Experimental	Correlated
750	30	0	54.5	54.3
800	30	0	46.2	46.9
800	60	0	39.9	39.6
825	30	0	41.1	41.0
750	30	1	25.2	25.3
800	30	1	22.6	22.0
800	60	1	18.1	18.1
825	30	1	20.0	20.4

Figure 13 graphically summarizes the indicated residual oil secondary rate constants calculated using the primary formation value given above.

Microautoclave Tests with Liquid Products From CTSL™ Bench Unit Operations

The second stage product liquid (recycle solvent) from CTSL™ Bench Unit operations using Black Thunder Mine coal were tested in the 20 cc microautoclave to obtain additional data concerning the reactivity of the residual oil component of the oil. The bulk of these tests were with the filtered oil product (PFL) from Period 23A of Run 227-55(CC-1) which had the following composition:

<u>D-1160 Distillation</u>	<u>W%</u>	<u>Hydrogen Content, W%</u>
IBP-650°F	8.5	10.64
650-850°F	46.8	9.85
850-975°F	14.4	8.32
975°F+ Residuum	29.8	6.55
TGA Analysis		
Residuum, W%	31.1	

The net yield of the residual oil from this CTSL™ operations was 4.4 W% of dry coal fed.

Experiments were also used the PFL which had been diluted with one part of its gas oil components to two parts of the PFL. The residuum content of the diluted feed was 21.0 W%, by TGA analysis. The TGA (Thermogravimetric) analytical method, which was also used in analyzing the microautoclave products, had been developed by appropriate temperature/time programming to obtain linear correlation with 975°F+ residual oil contents by D-1160 distillation for samples containing 15 to 60 W% residuum. The microautoclave experiments were at 2,000 psig hydrogen pressure for 30 and 60 minutes using 0.25 and 1.0 grams of presulfided Shell S-317 catalyst per gram of PFL.

Figure 14 summarizes the results of these experiments with the PFL and diluted PFL in terms of logarithm of the residual concentration against reaction severity. Two factors are evident in this plot. First, simple first order kinetics, which would result in a linear plot, does not fit the data. Second, simple higher order kinetics would also be inapplicable since results with the diluted feed, in terms of product/feed concentrations, are virtually identical with those of the undiluted feed. Also, there is very little non-catalytic contribution to residual oil conversion since the amount of apparent residual oil conversion without catalyst, indicated

in the figure, would be obtained in about 10% as great residence time when catalyst was present.

Figure 14 also indicates the fit of a first kinetic order model which assumes two reactive residual species of the residual oil. The correlating parameters for this correlating curve are the following:

Residual Oil Distribution	
High Reactivity Component	50 W%
Low Reactivity Component	50 W%
Reaction Rate Constants	
1/min/(gm cat/gm oil)	
High Reactivity Component	0.10200
Low Reactivity Component	0.00590

In general terms this correlation for product residual oil corresponds to the correlation of the residual oil yields in the Microautoclave tests with Black Thunder coal, in indicating at least two species of residual oil of reactivities differing by a factor of about 20. However, the indicated proportion of high reactivity component remaining in the product PFL used in these microautoclave tests is much higher than would be projected from the parameters developed from correlation of the results of the tests with the fresh coal.

FIGURE 13

MICROAUTOCLAVE RESIDUAL OIL REACTION RATES

Black Thunder Coal – 57.3% Primary Residuum

FIGURE 14

REACTION OF 227-55-23A RESIDUUM

MicroA. - 825 F - 1990 Experiments Reanalyzed

Residuum Yields in Microautoclave Tests of Coals

The results of coal evaluation tests during the current program of various coals have been reviewed comparing the residual oil yields of the catalytic and thermal (non-catalytic) tests. The conditions for these tests have been 2,000 psig H₂ pressure, 30 minutes residence time, 800°F, 4 grams of coal liquefaction derived distillate oil per gram of coal, and 1 gram presulfided S-317 catalyst per gram of coal. This analysis indicated apparently significant differences in residual oil yield for various coals, and in the catalytic and thermal yields, as summarized in the following table:

Coal	Resid Yield, W% of Conv. Coal		
	Thermal Test	Catal. Test	Ratio
Illinois No. 6	46.4	32.1	0.69
Black Thunder			
Untreated	37.1	23.2	0.63
Thermally Treated	50.2	25.4	0.51
Other Sub-Bituminous	38.1	20.0	0.52

These results are the averages of 37 pairs of the thermal and catalytic tests, 12 with the Black Thunder Coal, 14 with the Illinois Coal (cleaned and uncleaned), and 11 with 6 other Sub-bituminous coals.

Statistically, the higher residual oil yields with Illinois No. 6 coal than Black Thunder coal has a confidence level of 99.0%. The higher residual oil yield for thermally treated (at 400-600°F) Black Thunder coal compared to the untreated coal has a statistical confidence level of 99.5%, but the difference in catalytic results is not significantly different. Nominally, the thermal treatment does increase the potential for residual oil yield, but this is readily overcome in the catalytic operation. The relative residual oil yields of catalytic and thermal operation differ from coal to coal on the average, but the variability of the data (the standard error of the yields was 5.6%) indicates only a 40% confidence level in the significance of such apparent differences.

A similar comparison was made of the results for Illinois No. 6 and Ohio 5/6 coals in tests made during the previous program. Here, the test program included tests at 750°F and 825°F in addition to the tests at 800°F, so that the correlation against severity could be developed. *Figure 15* compares the thermal and catalytic results for the two coals, by plotting the residual oil yield (logarithmic scale) and against nominal thermal severity, STTU (test time adjusted to equivalent time at 840°F, using an Arrhenius activation energy of 49.7 Kcal/mole.

In *Figure 16*, the residual oil yields in the tests with the Ohio Coal was generally higher than those with the Illinois Coal at comparable condition. The trends of residual oil yields in the thermal tests against severity correspond reasonably closely to a liner trend of the logarithm of the residual oil formation against severity (STTU) indicating the activation energy used in the calculation of STTU is appropriate.

These results were correlated using a very simple kinetic model, which assumed that the conversion reaction of the coal is very rapid and produces a fixed proportion of the residual oil subject to secondary reaction. This primary quantity of residual oil then undergoes secondary reaction following simple, single species, first order kinetics. With this model, extrapolation of the thermal tests results to a 0.0 value of STTU indicates the amount of primary residual oil formation, with a value of about 72% of converted coal for the Ohio Coal, and of about 62% for the Illinois coal. The lower yields of residual oil in the catalytic tests indicate additional reaction rate because of the catalyst tests, and permit calculation of apparent relative reaction rate constants for the thermal and catalytic tests.

The following apparent first order rate constants (1/hours) for the various tests were then calculated:

Temp., °F (STTU)	Ohio Coal		Illinois Coal	
	Thermal	Catalytic	Thermal	Catalytic
750 (2.3)	0.060	1.012	0.070	0.926
800 (10.0)	0.860*	1.341	0.244	1.284
	0.268	1.454	0.340	1.444
825 (20.0)	0.538	1.976	0.618	1.752

* Disregarded

Taking the increment between the catalytic result and the thermal result as the contribution of the catalyst itself indicates a value of 1.13-1.44 hr⁻¹ at 825°F, with an activation energy of about 7-10 Kcal/mole for the catalytic rate constant.

FIGURE 15

RESIDUUM YIELD — OHIO AND ILLINOIS COALS

Microauto. — 30 Min. — 1 gm Cat/gm Coal

FIGURE 16

MICROAUTOCLAVE RESIDUUM CONVERSION RATES

Primary Yields - Ohio 72.5% - Ill. 61.6%

Evaluation of Recovered CTSL™ Catalysts

In addition to the evaluation of the first and second stage catalysts from CTSL™ Run CC-12, which was discussed in the section above, first and second stage catalysts from Runs CC-8, and CC-11 were similarly evaluated in the microautoclave. *Table 1* summarizes the results of these microautoclave tests.

CTSL™ Bench Unit Run CC-8 processed Illinois No. 6 Coal that had been cleaned by the OTISCA Process to reduce the ash content to 3.5 W%. CTSL™ Bench Unit Run CC-11 processed Black Thunder Mine (Wyoming) coal. The catalyst for both runs was Shell S-317 catalyst, which was presulfided, using TNPS doped gas-oil at temperatures of 450-650°F, as part of the start-up operations of the run. During Run CC-11 H₂S was added, corresponding to 2 W% of the coal, for maintenance of the sulfided level of the catalyst. No H₂S was added during Run CC-8 since with the higher sulfur content Illinois Coal the H₂S formation was equivalent to this proportion.

The current microautoclave tests included a contemporary series of tests using Shell S-317 catalyst, HRI 5394P, which had been pre-sulfided somewhat similarly to the CTSL™ Bench Unit procedure, although in a small fixed bed. This series of tests was intended to supply a reference data base for "fresh" catalyst to use in comparison with the results for the recovered CTSL™ catalysts.

Referring to *Table 1*, all four of the recovered catalysts showed appreciable activity in converting the residual oil component in a recycle solvent obtained during CTSL™ Bench Unit operations with Black Thunder Mine coal in Run CC-1. The residual oil conversion levels with the recovered catalysts were higher than obtained with half as much "fresh" catalyst, but lower, in three cases, than obtained with about the same amount of "fresh" catalyst. The first and second stage catalysts from Run CC-8 had about the same catalyst effectiveness, 77-83% of that of "fresh" catalyst as these microautoclave tests have been correlated. In contrast, the first stage catalyst from Run CC-11 was considerably more effective than the second stage catalyst from that run. Actually, this first stage catalyst demonstrated an activity higher than that of the "fresh" catalyst, while the second stage catalyst was only 71% as effective as the "fresh" catalyst.

The relative effectiveness of the four recovered catalyst that were tested corresponded to their carbon contents (noted in *Table 1*), with the least effective catalyst containing 18.8% carbon, and the most effective 10.0% carbon, and the catalysts of intermediate effectiveness having intermediate carbon contents.

There were a pair of replicate tests with the "fresh" catalyst, Runs CM1O3 and CM1O5, which indicates the sensitivity of the microautoclave tests to the analytical results, where a difference of less than 1 W% in analyzed residual oil

content corresponds to a difference of over 20% in indicated catalyst effectiveness. This is because the conversion pattern with increasing catalyst/oil ratio does not follow simple first-order kinetics, so that deeper residual conversions require disproportionate increases in catalyst effectiveness. The correlating equations indicated in *Table 1* correspond to system with two residual oil components of differing reactivity, both following first-order kinetics.

TABLE 1

MICROAUTOCLAVE TESTS WITH RECOVERED CATALYSTS
FROM CTSL OPERATIONS

825°F, 2000 psig H₂, 30 Minutes with CTSL Recycle Solvent (PFL)

CTSL Run Stage	CC-8 First	CC-8 Second	CC-11 First	CC-11 Second	---Presulfided Shell S-317 Catalyst ---			
Coal Feed	Illinois No. 6		Black Thunder					
Cat. Age, Lb Coal/Lb	560	560	748	748				
Catalyst Analysis								
Carbon, Wt	12.56	13.61	10.04	18.82	-----	5.81	-----	
Sulfur, Wt	6.32	6.02	6.34	5.48		5.24		
Metal Contam., Wt	0.97	1.12	2.35	2.45		----		
Molybdenum, Wt	7.46	7.39	8.25	7.78		9.49		
Microautoclave Run	CM99	CM100	CM101	CM102	CM103	CM105	CM104	CM106
Catalyst/Oil As Charged	1.00	1.00	1.00	1.00	1.00	1.00	0.50	0.25
Equivalent*	0.79	0.78	0.87	0.82	1.00	1.00	0.50	0.25
Product Residuum, Wt**	20.73	20.68	18.39	20.94	18.61	19.58	21.39	24.64
Relative Catalyst Activity ***	0.81	0.83	1.39	0.74	1.14	0.86	(1.00)	(1.00)
Activity ****	0.77	0.79	1.21	0.71	1.00	0.79	(1.00)	(1.00)

* Relative contaminant-free catalyst, based on Molybdenum content relative to that of Presulfided catalyst.

** TGA analysis, CTSL feed to tests contained 29.87 Wt residuum (Run CC-1, Period 23 PFL).

*** Presulfided Catalyst correlated as $C = Co * (0.70 * \text{Exp}(-0.1165 * (\text{Cat}/\text{Oil}) + 0.30 * \text{Exp}(-2.996 * \text{Cat}/\text{Oil}))$

**** Presulfided Catalyst correlated as $C = Co * (0.70 * \text{Exp}(-0.1462 * (\text{Cat}/\text{Oil}) + 0.30 * \text{Exp}(-2.813 * \text{Cat}/\text{Oil}))$

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SECTION V

MODELLING C₁-C₃ GAS YIELDS

Illinois No. 6 Coal Operations

In Runs 227-32(I-12) and 227-32(I-13) C₁-C₃ gas yields were principally affected by the individual stage temperatures and the coal feed rate. Solvent/coal ratio and catalyst age had correlations of low statistical significance, with 69% and 85% confidence levels, respectively.

The pattern of the variation in C₁-C₃ gas yields corresponded closely to a model in which some gas is formed as part of the primary conversion of the coal, with additional formation from the reaction of the other slurry phase components. The selectivity of the gas formation in the primary conversion reaction of the coal was assumed to be independent of temperature, while the formation from the slurry phase components was taken to have temperature dependence common to both the first and second stages.

The values of the correlating parameters were the following;

Primary Formation	3.07
W% of Converted Coal	
Slurry phase Reaction Rate	
Lbs/hr/ft ³ @ 750°F	0.102
Activation Energy, Kcal/mole	56.1

Figure 1 is a parity plot comparing the correlated gas yields, using these correlating parameters, with the experimental yields of Runs 227-30(I-12) and 227-32(I-13). The correlation has R-squared (variance reduction) value of 84.3%, with a standard error of 0.63 W% yield for the experimental gas yields which range from 5.0 to 10.6 W% of dry coal fed.

The correlation was modified after consideration of the experimental results of Run 227-33(I-14) in which there was catalyst only in the first stage. The values of the correlating parameters for the C₁-C₃ gas yields considering the results of Runs 227-30(I-12), 227-32(I-13) (both with catalyst in both stages), and 227-33(I-14) were then:

Primary Formation	4.06
W% of converted coal	
Slurry phase Reaction Rate	
Lbs/hr/ft ³ @ 750°F	0.083
Activation Energy, Kcal/mole	57

Figure 2 compares the changes the experimental trends for the three runs in space-time gas yield with changes in reaction severity (stage temperatures and amount of reacted coal) with the projected trends. The lower exhibit of the figure summarizes the total gas yield against amount of reacted coal for various combinations of first and second stage temperatures. In this exhibit, slopes of the curves that are shown corresponds to primary formation of gas of 4.06 W% of the converted coal. This exhibit reflect a good correspondence of the correlated impact of changes in the first and second stage temperatures to that indicated by the experimental results. The upper exhibit of *Figure 2*, the apparent secondary formation of gas by slurry phase constituents against combined reaction severity of the two stages (adjusted to a common temperature of 825°F by means of the correlated activation energy) shows a reasonable correspondence to the linear relation that is to be expected. The upper exhibit also shows a very close correspondence to the correlation of the results with no catalyst in the second stage, indicating a relatively small impact by the catalyst upon gas formation.

FIGURE 1

PARITY PLOT FOR CORRELATED C1-C3 GAS YIELDS

Run 227-30 and 227-32 - Illinois Coal Operations

CORRELATION OF C₁-C₃ GAS YIELDS - RUNS 1-12 to 1-14

FIGURE 2

Clovis Point Mine - C₁-C₃ Gas Yields

The determination of the activation energy used the data for Run 227-21 and 227-22, which had the full range of first stage temperature (650-775°F), second stage temperature (810 to 825°F), and coal feed rate. A linear least squares fit of the space-time yield of gas against space-time amount of coal converted, with each level of stage temperature treated as an independent variable, resulted in a correlation pattern with good correlation against converted coal (99.8% confidence level), and second stage temperature (97.7% confidence level), and fair correlation with first stage temperature (84.4% confidence level). However, the amounts of secondary reaction assignable to first stage temperature changes were consistent with the amounts assignable to second stage temperature changes in indicating a common activation energy, 57 Kcal/mole.

Using this value for the activation energy, the final correlation of the gas yields for all of the five runs with this coal resulted in the equation:

$$C_1-C_3(STY) = 0.519 * Severity + 0.0380 * CoalReacted$$

C ₁ -C ₃ (STY)	- Space-time yield of gas, Lbs/hr/ft ³ (reactor)
Severity	- Summation of first and second stage severity Contribution, unity at 810°F, and 57 Kcal/mole activation energy for other temperature
CoalReacted	- Reacted coal, Lbs/hr/ft ³ (reactor)

There was no statistically discernable effect of catalyst age upon the C₁-C₃ gas yield.

The significance of the terms in the equation is as follows: the 0.519 factor represents the secondary rate of gas formation at 810°F; the 0.0380 factor represents the proportion of the primary coal conversion going to gas. However, the correlation indicated significant differences for the individual runs from this equation, statistical analysis indicating a 99.99% probability of a run effect. These deviations for the individual runs correspond to the following factors to be multiplied by the nominal rate constant at 810°F (in effect, assuming the proportion of primary conversion to gas was the same for all of these runs):

<u>Run</u>	<u>Adjustment</u>
227-21	1.31
227-22	1.02
227-25	0.68
227-26	1.07
227-27	1.11

It is not evident that variables caused these deviations. Run 227-21 was the only run in which the unfiltered product slurry (topped separator bottoms) was used as a portion of the recycled slurrying solvent, but some filtered solvent was also used in that run so that the mineral matter content of the slurries in the reactors was virtually the same as in the other runs. (Run 227-21 and 227-22 used the same shipment of coal, while runs 227-25, 227-26 and 227-27 used a second shipment of the coal. A large proportion of Run 227-25 was with coal that was put undried into the slurry preparation tank, so that moisture removal was affected in the presence of the slurrying oil at the slurrying temperature, rather than by pre-drying in a nitrogen swept oven as in most of the other operations. However, during Run 227-25 the gas yields were not significantly different for operations with feeds dried by either of the two methods.

The standard error of the gas yields for the correlation of the pooled data for the five runs corresponded to a gas yield of 1.1 W% of dry coal. Consideration of the differences between the results of these runs lowered this standard error to 0.7 W% of dry coal.

Figure 3 summarizes the gas yields for runs 227-21 and 227-22 in terms of the correlating parameters discussed above.

GAS YIELDS IN TWO STAGE LIQUEFACTION OF CLOVIS POINT COAL

FIGURE 3

● 810 °F Second Stage Temp. ○ 825 °F Second Stage Temp.

Black Thunder Mine Coal - C₁-C₃ Gas Yields

The pooled data for gas yields from Run 227-55 (CC-1) and 227-57 (CC-2) were correlated by modification of the kinetic model previously developed for these yields for Clovis Point (Wyoming) and Illinois No. 6 coal. The resulting least-squares values of the correlating parameters were the following:

Primary yield - 2.8 W% of converted coal

Secondary formation from slurry phase reactions

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

Temperature Dependence

Arrhenius Activation Energy - 37.8 Kcal/mole

The correlation has a high statistical confidence level, 99.99%, with an R-squared value of 0.495, and a standard error of 1.15 W% for the gas yields which ranged from 5.7 to 12.5 W% of dry coal. The low value of R-squared (the deviation from the means values removed by the correlation) is for the most part due to the poor replication of results at a given set of conditions, since an analysis of variance indicates that the experimental standard error is about 1.07 W%, only slightly less than the standard error of the correlation.

Figure 4 is a parity plot comparing to the correlated and experimental gas yields for these two runs with Black Thunder Mine coal.

There was no strong evidence on a synergistic effect upon gas yield of the redistribution of reactor volumes (the two stage volumes were equal in Run CC-1, while in Run CC-2 the first stage had twice the volume of the second stage) beyond that projected considering the severity of conditions in each of the two stages. The scatter of the yields in Run CC-2 was considerably less than that for Run CC-1, probably associated with the improved product gas sampling procedure that was instituted for the later run.

FIGURE 4

PARITY PLOT FOR CORRELATED GAS YIELDS

Black Thunder Coal – Runs 227-55(CC-1) and 227-57(CC-2)

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SECTION VI

MODELLING C₄-390°F NAPHTHA YIELDS

Illinois No. 6 Coal Operations

The yields of C₄-390°F naphtha for the operations with Illinois No. 6 coal in runs 227-30 (I-12), 227-32 (I-13) and 227-33 (I-14) were correlated by means of a model similar to that used for C₁-C₃ gas yields, in which a portion of the naphtha was produced during the primary reaction of the coal, and the balance of the naphtha was formed by secondary reaction of the slurry phase components in the reactors. In Runs 227-30 and 227-32 there was catalyst in both stages, while in run 227-33 there was catalyst in the first stage and no catalyst in the second stage.

C₄-390°F naphtha yield ranged from 13.5 W% to 26.5 W% of dry coal for the three runs considered in the model development. The highest yield was obtained in the operations with the lowest coal rate, with the highest second-stage temperature with catalyst in that stage. The lowest yield was obtained at the highest coal rate used, at comparable first and second stage temperatures, but with no catalyst in the second stage. There were evident effects of second stage temperature (an increase of 5-8 W% with an increase of 16°F in temperature in Run 227-32), of first-stage temperature (1-2 W% changes for 25°F changes in first-stage temperature in Run 227-32), and of coal rate (9 W% increase when the coal rate was halved in Run 227-30). There was a probable impact of catalyst age, with about 5 W% lower yield after twenty-five days during Run 227-30 at nominally comparable conditions. Also, elimination of catalyst from the second stage apparently lowered this yield, by about 6 W% for comparable operations in Runs 227-30 and 227-33.

The correlation was based on a model of naphtha formation as a portion of the products from the primary reaction of the coal, plus additional formation from the first-order reaction of the slurry phase liquids in each stage. The correlation actually was in terms of a total slurry phase secondary naphtha formation rate, in effect assuming that all of the slurry phase components had a common rate of naphtha formation. The impact of the variables was appraised in general terms by a least square multiple linear regression of the space-time naphtha yield against space-time coal conversion, days of coal operations, a reaction severity factor combining the first and second stage temperatures by use of an activation energy, and the presence or absence of catalyst in the second stage. With an activation energy giving the closest fit to the data these variables all proved to have highly significant effects, of greater than 99.99% statistical confidence levels, an R-squared value of 0.931, and a standard error corresponding to about 1.2 W% of dry coal.

The linear regression fitting of the data was continued, considering only the data with catalyst in the second stage, targeting a set of parameters that corresponded to a zero yield of naphtha with zero coal converted and a zero secondary reaction severity. This resulted in a set of best values for the correlating parameters of 8.4% being the proportion of primary coal conversion going to naphtha, and 51 Kcal/mole for the activation energy of the secondary slurry phase reaction. These parameters were used in developing *Figure 1*, as a summary of the apparent kinetics of the secondary naphtha formation, in terms of the relation of the secondary rate constant and catalyst age (days of coal operations). In *Figure 1*, the ordinate is nominal secondary formation rate of naphtha per unit single stage volume (that is, the total formation less the nominal primary formation from the coal reaction) divided by the relative reaction severity (the sum of the first and second stage severities, with a unit value for 825°F, adjusted for temperatures using an activation energy of 51 Kcal/mole). This parameter is plotted against time of coal operations.

In *Figure 1* it is evident that with catalyst in both stages the secondary naphtha formation rate declined with increasing catalyst age, approaching a lower limit represented by the apparent second stage performance with no catalyst in that stage during Run 227-33 (I-14). The degree of this decline with increasing catalyst age was possibly more moderate during Run 227-32 (I-13), operating at 800-816°F temperatures, than during Run 227-30 (I-12), operating 825°F. An improved fit of the correlation was obtained with an allowance for differing rates of deactivation dependent upon stage temperatures.

The relation of the catalyst rate constant (that is, the apparent secondary rate of naphtha formation less the rate with no catalyst in the reactor) to catalyst age was assumed to follow an equation of the form:

$$K = K_o \exp (-D \cdot \text{Age})$$

- K - Rate Constant at Catalyst Age, Age
- K_o - Rate Constant for Fresh Catalyst
- D - Deactivation Factor (Temperature Dependent)
- Age - Catalyst Age, Days of Coal Operations

Taking the temperature dependence of the rate of deactivation for catalytic naphtha formation to be the same as that for the deactivation of secondary residual oil reaction, 39 Kcal/Mole, resulted in an improved fit to the naphtha yield data, with a statistical confidence level of 99.0%.

The final values of the parameters for the naphtha formation rate were the following:

Primary Formation, W% of Coal Converted	8.4
Secondary Reaction Rate At 825°F, Lbs/hr/ft ³ (reactor)	
Thermal Contribution	1.20
Fresh Catalyst Contribution	2.88
Activation Energy, Kcal/mole	51
Deactivation Factor, D	
For Catalytic Rate Constant at 825°F	0.052
Activation Energy for Effect of Temperature	39

Figure 2 is a parity plot of the experimental naphtha yields compared to the yields projected using the above correlating parameters.

FIGURE 1

APPARENT NAPHTHA FORMATION RATE VERSUS TIME OF COAL OPERATIONS

- Run 227-30(1-12), 825 °F Second Stage Temperature
- Run 227-32(1-13), 800 °F, 816 °F Second Stage Temperature
- ▲ Run 227-33(1-14), No Catalyst In Second Stage, Overall Performance
- ▲ Run 227-33(1-14), Second Stage Performance Adjusting for Estimated First Stage Performance

FIGURE 2

PARITY PLOT FOR CORRELATION OF C_4 -390 °F NAPHTHA YIELD

Illinois No. 6 Coal - Runs 227-30, 227-32, and 227-33

Clovis Point Mine Coal Operations

Correlation of the C_4 -390°F naphtha yields in CTSL™ Operations with Clovis Point Mine Coal in Runs 227-21, -22, -25, -26, and -27 used the same activation energy for the secondary formation of the naphtha by the reaction of the slurry phase components, 57 Kcal/mole, that had been used in the correlation of C_1 - C_3 gas yields. The effect of stage temperatures using this activation energy had a high statistical confidence level, 99.8%, and the best fit to the data was obtained with this activation energy, although the degree of fit was only slightly poorer with changes in the activation energy by 10 Kcal/mole. There was a statistically significant, 99.9% confidence level, effect of catalyst age.

The values of the correlating parameters for the pooled data for the five runs were the following:

Primary Formation, W% of Coal Converted	12.3
Secondary Reaction Rate At 810°F, Lbs/hr/ft ³ (reactor)	1.50
Activation Energy, Kcal/mole	57
Deactivation Factor, D	0.013

The relation of the catalyst rate constant (that is, the apparent secondary rate of naphtha formation less the rate with no catalyst in the reactor) to catalyst age was assumed to follow an equation of the form:

$$K = K_o \exp (-D \cdot \text{Age})$$

K	-	Rate Constant at Catalyst Age, Age
K	-	Rate Constant for Fresh Catalyst
D	-	Deactivation Factor
Age	-	Catalyst Age, Days of Coal Operations

The standard error of this correlation of the pooled data was 2.0 W% of dry coal over a range of naphtha yields of 13.0 to 25.0 W% of dry coal.

However, there were significant differences in the yields in each of the five runs from the values projected using the above correlating parameters. These deviations for the individual runs from the pooled correlation correspond to the following factors to be multiplied by the secondary reaction rate constant for the pooled correlation. The tabulation also indicates the average adjustment in naphtha yield for each of the runs to that projected using parameters of the pooled correlation.

<u>Run</u>	<u>Rate Adjustment</u>	<u>Yield Adjustment W% of Dry Coal</u>
227-21	1.30	+2.1
227-22	1.15	+0.7
227-25	0.90	-1.3
227-26	0.94	-0.7
227-27	0.94	-1.1

There is a rough parity of these run adjustments for naphtha yields to those for gas yield correlations, with highest and lowest yields of gas and of naphtha being in runs 227-21 and 227-25, respectively. The general difference of the Run 227-21 and Run 227-22 results from those of the later runs might be associated to the second coal shipment used in the later runs.

The standard error of the naphtha yields projected using the correlation considering the differences from Run-to Run was 1.1 W% of dry coal.

Figure 3 summarizes the naphtha yields for Runs 227-21 and 227-22 in terms of the correlating parameters discussed above. *Figure 4* is a parity plot for the projected and experimental naphtha yields for the data of the five runs that were considered (these projections include the run effect factors given above).

C₄-390°F YIELDS IN TWO STAGE LIQUEFACTION OF CLOVIS POINT COAL

PARITY PLOT FOR CORRELATED NAPHTHA YIELDS

Clovis Point Coal -- Runs 227-21, -22, -25, -26, -27

Black Thunder Mine Coal Operations

The yields of C_4 -390° naphtha for the operations with Black Thunder Mine coal in Runs 227-55 (CC-1), and 227-57 (CC-2) were correlated by means of a model similar to that used for C_1 - C_3 gas yields, in which a portion of the naphtha was product during the primary reaction of the coal, and the balance of the naphtha was formed by secondary reaction of the slurry phase components in the reactors. In Run 227-55 the two stages were of equal volumes, while in Run 227-57 the first stage volume was twice that of the second stage. The correlating parameters projected average yields for each of the two runs that were within 0.1 W% of dry coal of the average experimental yields.

The values of the correlating parameters for the pooled data for the two runs were the following:

Primary Formation, W% of Coal Converted	7.5
Secondary Reaction Rate	
At 825°F. Lbs/hr/ft ³ (reactor)	2.22
Activation Energy, Kcal/mole	36
Deactivation Factor, D	0.013

The relation of the catalyst rate constant (that is, the apparent secondary rate of naphtha formation less the rate with no catalyst in the reactor) to catalyst age was assumed to follow an equation of the form:

K	-	$K_o \exp (-D \cdot \text{Age})$
K	-	Rate Constant at Catalyst Age, Age
K_o	-	Rate Constant for Fresh Catalyst
D	-	Deactivation Factor
Age	-	Catalyst Age, Days of Coal Operations

The value of the deactivation factor was taken from the value obtained in the correlation of the naphtha yields in Clovis Point Mine coal operations. While some deactivation was apparent in the Run 227-55 data, a decline of about 1.0 W% in collected naphtha yield between 9 and 19 days of operations at a common set of operating conditions, it was not considered that there was sufficient data base to justify a modification of the deactivation factor.

The R-squared value of the correlation was 0.806, with a standard error of 1.1 W% of dry coal. *Figure 5* is a parity plot comparing the experimental yields with those project with these correlating parameters.

FIGURE 5

PARITY PLOT FOR CORRELATED NAPHTHA YIELDS

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

SECTION VII
Economic Studies

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SECTION VII ECONOMIC STUDIES

INTRODUCTION

In the late 1980's, under DOE Contact DE-AC22-83PC-60017, HRI conducted two conceptual plant designs and economic studies on applying the CTSL™ Process to commercial scale: one on bituminous, and the other on sub-bituminous coal. Both plants were set up to be grass-roots complexes, supplying their own hydrogen, and generating all utilities except for electricity on site. The schematic flow diagram shown in *Figure 1* is applicable to both studies. The Wyoming sub-bituminous coal study, reported in DE/80002-TOP-1, September, 1988, was sized for 10,000 T/Day of coal to liquefaction, producing 37,768 B/D of liquid products. The Illinois bituminous coal study, reported in DOE/PC/80002-T4, September 1988 was sized for 8,400 T/D of coal to liquefaction, and produced 41,948 B/D liquid products. Both studies were based on results of bench-scale coal liquefaction runs at equilibrium catalyst activity.

The feed requirement, product rates and net utility needs are summarized in *Table 1*, for each study. *Table 2* presents the coal analyses for both studies. *Table 3* summarizes the yields obtained in coal liquefaction. *Table 4* lists the major process units and the off-sites in the plant. *Table 5* is a breakdown of the Total plant investment, based on a US Gulf Coast location in 1984. *Table 6* gives the product cost. Finally, *Table 7* is a summary of the economic basis in determining the project rate of return.

Since publication of these reports, the economics have been updated and revised to incorporate new technologies, particularly in heavy-wall pressure vessel fabrication, up-to-date cost and operating requirement information on process facilities, as well as changing financing concepts. The purpose of the present report is to summarize the economics updates for both types of coal.

RESULTS WITH SUB-BITUMINOUS COAL

The economics were updated in a 1990 study, in which the size of the liquefaction reactors was increased to reflect improvements in pressure-vessel fabrication metallurgy. Use of larger-diameter reactors allowed a decrease in the number of operating trains from five to four, thereby cutting plant costs. Results are shown in *Table 8*, showing considerable reduction in both capital investment and operating costs.

A brief study in 1990 compared the economics of producing hydrogen by steam reforming natural gas against partial oxidation. Results, shown in *Table 9* show a clear economic advantage for steam reforming.

The 1988 study was based on a reactor space velocity of 20 lbs/hr/ft³, or an equivalent catalyst space velocity of 45 lbs/hr/ft³. In a 1990 study, the space velocity was increased 50% while assuming the same liquefaction yields. Two plant sizes were investigated: a 2,000 T/D demonstration plant partially DOE-funded, and a 10,000 T/D unit, financed fully by private equity. *Table 10* shows the results of this study for hydrogen production by partial oxidation, and *Table 11* for hydrogen by steam reforming. Again, both the investment cost and the product cost are lower using steam reforming. The economic advantage of the decreased reactor severity is seen with both hydrogen-manufacturing techniques.

In these updated studies, the DCF rate of return is calculated with an assumed liquids product price of \$1.40/gallon. *Figures 2 and 3* show the effect of product pricing on the rate of return, at two plant sizes and with two reactor space velocities. *Figure 4* shows the effect on rate of return of several pricing bases, chiefly projections on the price of the liquid product. *Table 12* is a sample of the cash flow analysis.

RESULTS WITH BITUMINOUS COAL

Investment costs and operating requirements were updated to a 1991 level, using information derived from the Bechtel study entitled "Direct Coal Liquefaction Baseline Design and System Analysis", under Contract No. DEAC22 90PC89857. Bechtel's report designed off-site facilities in much greater detail than available to HRI in the earlier study.

Table 13 is a summary of results for the updated economics, comparing various hydrogen manufacturing methods. As with sub-bituminous coal, steam reforming is the most attractive option, with the given financing parameters. *Table 14* shows the economic effect of varying plant size and reactor severity. *Figures 5 and 6* show the effect of assumed product price, while *Figure 7* shows capital cost sensitivity.

For completeness, economics are shown in *Table 15*, updated to the 1991 basis, with the Bechtel information, for sub-bituminous coal.

CONCLUSIONS

- Larger diameter reactor available with current technology permit lower the capital cost by reduction of the number of trains required.
- Steam reforming of natural gas is more economically cost effective a partial oxidation.
- An increase in sub-bituminous coal space velocity of 50% lower product cost by ~\$2/bbl.
- Economics are quite sensitive to product price. A 10% increase in product price increases the rate of return 10% over the original.

TABLE 1**Feed Products and Utilities**

	<u>Sub-Bituminous</u>	<u>Bituminous</u>
DRY COAL FEED, TPSD		
To Liquefaction	10,000	8,400
To Partial Oxidation	-0-	4,405
	<hr/>	<hr/>
TOTAL	10,000	12,805
	108	106
Purchased Electric Power, MW	92	---
Purchased Natural Gas, MMSCFD		
LIQUID PRODUCTS, BPSD		
Gasoline	12,360	13,170
Diesel	24,160	28,778
Turbine Fuel	948	---
	<hr/>	<hr/>
TOTAL	37,768	41,948
BY-PRODUCTS		
Sulfur, TPSD	100	329
Ammonia, TPSD	80	143
Ash to Disposal, TPSD	914	1,498
LPG, BPSD	---	289

TABLE 2**Coal Feed Analysis**

COAL TYPE	<u>Sub-Bituminous</u>	<u>Bituminous</u>
	Wyoming Clovis Point	Illinois No.6 Burning Star
PROXIMATE ANALYSIS, W% DRY COAL		
Volatile Matter	46.28	40.30
Fixed Carbon	43.83	53.93
Ash	9.89	5.77
TOTAL	100.00	100.00
ULTIMATE ANALYSIS, W% DRY COAL		
Carbon	65.36	73.92
Hydrogen	4.81	4.93
Nitrogen	0.92	1.51
Sulfur	1.13	2.75
Ash	8.78	5.77
Oxygen (by difference)	19.00	11.12
TOTAL	100.00	100.00
HEATING VALUE (HHV), BTU/LB DRY	11,351	13,181
MOISTURE, W% ON COAL FEED TO LIQUEFACTION	5.0	3.08
SULFUR FORMS, W% DRY COAL		
Organic	0.68	2.02
Pyritic	0.43	0.72
Sulfate	0.02	0.01

TABLE 3

Liquefaction Yields

		<u>Sub-Bituminous</u>	<u>Bituminous</u>
W% DRY COAL			
H ₂ S		0.77	2.50
NH ₃		0.73	1.38
H ₂ O		18.17	10.57
CO + CO ₂		1.80	0.10
C ₁ - C ₃		7.34	8.44
Naphtha		17.38	21.23
Mid-distillate		27.81	30.14
650 - 975°F		10.94	21.61
975 ⁺		4.19	2.89
Unconverted Coal		9.00	2.77
Ash		<u>8.78</u>	<u>5.77</u>
TOTAL		106.91	107.40
C ₄ - 975°F			
Bbls/Ton maf Coal		4.1	5.3
Bbls/Ton mf Coal		3.8	5.0

TABLE 4

PROCESS UNITS

Coal Preparation (cleaning, drying, grinding)
Liquefaction
Solid-liquid Separation
Gas Plant
Hydrotreating (gas oil & naphtha)
Hydrogen Production
Air Separation
Sulfur Plant

OFF - SITES

Relief & Blowdown Facilities
Tankage
Interconnected Piping Systems
Product Shipping & Loading
Coal Refuse & Ash Disposal
Phenol Recovery
Ammonia Recovery
Electric Power Distribution
Steam Generation
Raw, Cooling Water & Potable Water Systems
Fire Protection
Sewage & Effluent Water Treatment
Instrument & Plant Air
Purge & Flush Oil
General Site Preparation
Buildings

TABLE 5**Total Plant Investment Summary**

	Cost, \$ MM⁽¹⁾	
	<u>Sub-Bituminous</u>	<u>Bituminous</u>
Coal Preparation	193	176
Liquefaction	724	619
Partial Oxidation	103	283
Oxygen Plant	59	130
Steam Reforming	88	---
Product Treating	49	77
Product Upgrading	110	157
Utilities	94	109
Tankage	81	81
General Off-sites	386	477
TOTAL	1,887	2,109

(1) 1984 U.S. dollars at a U.S. Gulf Coast location.

TABLE 6**Product Cost**

<u>OPERATING COST, MM\$/YR</u>	<u>Sub-Bituminous</u>	<u>Bituminous</u>
Coal ⁽¹⁾	34.1	126.8
Electric Power @ 0.035/Kwh	29.8	29.3
Natural Gas at \$2.50/MMBtu	76.8	---
Raw Water @ 0.50/MGal	0.5	0.8
Catalyst and Chemicals	31.1	28.8
Ash Disposal @ \$2/Ton	0.6	1.0
Labor, Supervision and Overhead	56.6	63.3
Maintenance	58.1	63.7
Capital Charges ⁽²⁾	<u>207.6</u>	<u>232.0</u>
TOTAL	495.2	545.7
BY-Product Revenues, MM\$/Yr		
LPG @ \$20/B	---	1.9
Sulfur @ \$60/LT	1.8	5.8
Ammonia @ \$150/T	<u>3.9</u>	<u>7.1</u>
TOTAL	5.7	14.8
Product Cost⁽³⁾		
MMS/Yr	489.5	530.9
\$/B	39.30	38.35

(1) \$10/Ton for Sub-Bituminous. \$30/Ton for Bituminous coal

(2) Equivalent capital charge factor is 11% of TEC/Yr.

(3) First year product cost.

TABLE 7
ECONOMIC BASIS

Type of Financing, % Equity	100
Construction Period, Years	4
Draw-Down, %	
• First Year	4
• Second Year	26
• Third Year	45
• Fourth Year	25
Escalation Rate During Construction	5
Depreciation Period, years	25
Depreciation Type	Straight Line
Capacity Factor, %	
• First Year	65
• Second Year	80
• Thereafter	100
Inflation Rate, %	4
Income Tax Rate, %	33
Operating Days per Year	320

TABLE 8**Sub-Bituminous Coal****Economic Effect of Lower Space Velocity**

	Space Velocity = 20	Space Velocity = 30
Number of Reactors	10	8
Per Reactor		
I.D.	13'0"	14'0"
Thickness, in.	12.75	12.875
Height, ft.	63	44
Weight, tons	1012	844
Investment Cost, \$MM (1988 Basis)		
Liquefaction	804	700
Other On-Sites	571	571
Off-Sites	<u>390</u>	<u>369</u>
TOTAL	1765	1640
Rate of Return, % ⁽¹⁾	11.2	12.1
Product Cost, \$/B ⁽²⁾	39.30	38.12

⁽¹⁾ Product price basis = DOE projection for crude oil x 1.3.

⁽²⁾ See report DE-80002-TOP-1

TABLE 9

**Sub-Bituminous Coal
Comparison of
Hydrogen Manufacturing Techniques**

Coal (dry), Tons/Day B/D Liquids H ₂ Manufacture \$MM Investment		Cost, \$/Unit	10,000 39365 Steam Reforming <u>1344.8</u>		10,000 39365 Partial Oxidation <u>1567.3</u>	
			Consumed, Units/Bbl	Cost, \$/Bbl	Consumed, Units/Bbl	Cost, \$/Bbl
	Units					
Coal	Tons	5.00	0.254	1.27	0.254	1.27
Power	Kw	0.04	50.641	2.03	69.537	2.78
Nat'l Gas	MMBTU	1.97	2.615	5.15	1.087	2.14
Raw Water	1000 Gal	0.50	0.084	0.04	0.069	0.03
Vac Btms	Tons	1.00	0.050	0.05	0.000	0.00
Cat & Chem				2.33		2.19
Labor				2.40		2.79
Maintenance				3.19		3.53
Taxes				3.00		3.49
Sulfur	Tons	60.00	0.002	-0.12	0.002	-0.12
Ammonia	Tons	150.00	0.002	-0.35	0.002	-0.35
Product Cost, ex Capital				18.9		17.76

RATE OF RETURN

100% Equity		
Liquid @ \$1.20/Gal	18.9	17.0
Liquid @ \$1.40/Gal	22.0	19.9
50% Equity/50% Debt		
Liquid @ \$1.20/Gal	25.5	22.7
Liquid @ \$1.40/Gal	30.4	27.2

TABLE 10
Sub-Bituminous Coal
Economic Results Using Partial Oxidation for Hydrogen Manufacture

Plant Size, T/D Dry Coal	2000	2000	10000	10000
Catalyst Sp Vel	45	67	45	67
No. of Reactor Trains	1	1	5	4
Total Reactors	2	2	10	8
Investment Cost \$ MM, (1988)				
Liquefaction	160.7	140.0	804	700
Other On-Sites	153.9	153.9	571	571
Utilities	21.5	21.5	107	107
Other	67.2	63.1	296	276
Total	403.3	378.5	1778	1654
DOE Contribution	161.3	151.4	0.0	0.0
Operating Cost, \$MM/Yr				
Coal, \$5/Ton	3.20	3.20	16.00	16.00
Power, \$0.04/kw	6.29	6.29	31.44	31.44
Gas, \$1.40/MMBtu	3.91	3.91	19.53	19.53
Water, \$0.50/Mgal	0.11	0.11	0.55	0.55
Catalyst & Chem	5.68	5.68	28.42	28.42
Labor	12.10	11.35	53.33	49.61
Maintenance	11.28	10.37	51.63	47.07
Capital Charges ⁽¹⁾	44.37	41.63	195.56	181.90
Total	86.93	82.54	396.46	374.52
Byproduct Credit, \$MM/Yr				
Sulfur, \$60/T	0.31	0.31	1.57	1.57
Ammonia, \$150/Ton	0.86	0.86	4.37	4.37
Total	1.17	1.17	5.94	5.94
Product Cost, \$MM/Yr	85.76	81.37	390.52	368.58
\$/Bbl ⁽²⁾	34.04	32.30	31.00	29.26
Rate of Return, % ⁽³⁾	23.8	25.0	18.2	19.3

⁽¹⁾ Equivalent 11% of TEC/Yr

⁽²⁾ First-Year Product Cost

⁽³⁾ Product selling Price = \$1.40/Gal

TABLE 11
Sub-Bituminous Coal
Economic Results Using Steam Reforming for Hydrogen Manufacture

Plant Size, T/D Dry Coal	2000	2000	10000	10000
Catalyst Sp Vel	45	67	45	67
No. of Reactor Trains	1	1	5	4
Total Reactors	2	2	10	8
Investment Cost \$ MM, (1988)				
Liquefaction	160.7	140.0	804	700
Other On-Sites	107.1	107.1	392	392
Utilities	15.6	15.6	78	78
Other	56.7	52.5	255	234
Total	340.1	315.2	1528	1404
DOE Contribution	136.0	126.1	0.0	0.0
Operating Cost, \$MM/Yr				
Coal, \$5/Ton	3.20	3.20	16.00	16.00
Power, \$0.04/kw	6.68	6.68	33.41	33.41
Gas, \$1.40/MMBtu	9.20	9.20	46.00	46.00
Water, \$0.50/Mgal	0.10	0.10	0.49	0.49
Ash Disposal, \$1/T	0.13	0.13	0.63	0.63
Catalyst & Chem	6.06	6.06	30.28	30.28
Labor	10.20	9.46	45.84	42.12
Maintenance	10.02	9.10	46.63	42.08
Capital Charges ⁽¹⁾	37.41	34.68	168.09	154.43
Total	82.99	78.60	387.37	365.43
Byproduct Credit, \$MM/Yr				
Sulfur, \$60/T	0.31	0.31	1.57	1.57
Ammonia, \$150/Ton	0.86	0.86	4.37	4.37
Total	1.17	1.17	5.94	5.94
Product Cost, \$MM/Yr	81.82	77.43	381.43	359.49
\$/Bbl ⁽²⁾	32.48	30.74	30.28	28.54
Rate of Return, % ⁽³⁾	26.0	27.6	19.7	21.1

(1) Equivalent 11% of TEC/Yr

(2) First-Year Product Cost

(3) Product selling Price = \$1.40/Gal

TABLE 12

Cash Flow

YEAR	GROSS REVENUE	OPERATING COST	GROSS INCOME	DEPREC'N	TAXABLE INCOME	TAX	AFTER-TAX INCOME	CASH FLOW	9.25 PRESENT VALUE	14.50 PRESENT VALUE
1										
2								-7.60	-7.60	-7.60
3								-21.20	-19.41	-18.52
4								-130.70	-109.50	-99.70
5	77.84	52.28	25.56	41.78	-16.23	0.00	-16.23	-100.04	-76.72	-66.65
6	97.97	62.49	35.48	39.69	-4.21	0.00	-4.21	25.56	17.94	14.87
7	125.18	72.72	52.46	37.60	14.86	0.00	14.86	35.48	22.80	18.03
8	127.89	75.15	52.74	35.51	17.23	3.84	13.39	52.46	30.85	23.29
9	130.61	77.66	52.95	33.42	19.53	6.44	13.08	48.90	26.32	18.96
10	133.33	80.25	53.08	31.34	21.74	7.17	14.57	46.51	22.92	15.75
11	137.28	83.13	54.15	29.25	24.90	8.22	16.68	45.90	20.70	13.58
12	141.22	86.10	55.13	27.16	27.97	9.23	18.74	45.93	18.96	11.86
13	145.18	89.16	56.02	25.07	30.95	10.21	20.74	45.90	17.34	10.35
14	149.13	92.31	56.82	22.98	33.84	11.17	22.67	45.81	15.84	9.03
15	153.09	95.56	57.52	20.89	36.63	12.09	24.54	45.65	14.45	7.86
16	158.48	99.16	59.32	18.80	40.52	13.37	27.15	45.44	13.17	6.83
17	163.87	102.86	61.02	16.71	44.30	14.62	29.68	45.95	12.19	6.03
18	169.27	106.67	62.60	14.62	47.98	15.83	32.14	46.40	11.26	5.32
19	174.67	110.60	64.07	12.53	51.54	17.01	34.53	46.77	10.39	4.68
20	180.07	114.65	65.43	10.45	54.98	18.14	36.84	47.06	9.57	4.12
21	185.48	118.82	66.66	8.36	58.30	19.24	39.06	47.28	8.80	3.61
22	190.89	123.13	67.76	6.27	61.50	20.29	41.20	47.42	8.08	3.16
23	196.31	127.58	68.74	4.18	64.56	21.30	43.25	47.47	7.41	2.77
24	201.73	132.16	69.57	2.09	67.48	22.27	45.21	47.43	6.77	2.41
25	207.16	136.89	70.27	0.00	70.27	23.19	47.08	47.30	6.18	2.10
26	212.59	141.78	70.81	0.00	70.81	23.37	47.44	47.08	5.63	1.83
27	218.03	146.83	71.20	0.00	71.20	23.50	47.70	47.44	5.20	1.61
28	223.47	152.04	71.43	0.00	71.43	23.57	47.86	47.70	4.78	1.41
29	228.92	157.42	71.49	0.00	71.49	23.59	47.90	47.86	4.39	1.24
TOTAL	4129.67	2637.39	1492.27	438.70	1053.57	347.68	705.89	78.75	6.61	1.78
								915.89	115.35	-0.00

2000 T/D COAL
DOE BASIS
14.50 DF FOR PV=0

TABLE 13

ECONOMIC RESULTS USING VARIOUS HYDROGEN PRODUCTION METHODS

8,400 T/D Coal, Reactor Space Velocity = 20 lb/hr/ft³

Product, B/D	41,950	41,950	41,950	41,950
H₂ via:				
Vacuum Bottoms POX	X	X		X
Coal POX				X
Process Gas SR	X		X	
Import Gas SR	X	X	X	
Cost, \$MM				
Liquefaction	731	731	731	731
H ₂ Manufacture	118	118	114	302
Other on-sites	418	418	421	450
Utilities	287	287	331	298
Other off-sites	366	366	366	366
Home Office	162	162	166	181
Contingency	273	273	279	306
Total	2,355	2,355	2,408	2,634
Operating Cost, MM\$/yr				
Coal, \$30/Ton	83.16	83.16	83.16	126.86
Electricity, \$0.04/kw	47.92	47.92	43.78	77.72
Natural Gas, \$1.50/MMBTU	53.31	53.16	60.45	3.82
River Water, \$0.50/Mgal	1.14	1.14	1.16	1.78
Catalyst & Chemicals	32.02	32.02	32.36	29.13
Ash Disposal, \$2.00/Ton	0.32	0.32	0.63	0.71
Maintenance	55.16	55.16	56.05	59.71
Labor	57.55	57.55	58.88	64.38
Capital Charges ⁽¹⁾	211.03	211.03	215.91	236.06
Total:	541.61	541.46	552.38	600.17
By-product Credit, \$MM/yr				
Ammonia, \$150/Ton	7.43	7.43	7.43	7.43
Sulfur, \$60/L Ton	4.06	4.06	3.97	6.12
Product Cost, \$MM/yr	530.12	529.97	540.98	586.62
\$Bbl	38.29	38.28	39.08	42.37
Rate of Return, % ⁽²⁾	16.13	16.14	15.74	14.47

Notes: (1) Capital charges are equivalent to 11% per year
(2) Product selling price assumed \$1.40/gal

TABLE 14**ECONOMIC RESULTS AT VARYING PLANT SIZE & SPACE VELOCITY****Hydrogen manufacture via Steam Reforming**

Coal Feed Rate, T/D	8400	8400	10,080	10,080
Product, B/D	41,952	41,952	50,342	50,342
Space Velocity, lb/hr/ft ³	20	30	20	30
Number of Reactor Trains	5	4	6	5
Total Reactors	10	8	12	10
Reactor Weight, ST	954	919	954	889
Cost, \$MM				
Liquefaction	731	648	876	785
H ₂ Manufacture	114	114	130	130
Other on-sites	421	421	540	540
Utilities	331	331	412	412
Other off-sites	366	366	449	449
Home Office	166	159	203	196
Contingency	279	268	343	330
Total	2,408	2,307	2,953	2,842
Operating Cost, MM\$/yr				
Coal, \$30/Ton	83.16	83.16	99.79	99.79
Electricity, \$0.04/kw	43.78	43.78	52.6	52.6
Natural Gas, \$1.50/MMBTU	60.45	60.45	72.18	72.18
River Water, \$0.50/Mgal	1.16	1.16	1.34	1.34
Catalyst & Chemicals	32.36	32.36	38.84	38.84
Ash Disposal, \$2.00/Ton	0.63	0.63	0.75	0.75
Maintenance	56.05	52.72	68.46	64.83
Labor	58.88	56.39	72.21	69.49
Capital Charges ⁽¹⁾	215.91	206.75	264.78	254.79
Total:	552.38	537.40	670.95	654.61
By-product Credit, \$MM/yr				
Ammonia, \$150/Ton	7.43	7.43	8.92	8.92
Sulfur, \$60/L Ton	3.97	3.97	4.76	4.76
Product Cost, \$MM/yr	540.98	526.00	657.27	640.93
\$Bbl	39.08	37.99	39.56	38.58
Rate of Return, % ⁽²⁾	15.74	16.37	15.45	16.01

Notes: (1) Capital charges are equivalent to 11% per year.
(2) Product selling price assumed \$1.40/gal.

TABLE 15

Sub- Bituminous Coal Economics

ECONOMIC RESULTS USING VARIOUS HYDROGEN PRODUCTION METHODS
10,000 T/D Coal, Reactor Space Velocity = 20 lb/hr/ft³

Product, B/D	37,768	37,768	37,768	37,768
H2 via:				
Vacuum Bottoms POX	X	X		X
Coal POX				X
Process Gas SR	X		X	
Import Gas SR	X	X	X	
Cost, \$MM				
Liquefaction	845	845	845	845
H ₂ Manufacture	159	159	116	308
Other on-sites	448	448	452	472
Utilities	231	231	387	306
Other off-sites	363	363	363	363
Contingency, Fee	464	464	491	520
Total	2,510	2,510	2,654	2,814
Operating Cost, MM\$/yr				
Coal, \$5/Ton	16.50	16.50	16.50	25.06
Electricity, \$0.04/kw	63.31	63.31	48.46	83.14
Natural Gas, \$1.50/MMBTU	38.67	38.51	64.19	4.99
River Water, \$0.50/Mgal	1.21	1.21	1.28	1.82
Catalyst & Chemicals	34.93	34.93	36.17	32.86
Ash Disposal, \$2.00/Ton	0.59	0.59	1.43	1.33
Maintenance	60.58	60.58	62.93	65.53
Labor	61.36	61.36	64.89	68.78
Capital Charges ⁽¹⁾	224.99	224.99	237.92	252.21
Total:	502.14	501.98	533.77	535.72
By-product Credit, \$MM/yr				
Ammonia, \$150/Ton	4.82	4.82	4.82	4.82
Sulfur, \$60/L Ton	1.97	1.97	1.29	2.91
Product Cost, \$MM/yr	495.35	495.19	527.66	527.99
\$Bbl	39.74	39.73	42.34	42.36
Rate of Return, %⁽²⁾	14.25	14.26	13.23	13.00

Notes: (1) Capital charges are equivalent to 11% per year
 (2) Product selling price assumed \$1.40/gal

SCHEMATIC FLOW DIAGRAM

FIGURE 1

FIGURE 2

FIGURE 3

2000 T/D DEMONSTRATION PLANT

FIGURE 4

FIGURE 5

CTSL ECONOMICS, BITUMINOUS COAL

Effect of Product Pricing

FIGURE 6

CTSL ECONOMICS, BITUMINOUS COAL

Effect of Product Pricing

FIGURE 7

CTSL ECONOMICS, BITUMINOUS COAL

Effect of Capital Investment

REFERENCE REPORTS THIS CONTRACT

1. Catalytic Two-Stage Liquefaction (CTSL™) Process Bench-Studies and PDU Scale-Up with Sub-Bituminous Coal, DE-88818-TOP-1, March, 1993 for U.S. DOE, Contract No. DE-AC22-88PC88818.

ABSTRACT

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

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

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

2. Catalytic Two-Stage Liquefaction (CTSL™) Process Bench Studies with Bituminous Coal, DE-88818-TOP-1, March, 1993 for U.S. DOE, Contract No. DE-AC22-88PC88818.

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.

3. Catalytic Two-Stage Liquefaction (CTSL™) Process Laboratory Scale Studies, Modelling and Technical Assessment, DE-88818-TOP-1, June, 1993 for U.S. DOE, Contract No. DE-AC22-88PC88818.

ABSTRACT

Reported herein are the details and results of Laboratory experiments using sub-bituminous and bituminous coal concluded at Hydrocarbon Research, Inc., under DOE Contract No. DE-AC22-88PC88818 during the period October 1, 1988 to June 30, 1993,. The work described is primarily concerned with tests on a Laboratory Scale primarily using microautoclaves. Experiments were conducted evaluating coal, solvents, start-up oils, catalysts, thermal treatments, CO₂ addition and sulfur compound effects.

Other microautoclave tests are included in the companion topical reports for this contract, DE88818-TOP-1&2 on Sub-Bituminous and Bituminous Bench-Scale and PDU activities.

In addition to the Laboratory Scale Studies, kinetic data and modelling results from Bench-Scale and Microautoclave tests are interpreted and presented along with some economic updates and sensitivity studies.

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9. "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.
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