**A Characterization and Evaluation of
Coal Liquefaction Process Streams**

Quarterly Technical Progress Report

April 1 through June 30, 1998

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ABSTRACT

This is the Technical Progress Report for the sixteenth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period April 1 through June 30, 1998. Described in this report are the following activities:

- CONSOL characterized nine process stream samples received from Exxon Recycle Coal Liquefaction Unit (RCLU) operations conducted in 1994 with Rawhide Mine Wyoming subbituminous coal and all-dispersed Fe and Mo catalysts.
- The University of Delaware subcontract related to resid reactivity was completed with issuance of the Topical Report covering work performed by Delaware.
- Computational studies of the coal liquefaction resid models developed at the University of Delaware were continued at CONSOL R&D. The two reaction models, consisting of the "reaction optimization" and "reaction once-through" programs, were the focus of these studies. The updated resid structure data and results were used in the reaction models to predict percent conversion values that were compared with the experimentally-measured values from the University of Delaware.
- Small samples of high-sulfur Hondo resid and anthracene oil were shipped to John Verkade of Iowa State University at his request. Verkade is testing a desulfurization method.

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Section 1

EXECUTIVE SUMMARY

CHARACTERIZATION OF SAMPLES FROM EXXON RCLU OPERATIONS

CONSOL characterized nine process stream samples received from Exxon Recycle Coal Liquefaction Unit (RCLU) operations conducted in 1994 with Rawhide Mine Wyoming subbituminous coal and all-dispersed Fe and Mo catalysts. The major conclusions from CONSOL's analyses of these samples follow.

- The product and recycle oils produced during Conditions 1, 3, and 4 have very similar characteristics, although several process variables differed during these conditions.
- Coal conversions to THF solubles during Exxon Run RCLU-1 ranged from 93.6 to 96.7% MAF. Exxon did not report coal conversions; therefore, CONSOL calculated coal conversions from two sources. Coal conversions based on CONSOL analyses were 96.5-96.7% for Conditions 1, 3, and 4. Coal conversions derived from Exxon yield data were 94.5-95.4% for Conditions 1, 3, and 4, and were 93.6-95.4% for the entire run.
- A comparison of process stream sample characteristics from Condition 4 of Exxon Run RCLU-1, Condition 6 of HTI Run CMSL-9 (a tie point to the RCLU run), and Period E of Wilsonville Run 263 showed many similarities. All three runs used dispersed Fe and Mo catalysts for processing subbituminous coal. The process stream characteristics, like the process yield data, indicated that all three plants arrived at approximately the same point when similar operating conditions were used.
- The Exxon materials tended to be more aromatic than their HTI counterparts. The Exxon recycle distillate was more similar to the Wilsonville recycle distillate than either was to the corresponding HTI oil. However, the lighter product distillate from the Exxon run was less like the HTI and Wilsonville oils.

STRUCTURE AND REACTIVITY MODEL PROGRESS

Computational studies of the coal liquefaction resid models developed at the University of Delaware were continued at CONSOL R&D. The two reaction models, consisting of the “reaction optimization” and “reaction once-through” programs, were the focus of these studies. The computations were performed on a Hewlett Packard Apollo HP-735 RISC workstation and a Silicon Graphics Octane RISC workstation. The updated resid structure data and results presented in the previous quarterly technical progress report were used in the reaction models to predict percent conversion values that were compared with the experimentally measured values from the University of Delaware. Parity plots of conversion (predicted vs. experimental) were generated using different sets of five resids to produce the starting vectors used to calculate conversion for all fifteen resids. These plots show that the data fit the parity line well (but differently) for all five resid starting sets.

Section 2

INTRODUCTION

This is the Technical Progress Report for the sixteenth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period April 1 through June 30, 1998.

CONTRACT OVERVIEW

The objectives of this project are to support the DOE direct coal liquefaction process development program and to improve the useful application of analytical chemistry to direct coal liquefaction process development. This project builds on work performed in DOE Contract No. DE-AC22-89PC89883. Independent analyses by well-established methods are obtained of samples produced in direct coal liquefaction processes under evaluation by DOE. Additionally, new analytical instruments and techniques to examine coal-derived samples are being evaluated. The data obtained from this study are used to guide process development and to develop an improved data base on coal and coal liquids properties. A sample bank, established and maintained for use in this project, is available for use by other researchers. The reactivity of the non-distillable resids toward hydrocracking at liquefaction conditions (i.e., resid reactivity) was examined. From the literature and experimental data, a kinetic model of resid conversion was constructed and is being refined. Such a model will provide insights to improve process performance and the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS PERIOD

- CONSOL characterized nine process stream samples received from Exxon Recycle Coal Liquefaction Unit (RCLU) operations conducted in 1994 with Rawhide Mine Wyoming subbituminous coal and all-dispersed Fe and Mo catalysts. Those results are described in the Results and Discussion section of this report.
- The University of Delaware subcontract was completed with issuance of the Topical Report covering work performed by Delaware.
- Computational studies of the coal liquefaction resid models developed at the University of Delaware were continued at CONSOL R&D. The two reaction models, consisting of

the “reaction optimization” and “reaction once-through” programs, were the focus of these studies. The computations were performed on a Hewlett Packard Apollo HP-735 RISC workstation and a Silicon Graphics Octane RISC workstation. The updated resid structure data and results were used in the reaction models to predict percent conversion values that were compared with the experimentally measured values from the University of Delaware.

- Small samples of high-sulfur Hondo resid and anthracene oil were shipped to John Verkade of Iowa State University at his request. Verkade is testing a desulfurization method.
- The Task 2.1 Topical report was drafted and is in internal review. Literature describing new (1994 to the present) analytical techniques applicable to resids and similar materials was reviewed.

ACTIVITIES IN PROGRESS

- Characterization work began on process stream samples from HTI Run PB-02. In Run PB-02, hybrid catalyst (dispersed plus supported catalyst) operation was tested with combinations of Black Thunder Mine coal, Hondo petroleum resid, and municipal solid waste plastics as feedstocks.
- CONSOL continues to work through FETC to obtain samples from the Japanese NEDOL pilot plant.

Section 3

RESULTS AND DISCUSSION

CHARACTERIZATION OF PROCESS STREAM SAMPLES FROM EXXON RCLU OPERATIONS WITH RAWHIDE SUBBITUMINOUS COAL

INTRODUCTION AND RUN BACKGROUND

In 1994, the Exxon Research and Development Laboratory (ERDL) liquefied Rawhide Mine Wyoming subbituminous coal in its Recycle Coal Liquefaction Unit (RCLU) in 24 yield periods (days) at eight sets of conditions.^{1,2} CONSOL received a sample of the feed coal and nine oil samples representing three sample points and yield periods of three operating conditions.³ The oil samples were characterized via standard methods employed by CONSOL for analyses of a variety of process streams from many different liquefaction processes.

A diagram of the RCLU is provided in Figure 1.^{1,2} The RCLU, located in Baton Rouge, LA, was designed to process 34 kg (75 lb) of coal per day. It consists of slurry mix and feed vessels, a catalyst pretreater followed by two liquefaction reactors in sequence, a letdown system consisting of hot and cold separators, a bottoms stripper, and a fractionation system for the oils. Batches of feed slurry are prepared every 6-8 hours and transferred to the feed tank. The pretreater is operated to sulfide and condition the dispersed catalyst with a nominal residence time of 20-30 minutes. The upflow liquefaction reactors are heated by sand baths and operate with nominal residence times of 40-55 minutes. The bottoms stripper uses the cold separator off-gases to strip nominally 538 °C⁻ (1000 °F⁻) material from the hot separator bottoms. The liquids then are separated into a light oil and a vacuum gas oil in the fractionation tower. Recycle streams for slurry preparation consist of vacuum gas oil and stripped bottoms. The RCLU unit has been described in more detail elsewhere.^{1,2}

The operations of interest took place from August 7 through October 29, 1994, during which 24 yield periods were completed. Catalyst characteristics, run conditions, process yields, and related information, as reported by Exxon, are provided in Tables 1-4. Coal conversions were not reported by Exxon; they were calculated by CONSOL R&D from Exxon data (Table 4). The run was performed to demonstrate operation of the unit, to define suitable catalyst screening conditions, and to test two molybdenum and three iron catalysts.

The feed coal composite sample provided by Exxon to CONSOL was a composite from several drums of the Rawhide Mine subbituminous coal that was fed during the run. This coal was chosen to be similar to the Black Thunder Mine coal that was fed during runs at the Wilsonville pilot plant. Prior to its use during the run, the Rawhide Mine coal was partially dried from 30-33% moisture content to 7-10% moisture content.

Oil samples provided to CONSOL were taken from sample points identified on the containers as A100 (Recycle Bottoms), A101 (Gas Oil), A102 (Distillation Product). These represent all of the non-gas intermediate and final products from the unit. Conditions and Yield Periods (YP) represented were Condition 1 (YP409-411), Condition 3 (YP419-421), and Condition 4 (YP422-424). In Condition 1, the Reactor 1 temperature was 430 °C; in Conditions 3 and 4, the Reactor 1 temperature was 440 °C. The Reactor 2 temperature was 450 °C in Conditions 1, 3, and 4. The dispersed catalyst was Bailey iron oxide in Conditions 1 and 3, and Bayferrox iron oxide in Condition 4. The dispersed iron oxide dose was kept constant at about 1.0 wt % of dry coal through Condition 4, after which it was reduced to about 0.25 wt % dry coal for the remainder of the run. The molybdenum dose was kept constant at 100 mg/kg of dry coal throughout the run, although the Mo source was varied.

Condition 3 was operated with higher first-stage reactor temperature and higher space velocity than Condition 1. The solvent recycle:coal ratio (S/C) was 1.07 in Condition 1, and slightly lower in Condition 3 (S/C = 0.95) and Condition 4 (S/C = 0.94). The bottoms recycle:coal ratio (B/C) was 0.85 in Condition 1, and slightly lower in Condition 3 (S/C = 0.79) and Condition 4 (S/C = 0.76) (Table 3).

The source of dispersed molybdenum was Molyvan L in Condition 1 and Condition 4, but Molyvan A was used in Conditions 2A, 2B, and 3, because Molyvan L was unavailable (Table 3).

Exxon concluded that the decrease in recycle ratio in Condition 2A (1.92 in Condition 1 decreased to 1.65 in Condition 2A) had a significant effect on process yields, resulting in a heavier product slate and increased 538 °C⁺ conversion (Table 4). The recycle ratio remained low at 1.70-1.75 in Conditions 3 and 4, although other variables were changed. Although

Exxon also decreased the H₂S addition rate after Condition 2A, they did not attribute any changes in yields or 538 °C⁺ conversion to that change.

Exxon increased the first-stage temperature and mass velocity for Condition 3 through the rest of the run in order to make it easier to detect the impact of a better catalyst in Condition 3. The nominal residence time (NRT) was decreased from about 50 minutes to about 40 minutes after Condition 2B (Table 3). Exxon observed small decreases in 538 °C⁺ conversion (from 88.6% to 86.9%, MAF) and distillate yield (from 59.1% to 56.5%, MAF) when the first-stage temperature and mass velocity were increased in Condition 3, relative to Condition 1 (Table 4).

The change in iron oxide catalyst precursor from Bailey in Condition 3 to Bayferrox in Condition 4 was accompanied by some changes in process performance (Table 4). Other conditions were nominally the same in Condition 4 as in Condition 3, except for an unintended reactor 1 temperature drop of 2 °C that accompanied the change to Condition 4. 538 °C⁺ conversion, gas yield, and hydrogen consumption all decreased in Condition 4. Liquid yield showed little decrease, and gas selectivity (100 x C₁-C₄ gas yield/total conversion) decreased (Table 4).

Other changes noted by Exxon during conditions from which CONSOL received no samples have been described elsewhere.^{1,2} In general, Exxon concluded that the recycle ratio apparently had a greater effect on operating performance than catalyst source or catalyst addition rate in the ranges tested. It was speculated that the constant Mo addition rate of 100 mg/kg may have masked other catalyst effects.

Analytical Results

CONSOL R&D's analyses of the Rawhide Mine composite feed coal are provided in Table 5. Also provided for reference are the component ranges from daily coal analyses reported by Exxon for the run periods, CONSOL's analyses of the Black Thunder Mine coal used in HTI Run POC-2 and many bench unit runs, and HTI's analyses of the Black Thunder Mine coal. Values for carbon, nitrogen, and oxygen by difference obtained by CONSOL for Rawhide Mine coal are slightly outside the range of values observed for those elements by Exxon (CONSOL's carbon value is 0.56% absolute lower than the lowest one reported by Exxon). The low

hydrogen content obtained by CONSOL relative to the Exxon values result in CONSOL's atomic H/C ratio being lower than those based on Exxon analyses.

The Rawhide Mine coal contained about 0.3 wt % (dry basis) more ash than did the Black Thunder Mine coal. The analyses otherwise show that the Rawhide Mine coal was generally similar to the Black Thunder Mine coal fed at HTI.

Data shown in Tables 6 and 7 indicate that there is little or no difference in characteristics of process oils produced in Conditions 1, 3, and 4.

The Condition 1 Gas Oil 454 °C⁻ distillate has a slightly higher donor solvent quality (91% MAF conversion) than its Condition 3 and 4 counterparts (ca. 85% MAF conversion).

Minor differences are indicated over the three conditions in the aromatic proton categories for some whole oils or their distillate or resid components (Table 7). These data indicate that the oils generally were relatively higher in condensed aromatic hydrogen and lower in uncondensed aromatic hydrogen in Condition 1 than in Conditions 3 and 4.

There was virtually no difference in the component distribution data and phenolic -OH concentrations for the comparative streams that were produced in the three run conditions. The distillation product samples are quite high in phenolic -OH, indicating that they are high in phenolics (approximately 25 wt % phenolic compounds), and may be a good source of phenolics for chemical feedstocks.

The bottom line is that the product and recycle oils produced during Conditions 1, 3, and 4 have very similar characteristics.

Coal Conversion

Exxon reported 1000 °F⁺ conversions on a MAF coal basis (Table 4). CONSOL R&D used the yield of THF solids¹ (THF insolubles from 1000 °F⁺ bottoms fraction), as reported by Exxon, to calculate coal conversion to THF solubles (Table 4). These data show no change as a result of the recycle ratio change in Condition 2A, but do show a decrease of 0.6% or more after

Condition 2A, when the sulfiding agent (H_2S) rate was decreased. The most significant change in these coal conversions occurred in Condition 6, when there was a decrease of about 1%, apparently as a result of use of the Mach 1 catalyst.

CONSOL R&D also calculated coal conversion (Table 6) from its own analyses of the feed coal and from the IOM and ash contents of the A100 Recycle Bottoms samples obtained in Conditions 1, 3, and 4. These values were in the range 96.5% to 96.7%, about 1-2% higher than the coal conversions shown in Table 4.

Comparison with HTI and Wilsonville Results

The HTI and Wilsonville runs that are most directly comparable to the Exxon RCLU run are HTI Run CMSL-9, Condition 6, and Wilsonville Run 263, Periods C, D, and E. Condition 6 of HTI Run CMSL-9 was designed to be a comparison point with Condition 4 of the RCLU run. The RCLU conditions were based on Wilsonville operations in Run 263. CONSOL previously reported process stream characterization results for both the HTI⁵ and Wilsonville⁶ runs. However, the characterization data available for the Wilsonville plant did not include process streams that are analogous to the RCLU streams. The best available samples for comparison were the V-131B ashy recycle solvent stream from Periods C, D and E, when the first-stage temperature was 449 °C (840 °F), and the second-stage temperature was 432 °C (810 °F). This process stream is similar to a combined gas oil and recycle bottoms stream in the RCLU run (i.e., the materials being recycled, without fractionation into separate components). On the basis of yields (discussed below), Period E of Run 263 was chosen for the best comparison.

Run conditions and yield data for comparison periods of Exxon Run RCLU-1, Wilsonville Run 263, and HTI Run CMSL-9 are given in Table 8. Relative to the other two runs, the temperature in Run 263 was higher in the first stage (449 °C vs. 440 °C) and lower in the second stage (432 °C vs. 449 °C). Run 263 used a high/low temperature configuration, whereas Run RCLU-1 and Run CMSL-9 used a low/high configuration. The three runs also differed in iron catalyst type and amount, and in molybdenum catalyst source. Other differences included use of interstage separation in Run 263, and differences in solids separations methods and recycle component ratios among the three runs.

HTI compared their results from Condition 6 of Run CMSL-9 with Conditions 3 and 4 of the RCLU run and found (Table 8) that the Run CMSL-9 distillate yields were 2-3% MAF higher than those obtained by Exxon.⁷ Also in Run CMSL-9, light gas yields were slightly lower, the HTI 524 °C⁺ resid conversion was slightly higher than the Exxon 528 °C⁺ resid conversion, and hydrogen consumption was slightly higher than in the Exxon run. HTI attributed the improved performance to higher activity of their sulfated hematite catalyst. The iron catalyst source was the main difference in nominal operating conditions between the HTI and Exxon operations. However, there were other differences in operations (distillation temperatures, solids separation techniques, and recycle recipes) that may have contributed to performance differences.

As shown in Table 8, the process performance results from all three runs shown were generally similar to each other. This indicates that the three processes arrived at roughly the same point in terms of performance and yields.

Many characteristics of the Exxon RCLU process streams were similar to corresponding streams from one or both of the other two runs (Table 9). The donor solvent quality was ca. 10% lower in the whole recycle distillate from Run 263, relative to those from the other runs. The largest difference among the runs is in the condensed aromatic and uncondensed aromatic hydrogen contents of the recycle distillate, which ranged from 13.8% to 24.8% condensed aromatics and from 7.1% to 12.2% uncondensed aromatics. The combined aromatic hydrogen content ranged from 25.0% to 31.9% in the recycle distillate from the three runs.

The proton distribution of the recycle distillates from Exxon Run RCLU-1 and Wilsonville Run 263 were much more similar to each other than either one is to the proton distribution of the recycle distillate from HTI Run CMSL-9. The proton distribution of the distillate product materials from HTI Run CMSL-9 and Wilsonville Run 263 are more similar than those of the corresponding Exxon Run RCLU-1 material, which was higher in aromatic hydrogen content.

The Exxon bottoms material contains several percent more aromatic hydrogen than does the HTI bottoms material.

The bottoms sample from the RCLU run contained about 5% more ash than did the sample from the HTI run. The process streams from the RCLU run were generally a few percent more aromatic than their Run CMSL-9 counterparts. This could arise partly from differences in the iron catalysts used, in distillation temperatures, in solids separation techniques, and in recycle recipes.

We conclude that the generally similar process stream characteristics, like the process yield data, indicated that all three processes arrived at approximately the same point.

STRUCTURE AND REACTIVITY MODEL PROGRESS

Introduction

The coal liquefaction resid models developed at the University of Delaware involve complex computer programs for the generation of model-compound mixtures to represent resid structures and a set of model-reactions for the computation of resid reaction conversion values. The purpose of the structure model is to construct a physio-chemical description for each resid sample from analytical measurements on each resid sample.

Earlier work at CONSOL R&D⁸ involved using the resid structure model to generate a model compound representation of the 15 coal resid samples on the HP-735 RISC workstation. Each resid sample was run through the "structure optimization" and "structure once-through" programs. The results provided 33 structure parameters from the "structure optimization" and 18 characterization parameters from the "once-through" computation.

The resid reaction program requires the structure parameters for five separate resid samples as input data. From these data, the program produces an optimized set of 19 reaction parameters. The values of the reaction parameters that result from the optimization are used in the "reaction once-through" program, which produces a predicted percent conversion to 850 °F material for each resid. The predicted percent conversion can be compared with the experimentally-determined percent conversion values measured at the University of Delaware.

Computational studies of the coal liquefaction resid models developed at the University of Delaware were continued this quarter at CONSOL R&D. The two reaction models, consisting of the "reaction optimization" and "reaction once-through" programs, were the focus of these studies. The computations were performed on a Hewlett Packard Apollo HP-735 RISC workstation and a Silicon Graphics Octane RISC workstation. The updated resid structure data and results presented in the previous quarterly technical progress report were used in the reaction models to predict percent conversion values that were compared with the experimentally measured values from the University of Delaware.

Reaction Optimization Computations

The input data to the reaction optimization program consisted of five (5) resid structure characterization files, a reaction parameter starting vector, and lower and upper bounds for each reaction parameter.

The reaction optimization program attempts to minimize the difference between predicted and actual percent conversion values for the five resids defined as inputs by varying the values of 19 reaction parameters. A structure characterization file, which is the product of the structure optimization and structure once-through programs, is needed for each of the five resids that are used as input. Several groups of five resids were selected to permit an examination of the influence of the specific selections upon the predicted values for the percent conversion. One of the groups was run multiple times. The group/run combinations are summarized in Table 10.

The algorithm for reaction optimization is the “simulated annealing” algorithm. This algorithm also was used for the structure optimization studies to match experimentally obtained analytical data with the predicted resid properties. The algorithm requires a starting vector (initial guess) of parameter values. Table 11 shows the starting vectors used by the University of Delaware (U of D) and CONSOL for the various group/run combinations.

The progress of the optimization is measured by the “F-value” of a particular set of reaction parameter values. The F-value is a measure of the difference between the predicted and experimental conversion values. The reaction optimization was programmed to end when either the difference between successive F-values was less than 1×10^{-6} or the optimization computation completed 100,000 iterations.

Figure 2 shows the progress of some of the reaction optimization runs. As can be seen from this figure, most of the progress occurred within the first 40,000 iterations. Because of the considerable amount of time needed to run a reaction optimization on the HP workstation, several of the optimizations were ended at 50,000 iterations.

To do a complete reaction optimization on the HP-735 RISC workstation took approximately 39 days of computation time. The processor chip operated at a clock speed of 99 MHz. A Silicon Graphics Octane RISC workstation being evaluated by CONSOL R&D was used to perform reaction optimization calculations. This SGI workstation was considerably faster (clock speed of 250 MHz), and completed an optimization in approximately six days.

Six reaction optimization computer runs were completed at CONSOL. The results are presented in Table 12. Numeric optimized values are reported for each of the 19 reaction parameters.

Reaction Once-Through Computations

The input data for the "reaction once-through" program includes a structure characterization file and a corresponding optimal set of 19 reaction parameters. In addition to the standard structure parameters, the following four parameters are needed in the structure characterization file:

Frac THF Ins -	Insoluble portion of the resid
Conv @ t1 -	Experimentally determined conversion at time t1
t1 (sec) -	Conversion time
% Low Boilers -	Amount of volatile material in the model resid

The "reaction once-through" program must be run two times on the same data in order to calculate a predicted conversion percentage. The first time it is run, the following parameters are set to a value of zero:

Conv @ t1
t1 (sec)
% Low Boilers

The first time the "reaction once-through" program is run it produces a predicted conversion. This value is then assigned to the "% Low Boilers" in the structure characterization file.

"t1 (sec)" is set to 1800 and "Conv @ t1" is set to the experimentally determined conversion at 1800 seconds. The "reaction once-through" program then is re-run.

The six reaction optimization groups yielded six sets of 19 reaction parameters. Each combination of 15 coal resid structure characterizations and six reaction parameter sets were used as input to the "reaction once-through" program, producing 90 predicted conversions (Table 13).

Reaction Conversion Results

The resid reaction optimization and resid "reaction once-through" computer program runs are defined in Table 10 and the results are presented in Tables 11 through 13. Table 13 displays the percent conversion values and the experimental values for comparison. The convergence of the optimization computations as a function of the number of iterations is shown graphically in Figure 2. Figures 3 through 9 graphically display the percent conversion results. For each group of optimized reaction parameters, the predicted versus experimental conversions are shown. A $y=x$ parity line is shown on each graph to indicate where the data points would lie if the model's predicted conversion matched the experimentally-determined conversion. These results are discussed below.

Discussion

Groups of five resids were selected for reaction optimization computations (Table 10). The group of resids selected originally by the University of Delaware represents a random selection of five resid samples of the fifteen. Group 1 is composed of resids A through E simply because these were the first five resids for which reaction optimization computation data were available. Group 2 was selected as a diverse set so as to contain representatives of each of the three feed coals (Black Thunder Mine, Illinois No. 6, and Pittsburgh seam), each of the three sample types (interstage, second stage, and recycle), and each of the preparation facilities (Wilsonville and HTI). Groups 3 through 5 are defined in Table 10. They were selected to represent a specific coal (Group 3, Black Thunder Mine), a specific sample type (Groups 4 & 5, recycle steam samples), and a single preparation facility (Group 5, Wilsonville plant).

The reaction optimization run for each resid set requires a starting or initialization vector of 19 optimization parameters. This is sometimes called the “initial guess”. The Table 11 shows the starting vectors used in this work. In general, for a robust optimization program, the results will be independent of the starting vector. Testing with a few different starting vectors is important to help determine to what extent this independence exists.

The resid reaction optimization process generated an optimal set of 19 parameters in each run. The parameters are optimized when the objective function for the reaction model (the F-value) is minimized. As shown in Table 12, good (low) results were obtained for the F-value. The parameters among the runs vary and, for Runs 5-1 and 5-2, differ in spite of the fact that these sets of parameters represent the same set of resid samples (A,C,D,E,H). The effects of these differences result in noticeable differences in the computed percent conversion values, as described below.

There is only modest agreement between the predicted and experimental conversion percentages (Table 13). Tables 14 and 15 provide quantitative measures of the agreement between the predicted and experimental percent conversion values. The “Scatter” column of Tables 14 and 15 indicates the cumulative difference over all 15 resids between the predicted and experimental values for the given group of reaction parameters. The degree of scatter was substantial for all of the results obtained. The important influence of resids N and O is clearly seen in these tables. For Run 5-2 the scatter was 11.567 with resids N and O included and 5.007 without including resids N and O. Generally, the scatter was somewhat less for all of the results which excluded resids N and O. Resids N and O were obtained from the HTI process. All other resids were obtained from the Wilsonville pilot plant. It is known that the HTI resids have considerably different ash contents and hydrogen contents than the Wilsonville samples. The HTI samples have higher resin contents and lower asphaltene contents than the Wilsonville resids.

Slope and Intercept values are also shown in Tables 14 and 15 for the least-squares best straight line representing the conversion predictions. For the full set of 15 resid samples, the slope values ranged from 0.409 to 0.825. However, the intercept values ranged from 3.73 to 30.49, indicating that the prediction capability of the model tends to become unreasonable

outside of the range of experimental values present in this study. Somewhat poorer agreement was found for the straight line predictions without the N and O resid samples included.

As shown in Figure 2, the optimization computations converge quickly onto a minimum value for the objective function F. The ratio F-initial over F-current is seen to approach 0.9 within about 30,000 iterations and to have become effectively 1.0 within about 50,000. As shown in Table 12, some 85,000 to 93,000 iterations were needed to meet the stringent requirement that F change by less than one part in one million. For practical purposes in the examination of the overall performance of these models, it can be concluded that results obtained after 50,000 can be considered adequate for comparison with other similar results.

A y-versus-x parity plot is provided for each run performed to graphically display the predicted versus the experimental values for the percent conversion of the resid samples. It is indicated in Figures 3 through 9 that resids N and O provided a unique influence on the results obtained. The University of Delaware under-predicted values for resids N and O, while the CONSOL results generally over-predicted them.

A comparison of Figures 3 and 4 indicates that most of the results cluster about the parity line, except for resids N and O, which tend to be under-predicted in the case of the University of Delaware computations and over-predicted in the case of the CONSOL random set (Group 1).

The Figures 5, 6, and 7 show results for Group 2 resids (a random set), Group 3 resids (the Black Thunder Mine and Pittsburgh seam coals set), and Group 4 resids (Black Thunder Mine coal, recycle samples only, from both pilot plants). Considerable scatter is seen on these plots. Somewhat better agreement is seen with Group 4, which used data from only one coal and one sample type to construct the reaction model.

Figures 8 and 9 display the least-squares best-fit straight line through the percent conversion values for Runs 5-1 and 5-2. The r^2 values for these best-fit lines and the r^2 values for best-fit lines for all other cases are given in Tables 14 and 15. The "Slope" and "Intercept" columns of Tables 14 and 15 list the best linear fit between predicted and experimental percent conversion values for all of the runs performed in this work. Ideally, the slope should be 1.0

and intercept should be 0.0. However, due to the clustering of percent conversion values in the range of 35% to 60%, most of the computed slope and intercept values depart noticeably from these ideal values.

Runs 5-1 and 5-2 differed in two ways. First, the starting vectors differed. Second, the reaction optimization was performed on the SGI workstation in the case of Run 5-1 and on the HP workstation in the case of Run 5-2. These results suggest that a true global minimum value may not have been achieved with the initial starting vectors used in this work. Additional computational work is under way to investigate this possibility.

Run 5-1 yielded the best overall results (best match with experimental conversion values), as shown in the Table 13 and Figure 9. The resids included in this run set were A, C, D, G, and H. These are all recycle resids rather than interstage or second-stage resids. Each of these resids was generated at the Wilsonville plant. All three coals used to produce resids in the set of 15 are represented, Black Thunder (A, G, H), Illinois No. 6 (D) and Pittsburgh seam (C). The results for this same Group shown in Figure 9 also are reasonably good, except for the N and O resid samples of the HTI plant.

Differences in optimization results and predicted conversion behavior were observed between the HP-735 RISC workstation (Runs 1-1, 3-1, 5-2) and the SGI Octane RISC workstation (Runs 2-1, 4-1, 5-1). This may be due to differences between the operating systems of the HP (HP-UX 10.20) and SGI (IRIX 6.5) workstations for the same calculation sequences. Differences in the numerical word length, the precision of the numerical values and the algorithms for function evaluations would likely result in the somewhat different values obtained, particularly for the programs used in this work, in which random number generation is involved. It is known that these two workstations employ different application binary interfaces for interpretation of the compiled FORTRAN code to the central processing unit (cpu). The future work recommended below is intended to further resolve and explain these differences.

Recommended Additional Work

It is recommended that reaction optimization model runs be performed for the following sets of resid samples.

- (a) Run the University of Delaware group (resids B, D, E, H, L), which was previously run on an IBM-RS/6000, on the HP-735 RISC workstation for comparison with the other runs at CONSOL. This is important because the CONSOL runs utilized additional characterization data for the resid samples.
- (b) Run Group 1 (resids A, B, C, D, E) and Group 4 (resids A, G, H, N, O) using the second starting vector, for comparison with results already achieved with the first starting vector. This is important because vectors one and two resulted in somewhat different results for Group 5 (resids A, C, D, G, H).
- (c) Run Group 5 (resids A, C, D, G, H) with a third and fourth starting vector, to determine whether the results for the second starting vector can be further improved. These runs are needed to establish whether the optimal vector of 19 parameters obtained with the second starting vector is a local optimum or a global optimum.
- (d) A new group could be formed representing Black Thunder Mine coal only, to exclude the HTI plant samples. Such a set could include any five of the following resids: A, E, F, G, H, K, or L.

The results to date have clearly established that 50,000 iterations are adequate to provide converged results for the reaction optimization program. Thus, the total computer hours needed to complete these runs can be reduced by approximately 50% over the full run requirements, as was experienced with previous reaction optimization runs.

Section 5

CONCLUSIONS

Conclusions are provided in the Executive Summary section of the report.

Section 6

REFERENCES

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Section 7

LIST OF ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing and Materials
B/C	Recycle bottoms/coal ratio
CMSL	Run designation used by HTI for catalytic multi-stage liquefaction
DOE	Department of Energy
ERDL	Exxon Research and Development Laboratory
FTIR	Fourier-transform infrared
GC-MS	Gas chromatography-mass spectrometry
HTI	Hydrocarbon Technologies, Inc.
HTU	Hydrotreater unit
IBP	Initial boiling point
IOM	Insoluble organic matter
MAF	Moisture and ash free
MF	Moisture free
NMR	Nuclear magnetic resonance
NRT	Nominal residence time
PB	POC bench option, HTI run designation
PFC	Pressure filter cake
PFL	Pressure filter liquid
POC	Proof of concept
RCLU	Recycle coal liquefaction unit
S/C	Recycle solvent/coal ratio
SOH	Separator overhead; the hydrotreated net product
THF	Tetrahydrofuran
V-131B	Wilsonville recycle oil
VSB	Vacuum still bottoms
VSOH	Vacuum still overhead
YP	Yield period

TABLE 1

**PROPERTIES OF SLURRY CATALYSTS
FROM EXXON RUN RCLU-1**

Catalyst	Particle Size, Microns	Surface Area, m ² /g	Bulk Density, g/cm ³	Physical Form	Composition, wt %
Nanocat® Superfine Iron Oxide (SFIO)	0.003	250	0.05	Reddish-brown powder	100% Fe ₂ O ₃
Bayferrox PK 5210 Technical Iron Oxide	0.020	123	N/A	Reddish-brown powder	100% Fe ₂ O ₃
Bailey Iron Oxide	96 wt % <44	N/A	N/A	Reddish-brown powder	100% Fe ₂ O ₃
Molyvan L, Molybdenum-containing lubricant	N/A	N/A	1.08	Dark green liquid	8.1% Mo
Molyvan A, Molybdenum-containing powder	5 to 10	N/A	1.58	Yellow-orange powder	30.0% Mo
Ammonium heptamolybdate	N/A	N/A	2.50	White powder	54.3% Mo

Source: References 1, 2

TABLE 2

**SUMMARY OF EXPERIMENTAL DESIGN
FROM EXXON RUN RCLU-1**

Condition	Comment	Yield Periods of Interest
1	Initial conditions.	409-411
2A	Reduced solvent-to-coal ratio compared with initial conditions	412-414
2B	Reduced H ₂ S treat rate compared with conditions 1 and 2A	415, 416, 418
3	Increased first-stage reactor temperature and increased mass flow rate compared with previous conditions.	419-421
4	Switched from Bailey iron oxide to Bayferrox PK 5210 iron oxide catalyst.	422-424
5	Reduced iron oxide addition rate from 1.0 to 0.25 wt % on dry coal	425-427
6	Switched from Bayferrox PK 5210 to Mach 1-Nanocat SFIO catalyst	428-430
7	Switched from organic to inorganic source for molybdenum catalyst and switched back to Bayferrox PK5210 iron oxide.	431-433

Source: References 1, 2

TABLE 3

SUMMARY OF TEST CONDITIONS FROM EXXON RUN RCLU-1

Condi- tion	Fe ₂ O ₃ Type	Fe ₂ O ₃ wt % Dry Coal	Mo Type	S/C:B/C (a)	H ₂ S as S wt %	NRT, (b) min	Reactor Temp.	
							1st °C (°F)	2nd °C (°F)
1 (c)	Bailey	1.03	Molyvan L	1.07:0.85 (d)	5.8	49	430.6 (807.0)	450.6 (843.0)
2A	Bailey	0.99	Molyvan A	0.94:0.71	6.0	53	431.1 (808.0)	451.1 (844.0)
2B	Bailey	1.00	Molyvan A	0.90:0.75	2.7	50	431.3 (808.3)	449.3 (840.7)
3 (c)	Bailey	1.02	Molyvan A	0.95:0.79 (d)	3.4	41	441.3 (826.3)	450.0 (842.0)
4 (c)	Bayferrox	1.00	Molyvan L (e)	0.94:0.76 (d)	3.3	41	439.3 (822.7)	449.6 (841.3)
5	Bayferrox	0.25	Molyvan L	0.91:0.80	3.0	41	441.5 (826.7)	450.6 (843.0)
6	Mach 1	0.26	Molyvan L	0.91:0.83	3.1	42	440.9 (825.7)	450.4 (842.7)
7	Bayferrox	0.26	Inorganic	0.98:0.85	3.1	41	440.9 (825.7)	450.0 (842.0)

Source: References 1, 2, 3

Nominal reactor pressure for all conditions was 17.2 MPa (2500 psig).

- (a) S/C = Recycle Solvent (Gas Oil)/Coal Ratio,
B/C = Recycle Bottoms/Coal Ratio; both are DAF basis
- (b) NRT - Nominal residence time
- (c) Other conditions provided in Reference 3 were nominal space velocity of 480 kg/hr-m³ (30 lb/hr-ft³) in Condition 1 and 640 kg/hr-m³ (40 lb/hr-ft³) in Conditions 3 and 4, and hydrogen treat rate of 12 wt % in Conditions 1, 3, and 4. Basis is unknown, but presumed to be dry coal. See also notes d and e.
- (d) Reference 3 gave nominal ratios of 0.91:1.38 for Condition 1, and 0.85:1.15 for Conditions 3 and 4.
- (e) Listed as Molyvan A in Reference 3.

TABLE 4

SUMMARY OF RECONCILED YIELDS AND CONVERSION FROM EXXON RUN RCLU-1
(wt % Based on Dry Ash-Free Coal)

Condi- tion	Yield Period	H ₂	C ₁ -C ₄	C ₅ -177 °C (350 °F)	177-343 °C (350-650 °F)	343-538 °C (650-1000 °F)	538 °C* (1000 °F*) Conversion	Coal Conver- sion to THF Solubles (a)
1	409-411	-6.12	15.34	14.48	33.93	9.06	88.56	95.36
2A	412-414	-6.11	14.51	13.54	32.55	13.57	89.26	95.34
2B	415- 418	-5.77	13.69	12.86	31.35	14.87	88.60	94.74
3	419-421	-5.76	13.31	12.30	29.61	14.59	86.88	94.52
4	422-424	-5.43	12.48	12.71	31.33	13.70	85.62	94.21
5	425-427	-5.76	14.08	12.24	31.22	13.54	87.01	94.63
6	428-430	-5.46	12.82	11.66	30.69	14.67	85.19	93.61
7	431-433	-5.65	12.61	12.27	32.14	12.57	85.74	94.26

Source: References 1, 2.

- (a) Calculated by CONSOL R&D from Exxon data as 100%-Exxon's yield of THF solids;³ Exxon did not report directly coal conversion to THF solubles.

TABLE 5

**ANALYSES OF RAWHIDE MINE COAL FROM EXXON RUN RCLU-1
AND COMPARISON DATA FROM BLACK THUNDER MINE COAL**

Coal	Rawhide Mine		Black Thunder Mine	
Analysis by	CONSOL R&D	Exxon	CONSOL R&D	HTI
Reference	This report	1	4	5
Moisture Content, wt% As-Determined	9.00	Unreported	11.91	10.1
Ash, wt% Dry	6.62	5.26* - 6.07*	6.27 (4.97*)	6.19
<u>Elemental, wt% Dry</u>				
Carbon	67.66	68.22 - 70.00	69.96	70.12
Hydrogen	4.04	4.63 - 4.90	4.66	5.11
Sulfur	0.44	0.43 - 0.69	0.45	0.35
Chlorine	<0.02	NA	<0.01	NA
Nitrogen	0.93	0.95 - 1.19	0.97	0.99
Oxygen (by Diff.)	20.31	18.16* - 20.13*	17.69 (18.99**)	17.24
Heating Value, BTU/lb, Dry	11,420		11,636	
H/C Atomic Ratio	0.71	0.80 - 0.86	0.79	0.88

Results for ash and oxygen (by difference) are on a basis that includes ash-SO₃, except where otherwise noted.

NA = Not Available

* Ash SO₃ - free basis.

TABLE 6

**COMPONENT DISTRIBUTION, DONOR SOLVENT QUALITY, AND
FTIR PHENOLIC -OH DETERMINATIONS OF PROCESS STREAMS
FROM EXXON RUN RCLU-1**

Sample	Component Distribution, %					Conversion in Microautoclave to THF Solubles, % MAF (a)	
	454 °C ⁻ Dist	454 °C ⁺ Resid THFS	IOM	Ash	Total	Whole Sample	454 °C ⁻ Dist
A101 Gas Oil							
Cond. 1 (YP409-411)	81.1	17.8	0.1	0.0	99.0	83.7	91.2
Cond. 3 (YP419-421)	82.5	16.5	0.2	0.2	99.4	84.6	85.5
Cond. 4 (YP422-424)	81.9	17.5	0.1	0.0	99.5	86.9	84.4
						Coal Conversion to THF Solubles During Run RCLU-1, % MAF (c)	
A100 Recycle Bottoms							
Cond. 1 (YP409-411)	-	44.9(b)	15.8	39.3	100.0	96.7	
Cond. 3 (YP419-421)	-	46.9(b)	15.6	37.5	100.0	96.6	
Cond. 4 (YP422-424)	-	47.9(b)	15.6	36.5	100.0	96.5	
Phenolic -OH Determination by FTIR							
Sample	Whole Sample		454 °C ⁻ Distillate		454 °C ⁺ Resid THFS		
	Conc., meq/g	Peak Pos., cm ⁻¹	Conc., meq/g	Peak Pos., cm ⁻¹	Conc., meq/g	Peak Pos., cm ⁻¹	
A199 Recycle Bottoms							
Cond. 1 (YP409-411)	0.79(d)	3288	-	-	-	-	
Cond. 3 (YP419-421)	0.78(d)	3289	-	-	-	-	
Cond. 4 (YP422-424)	0.79(d)	3289	-	-	-	-	
A101 Gas Oil							
Cond. 1 (YP409-411)	-	-	0.99	3300	1.02	3293	
Cond. 3 (YP419-421)	-	-	1.00	3300	1.08	3293	
Cond. 4 (YP422-424)	-	-	1.11	3299	1.14	3294	
A102 Distillation Product							
Cond. 1 (YP409-411)	2.23(e)	3309	-	-	-	-	
Cond. 3 (YP419-421)	2.31(e)	3310	-	-	-	-	
Cond. 4 (YP422-424)	2.37(e)	3309	-	-	-	-	

- (a) Conversion to THF solubles at standard microautoclave Modified-Equilibrium test conditions: 399 °C (750 °F), 30 min, 9 g solvent, 6 g standard Old Ben Mine (Indiana 5 seam) coal.
- (b) Based on extraction of whole (undistilled) sample, calculated by difference.
- (c) RCLU unit coal conversion calculated via a simple ash balance procedure, and based on CONSOL data for the feed coal (Table 5) and the IOM and ash concentrations in the A100 Recycle Bottoms samples.
- (d) THF solubles of whole sample.
- (e) On "as-received" samples.

TABLE 7
PROTON DISTRIBUTIONS BY NMR OF PROCESS STREAMS
FROM EXXON RUN RCLU-1

Sample (a)	Distribution, % of Protons						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Whole Sample							
<u>A100 Recycle Bottom</u>							
Cond. 1 (YP409-411)	42.1	10.0	15.9	8.8	8.9	8.4	6.0
Cond. 3 (YP419-421)	38.0	12.1	16.4	9.6	9.8	8.9	5.2
Cond. 4 (YP422-424)	38.2	10.2	16.9	9.7	10.3	9.5	5.2
<u>A101 Gas Oil</u>							
Cond. 1 (YP409-411)	20.9	11.9	15.4	10.5	10.9	21.3	9.0
Cond. 3 (YP419-421)	18.8	12.5	14.8	10.7	11.4	21.4	10.3
Cond. 4 (YP422-424)	20.1	12.2	14.8	11.0	11.5	21.2	9.2
<u>A102 Distillation Product</u>							
Cond. 1 (YP409-411)	7.5	13.7	12.1	13.4	14.5	24.0	14.8
Cond. 3 (YP419-421)	6.4	9.3	11.7	15.0	15.2	25.4	16.9
Cond. 4 (YP422-424)	5.6	13.8	10.9	13.7	15.2	24.4	16.4
454 °C⁻ Distillate							
<u>A101 Gas Oil</u>							
Cond. 1 (YP409-411)	20.4	9.9	15.8	10.1	11.3	23.2	9.3
Cond. 3 (YP419-421)	17.2	12.1	15.9	10.8	11.5	23.8	8.7
Cond. 4 (YP422-424)	18.5	11.8	14.6	10.8	11.1	23.3	9.9
454 °C⁺ Resid							
<u>A101 Gas Oil</u>							
Cond. 1 (YP409-411)	32.5	8.0	19.5	9.8	10.8	13.0	6.4
Cond. 3 (YP419-421)	27.4	10.1	18.2	10.7	11.2	14.4	8.0
Cond. 4 (YP422-424)	29.0	9.6	18.1	10.3	11.7	14.0	7.4

(a) The A100 samples were dissolved in 99.96% d₅-pyridine and filtered prior to running NMR spectra; the other samples were dissolved in 99.8% CDCl₃ and run unfiltered.

TABLE 8

**RUN CONDITION AND YIELD COMPARISON BETWEEN HTI RUN CMSL-9,
EXXON RUN RCLU-1, AND WILSONVILLE RUN 263**

Run	HTI CMSL-9	Exxon RCLU-1	Exxon RCLU-1	Wilsonville Run 263
Condition	6	3	4	E
Residence Time, min	40	41	41	N/A
<u>Temperatures, °C</u>				
Pretreater	300	300	300	N/A
Reactor K-1	440	441	439	449
Reactor K-2	449	450	450	432
Hydrotreater	379	N/A	N/A	N/A
<u>Dispersed Catalysts</u>				
Molybdenum Precursor	Molyvan A	Molyvan A	Molyvan L	Molyvan L
mg/kg as Mo	100	100	100	100
Iron Precursor	FeOOH/SO ₄	Bailey	Bayferrox	Bailey
wt % of Precursor	1%	1%	1%	2%
<u>Yields (% MAF) (a)</u>				
C ₁ -C ₃	9.8	10.8	10.2	9.0
C ₄ -538 °C	62.6	59.0	60.0	60.7
C ₄ -177 °C	12.8	14.8	15.0	11.3
177-343 °C	32.4	29.6	31.3	} 49.5
343-538 °C	17.4	14.6	13.7	
Coal Conversion, % MAF	96.1	94.5 (a)	94.2 (a)	94.1
538 °C ⁺ Resid Conv., % MAF (b)	87.6	86.9	85.6	83.8
Hydrogen Consumption, % MAF	6.1	5.8	5.4	5.5

- (a) Calculated by CONSOL from Exxon data as 100%- Exxon's yield of THF solids;³ coal conversion to THF solubles was not reported directly by Exxon.
- (b) HTI's data represents the C₄-524 °C distillate fraction and 524 °C⁺ resid conversion instead of C₄-538 °C yield and 538 °C⁺ resid conversions in Exxon's data.

This table was modified from a table in Reference 7.

TABLE 9

**COMPARISON OF PROCESS STREAM CHARACTERISTICS FROM EXXON RCLU-1,
HTI RUN CMSL-9, AND WILSONVILLE RUN 263**

Sample Type and Analyses	HTI Run CMSL-9, Cond. 6³	Exxon Run RCLU-1 Cond. 4 (YP422-424)	Wilsonville Run 263 Period E⁴
<u>Distillate Product</u> % Aromatic H % Hydroaromatic H % Paraffinic H % Cond Arom H % Uncond Arom H	<u>SOH Oil</u> 15.8 16.0 47.5 4.9 10.9	<u>Distillation Product, A102</u> 19.4 15.2 40.8 5.6 13.8	<u>V-161 Naphtha (a)</u> 15.2 19.3 46.4 3.0 12.2
<u>Recycle Distillate</u> % Aromatic H % Hydroaromatic H % Paraffinic H % Cond Arom H % Uncond Arom H	<u>VSOH (c)</u> 25.0 13.0 35.9 13.8 11.2	<u>Gas Oil, A101</u> 32.3 11.5 30.4 20.1 12.2	<u>V-131B Recycle Oil (b)</u> 31.9 11.9 31.0 24.8 7.1
<u>Recycle Distillate, Phenolic -OH Conc., meq/g</u> 454 °C ⁻ Dist Portion 454 °C ⁺ Resid Portion	<u>VSOH (c)</u> N/A N/A	<u>Gas Oil, A101</u> 1.11 1.14	<u>V-131B Recycle Oil (b)</u> 1.03 1.11
<u>Recycle Distillate, Donor Solvent Quality (e)</u> 454 °C ⁻ Dist Portion Whole Portion	<u>CASB (d), Substitute for VSOH</u> 80.6 86.3	<u>Gas Oil, A101</u> 86.9 84.4	<u>V-131B Recycle Oil (b)</u> N/A 75.8
<u>Bottoms (Pyridine-Soluble Portion)</u> % Aromatic H % Hydroaromatic H % Paraffinic H % Cond Arom H % Uncond Arom H	<u>Vacuum Still Bottoms, VSB</u> 43.1 11.1 17.4 36.2 6.9	<u>Recycle Bottoms, A100</u> 48.4 10.3 14.7 38.2 10.2	N/A
<u>Bottoms</u> % THF Solubles % IOM % Ash % Coal Conversion to THF Solubles Based on IOM and Ash	<u>Vacuum Still Bottoms, VSB</u> 51.0 17.2 31.8 95.6	<u>Recycle Bottoms, A100</u> 47.9 15.6 36.5 96.5	N/A

- (a) Produced in Period G (supported catalyst present in second-stage reactor), no sample was available from Periods C, D, or E (dispersed catalyst operations).
- (b) The undistilled V-131B oil and the CASB substituted here for VSOH were ashy streams; the A101 gas oil and VSOH were ash-free.
- (c) Vacuum still overhead.
- (d) Continuous atmospheric still (CAS) bottoms.
- (e) % MAF conversion to THF solubles in standard microautoclave tests.

TABLE 10**DEFINITION OF REACTION OPTIMIZATION GROUP/RUNS**

Group - Run	Structure Characterizations Selected	Optimization Platform	Reason for Combination
U of D -1	B, D, E, H, L	IBM/AIX	Random/Diverse Set Without N or O
1-1H	A, B, C, D, E	HP/HP-UX	Initial/Random Set Without N or O
2-1S	A, B, H, I, N	SGI/IRIX	Random/Diverse Set With N
3-1H	C, E, G, J, L	HP/HP-UX	Black Thunder & Pittsburgh Seam Coal Set
4-1S	A, G, H, N, O	SGI/IRIX	Black Thunder/Recycle/Both Plants Set
5-1S	A, C, D, G, H	SGI/IRIX	Three Coals/Recycle/One Plant Set
5-2H	A, C, D, G, H	HP/HP-UX	Three Coals/Recycle/One Plant Set

Legend:

IBM - IBM RS-6000 with AIX operating system.

HP - HP 9000/735 with HP-UX operating system.

SGI - SGI Octane/250 with IRIX operating system.

TABLE 11**INITIALIZATION VECTORS FOR REACTION OPTIMIZATION COMPUTATIONS**

	Reaction Parameter	U of D Initial (Run U of D -1)	CONSOL Initial (Runs 1-1 to 5-1)	CONSOL Initial (Run 5-2)
1	b1	1.2648	1.5	1.75
2	b2	2.1165	3.0	2.5
3	kpar	4.4793	5.0	6.0
4	kref(1)	2.2738	4.0	5.0
5	kref(2)	2.2595	3.0	3.0
6	kref(3)	3.8468	5.0	4.0
7	kref(4)	6.875	5.0	6.0
8	kref(5)	4.0195	6.0	7.0
9	kref(6)	8.8701	7.0	8.0
10	kref(7)	3.9551	5.0	6.0
11	alpha(1)	1.0223	0.8	0.9
12	alpha(2)	0.8233	0.5	0.75
13	alpha(3)	0.63033	0.5	0.25
14	alpha(4)	0.15498	0.5	0.75
15	s(1)	0.0047893	0.05	0.08
16	s(2)	0.34237	0.45	0.35
17	s(3)	0.2895	0.2	0.15
18	s(4)	0.55493	0.4	0.5
19	s2(1)	0.67306	0.75	0.9

TABLE 12
RESULTS OF REACTION OPTIMIZATION COMPUTATIONS

		U of D - 1	Run 1-1H	Run 2-1S	Run 3-1H	Run 4-1S	Run 5-1S	Run 5-2H
	Reaction Parameter		50,000 Iterations	93,101 Iterations	91,201 Iterations	85,986 Iterations	86,744 Iterations	50,000 Iterations
1	b1	1.2648	1.0279	1.9550	1.9386	1.8835	1.4666	1.0513
2	b2	2.1165	3.4849	2.1100	3.0766	2.6856	3.3021	3.2920
3	kpar	4.4793	6.9764	3.2854	6.8964	3.1180	3.5972	6.8067
4	kref(1)	2.2738	2.9837	2.0749	2.8804	2.2745	2.1694	2.2839
5	kref(2)	2.2595	2.9427	2.1766	2.9669	2.2013	2.8507	2.9063
6	kref(3)	3.8468	5.3798	4.9735	3.1507	6.0244	4.0469	5.8389
7	kref(4)	6.8750	5.8009	3.0010	3.6212	3.1611	3.8964	4.4889
8	kref(5)	4.0195	7.9669	4.4504	4.0135	4.0343	4.0680	5.9578
9	kref(6)	8.8701	5.0002	5.0006	5.3244	5.0026	5.0005	5.0013
10	kref(7)	3.9551	6.7200	3.4063	5.1352	3.3534	4.7528	4.6187
11	alpha(1)	1.0223	1.0993	0.9459	1.0963	0.9698	0.6792	1.0511
12	alpha(2)	0.8233	0.0026	0.9996	0.0043	0.9041	0.0002	0.0415
13	alpha(3)	0.6303	0.0001	0.9964	0.0028	0.9933	0.9368	0.6432
14	alpha(4)	0.1550	0.6078	0.2184	0.0549	0.0139	0.0272	0.9108
15	s(1)	0.0048	0.998	0.0930	0.9907	0.0015	0.0008	0.0955
16	s(2)	0.3424	0.4990	0.3040	0.4104	0.3189	0.5965	0.5574
17	s(3)	0.2895	0.1001	0.2060	0.1074	0.2869	0.2779	0.1839
18	s(4)	0.5549	0.2001	0.2865	0.2479	0.3659	0.2305	0.2080
19	s2(1)	0.6731	0.5003	0.9348	0.5805	0.9016	0.5000	0.5000
	F-value	18.3	5.1173	5.9929	0.8950	3.8117	22.0581	14.8156

TABLE 13

**PREDICTED PERCENT CONVERSION FROM
"REACTION ONCE-THROUGH" COMPUTATIONS**

	Experimental	U of D -1	Run 1-1H	Run 2-1S	Run 3-1H	Run 4-1S	Run 5-1S	Run 5-2H
A	35.0	33.5	27.714*	25.199*	41.206	26.252*	25.657*	29.755*
B	38.1	34.1*	32.531*	36.254*	47.267	37.156	35.001	34.402
C	33.1	31.4	32.340*	33.041	41.816*	32.358	31.704*	34.239*
D	32.9	44.8*	38.201*	56.764	58.592	57.089	44.054*	41.961*
E	32.1	39.5*	26.819*	35.633	37.614*	37.704	33.079	33.573
F	37.4	45.8	24.799	23.106	37.770	25.803	19.417	34.505
G	35.8	43.6	27.511	32.584	40.081*	34.609*	29.180*	37.554*
H	44.6	34.6*	29.468	36.441*	38.324	37.557*	33.888*	36.304*
I	42.7	36.3	38.774	47.626*	56.713	49.669	44.517	41.526
J	42.1	33.3	30.973	32.379	44.612*	35.190	33.488	37.105
K	35.2	40.0	28.825	30.730	42.508	32.570	27.168	35.423
L	36.4	35.6*	30.175	34.176	42.179*	35.392	31.886	31.700
M	35.3	37.4	32.746	37.577	49.072	39.738	34.689	42.031
N	47.6	64.6	58.623	49.432*	70.364	48.972*	50.522	67.574
O	34.3	64.2	51.513	39.030*	66.443	38.585*	35.561	68.553

* indicates that the structure optimization data for this resid was used in the reaction optimization computation for this group.

TABLE 14**COMPARISON OF REACTION RESULTS
(15 RESID SAMPLES)**

Run	r ²	Scatter	Slope	Intercept
U of D -1	0.0305	11.270	0.409	25.927
1-1H	0.1579	9.411	0.809	3.731
2-1S	0.0472	20.291	0.597	30.487
3-1H	0.0942	14.583	0.697	21.477
4-1S	0.0516	19.752	0.596	30.327
5-1S	0.0825	18.777	0.767	22.766
5-2H	0.1056	11.567	0.825	9.471

TABLE 15**COMPARISON OF REACTION RESULTS
(13 RESID SAMPLES; N and O EXCLUDED)**

Run	r ²	Scatter	Slope	Intercept
U of D -1	0.0971	7.042	-0.350	50.597
1-1	0.0229	8.278	0.160	24.935
2-1	0.0006	15.156	0.047	47.167
3-1	0.0036	10.901	0.103	40.633
4-1	0.0038	15.047	0.121	44.461
5-1	0.0260	12.840	0.258	37.847
5-2	0.0381	5.007	0.191	29.098

Figure 1. Schematic Flow Plan of RCLU Pilot Plant (Source: Reference 2)

Figure 2. Reaction Optimization Progress.

Figure 3. Coal Resid Model Conversion Results.
University of Delaware Run 1: B, D, E, H, L (Random/Diverse Set Without N or O)

Figure 4. Coal Resid Model Conversion Results.
Run 1-1H: A, B, C, D, E (Initial/Random Set Without N or O)

Figure 5. Coal Resid Model Conversion Results.
Run 2-1S: A, B, H, I, N (Random/Diverse Set with N)

Figure 6. Coal Resid Model Conversion Results.
Run 3-1H: C, E, G, J, L (Black Thunder Mine and Pittsburgh Seam Coal Set)

Figure 7. Coal Resid Model Conversion Results.
Run 4-1S: A, G, H, N, O (Black Thunder Mine/Recycle/Both Plants Set)

Figure 8. Coal Resid Model Conversion Results.
Run 5-1S: A, C, D, G, H (Three Coals/Recycle/One Plant Set)

Figure 9. Coal Resid Model Conversion Results.
Run 5-2H: A, C, D, G, H (Three Coals/Recycle/One Plant Set)