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**ADVANCED DIRECT LIQUEFACTION CONCEPTS
for PETC GENERIC UNITS**

**Quarterly Technical Progress Report
for Period October 1993 through December 1993**

by

**University of Kentucky
Center for Applied Energy Research**

Sandia National Laboratories

CONSOL Inc.

LDP Associates

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SUMMARY

PROCESS SIMULATION TESTING PLAN

Several promising leads that have developed during the course of this program are being evaluated in this phase of the study. These have been selected from those that can be economically evaluated within the time constraints of the program schedule. A detailed plan for evaluating these approaches was formulated.

The individual steps that will be evaluated are:

- Dewaxing of the distillate recycle solvent stream treating either 25% or 100% of the stream.
- Hydrotreating the dewaxed distillate streams in a downflow fixed bed reactor.
- Agglomerating the coal using both the 25% and 100% dewaxed-hydrotreated distillate streams.
- Liquefying the as-received coal and the agglomerated coals using two different Mo-promoted hematite particulate catalysts.
- Liquefying two different Mo-Fe impregnated coals.
- Liquefying the two oil-agglomerated, Mo-Fe impregnated coals.

The effect of the presence of molybdenum in the 1050 °F⁺ will be determined by making comparisons in both Mo-containing and Mo-free full range V-131B process solvent. The solvents that will be used in this study are the full-range reconstituted Mo-containing V-131B from Run 262E and a Mo-free V131B made up of 1050 °F⁺ bottoms from Run 258K V-131B and V-1074 distillate from Run 262E.

The series of experiments are described and a chart has been prepared summarizing this series of runs. The plan requires significant exchange of samples between the different participants in the program with the schedule timed for providing the data for economic evaluation within the next quarterly reporting period.

TASK 1.2 LABORATORY SUPPORT (CONSOL)

Two dewaxed oil samples were prepared and sent to Sandia for hydrotreatment in preparation for the Integrated Simulation Tests, IST. Basic nitrogen contents of two slack waxes were determined by the National Institute for Petroleum and Energy Research. These results were forwarded to Burns and Roe Services Corp. to help them to refine their predictions concerning FCC yields from slack wax feedstock. Revised analyses are reported for the Martin Lake lignite previously shipped to program participants. Float/sink fractions of Black Thunder coal, Martin Lake lignite, and Burning Star 2 coal produced by CONSOL were provided to CAER for examination by petrography to investigate maceral segregation effects.

TASK 2.1 CO-PRETREATMENT

In previous reports, we have concentrated our effort on demonstrating the effect of CO-pretreatment by evaluating the chemical and structural changes that occur within the coal structure and the potential beneficial impact of coal pretreatment on the liquefaction performance under various reaction conditions. The water-gas-shift (WGS) conversion results from some of these reactions have been previously reported, although they were not extensively discussed. These results of CO conversion were consistently high because of a systematic error in the sampling protocol. Consequently, considerable effort and time has been spent in the last quarter on re-checking equipment, volume capacities, analysis technique and construction of a new gas sampling system. A precise gas balance is required to ensure success in determining the CO_x gas make from the coal reaction in subsequent work with ^{14}C tracers. Test runs have been performed on the new system and the results have indicated a complete recovery and balance of gaseous products. Thus, the old results were re-evaluated and checked against results obtained from corresponding experiments in the newly installed gas sampling system. The revised CO conversion results from earlier experiments, calculated as a function of the recovery of total gas products, are in full agreement with the results from corresponding experiments obtained from the newly installed system. It is important to note that the revised numbers did not change the general trend and conclusions of the study. In this report, we present the results of the water-gas-shift (WGS) reaction and its implication on coal pretreatment. There is a strong correlation

between the WGS reaction and coal solubilization in THF for two different Wyodak coals. In addition both the coal and WGS reactions have a strong dependence on the reaction temperature. The results suggests that varying the reaction conditions may influence the kinetics of the WGS reaction such that the coal reaction may be further enhanced. A good correlation was found between THF solubility of the recovered products and CO conversion. In addition, THF solubility appears to be related to the missing hydrogen from the WGS reaction.

TASK 2.1.2.1 PRETREATMENT/ DEWAXING - (CONSOL)

Approximately 2.6 kg of V-1074 heavy distillate from Wilsonville Run 262E was dewaxed in acetone at -5 °C for use in integrated testing. Over 2 kg of dewaxed oil was recovered. Samples (~1 kg each) of the dewaxed oil and of a simulation of oil that would be produced by dewaxing a 25% slipstream of the total distillate were shipped to Sandia for hydrotreatment.

Examination of the ¹H-NMR proton distributions as a function of the degree of dewaxing suggests that there may be a peak in the hydroaromatic proton content at about 20 wt % wax removal. Coupled with solvent quality studies which showed that intermediately dewaxed (-5 °C in acetone) distillate is a better donor solvent than either shallower dewaxed (-35 °C in acetone/MEK) or deeper dewaxed (-35 °C in acetone) distillate, the NMR data suggest that ~20wt % wax removal is optimum for producing the best donor solvent from the Wilsonville Run 262E distillate.

Analyses of dewaxed distillate samples hydrotreated at different space velocities showed that increasing the space velocity from 0.79 to 1.44 hr⁻¹ resulted in a material with a greater concentration of aromatic protons (less hydrogenated) but with similar donor solvent properties (by microautoclave testing).

Use of Mo-free resid from Wilsonville Run 258K in microautoclave tests results in about 15 wt % lower coal conversions than when Mo-containing ashy resid from Run 262E is used.

Duplicate base case microautoclave tests (5-min, 824 °F, 1500 psig H₂, 1.5 S/C and Wilsonville Run 262E solvent blend) were run that suggest that some sample deterioration may have occurred over the past several months. Resid conversion when SC1 was used as the distillate in the base case test was 12.2 wt % compared with 6.5 wt % when V-1074 was used. A new aliquot of the Black Thunder coal sample was prepared for use in future microautoclave tests. Tests with this new coal aliquot will help determine if the observed decreases in coal conversion over time were due to deterioration of the coal sample.

A systematic error was found in the coal conversions, IOM conversions and total resid conversions reported for all microautoclave tests with Black Thunder coal. Correction of this error lowers the calculated coal conversions by 1.0 to 2.3 wt %, it lowers the calculated IOM conversions by 0.8 to 2.5 wt % and it lowers the calculated total resid conversions by 0.3 to 3.5 wt %. The corrections do not alter any conclusions drawn from these data.

Comparison of TGA-simulated distillations with microdistillations of THF soluble resids from earlier microautoclave tests was continued. TGA repeatability is excellent and data for samples containing 55 to 70 wt % resid fall close to the parity line. TGA data for samples that contain less than 55 wt % resid or more than 70 wt % resid appear to be biased low.

TASK 2.1.2.2 PRETREATMENT/ AGGLOMERATION - (CONSOL)

We applied an ash-SO₃ correction to agglomeration results from an early low-pH run with Black Thunder coal. Corrected ash rejection including dissolution was 31.2%. The product ash content was 3.9%; the feed coal ash content was 5.54% MF.

The results from two previous agglomeration runs (Run A45 with Burning Star 2 coal and Run A47 with Kemmerer coal) were revised, based on re-analysis of the products. Relative to the values reported last quarter, the product ash contents were higher, dissolved plus physical ash rejections were lower, and the ash balances were improved. The revisions were significant for the Burning Star 2 case, but were minor for the Kemmerer case. In both runs, physical ash rejection and organic recovery were unaffected.

TASK 2.1.3 SOLVENT PRETREATMENT (SANDIA)

Experiments performed this quarter have been used to evaluate the effects of solvent hydrotreating parameters on yield of hydroaromatic components in the hydrotreated product. Several operating parameters, such as hydrotreating temperature, liquid space velocities, and hydrogen gas treatment rates were investigated. A trickle-bed hydrotreater packed with a supported nickel/molybdenum on alumina catalyst was used to hydrotreat Wilsonville Run 262E V1074 heavy distillate and dewaxed V1074 distillate. The hydrotreated distillate was analyzed for hydrogen content and hydrogen distribution using elemental analysis and proton NMR spectroscopy. The results from these tests will be used as a prescriptive guide for the Integrated Simulation Testing which will commence in January of 1994.

In addition, proton NMR spectroscopic analyses were performed on hydrotreated dewaxed heavy distillate samples that were hydrotreated at 360°C using two different liquid flow rates. It was found that changing the liquid hourly space velocity (LHSV) from 0.7 hr⁻¹ to 1.1 hr⁻¹ had little effect on the hydroaromatic hydrogen concentration (cyclic $\alpha + \beta$ protons were 38.7% at LHSV = 0.7 hr⁻¹, and 40.5% at LHSV = 1.1 hr⁻¹). This indicates that, at these conditions (360°C, 1300 psig in hydrotreater), there appears to be no penalty for raising the liquid hourly space velocity.

This quarter a catalytic dehydrogenation test also was developed and used to quantify the amount of donor hydrogen in hydrotreated distillate samples.

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS

Particulate Catalyst Synthesis and Characterization

Screening reactions on two promoted sulfated hematite catalysts were chosen for evaluation in the process simulation testing aspect of the program. The 0.7 wt% Ni, 0.9 wt% Mo on α -Fe₂O₃ (P-1) was chosen because of the significant increase in catalyst activity at relatively low promoter metal loading. The second catalyst, a 10 wt% Mo on α -Fe₂O₃ (P-2), provided high conversion and very good selectivity to oils. These two catalyst compositions, therefore, were scaled up during this reporting period.

Results of the screening reactions in tetralin indicated that, although higher in activity than the unpromoted sulfated hematite, both of the catalysts exhibited lower catalytic activity than expected. In reactions utilizing Run 258K V-131B as the reaction solvent, the P-2 catalyst showed only slightly lower resid conversion than expected but the P-1 exhibited no promoter effect. The loss in activity for the P-1 catalyst may be related to the increased nickel content of the particles compared to the particles from the earlier preparation of this material. Based on the favorable results of the P-2 catalyst, this sample will be used in the integrated simulation testing process. However, work is continuing to improve the activity of the P-1 catalyst.

Experiments were conducted to compare the positive effect on liquefaction of impregnating ferrous sulfate on as-received coal using the incipient wetness technique, relative to the thermal conversion of coal or to either the addition of solid ferrous sulfate or an aqueous solution of ferrous sulfate. These experiments were done with tetralin as the hydrogen donor solvent in microautoclaves. Liquefaction results among the latter two, reported as total THF conversion, were within one standard deviation of each other, and were slightly better than the thermal case, indicating that adding ferrous sulfate in either a solid or dissolved form results in only a slight improvement in the conversion of coal. The yield of oil was not statistically different between the three. However, liquefaction was obviously enhanced for the samples where the ferrous sulfate was impregnated on the coal.

Further, a series of experiments was performed to compare the effect of impregnating ferrous sulfate onto a portion of the coal feed, including feed coal fractions of 10, 50 and 90%. The THF conversions of the mixed feed coals were very similar to the samples which were entirely impregnated with ferrous sulfate, implying that the impregnation of the iron on only a portion of the coal does not hinder the performance of the coal in tetralin solvent.

TASK 2.3.2 CATALYST STUDIES (CONSOL)

High organic recoveries were obtained when two forms of Fe-impregnated Black Thunder coal were agglomerated with Wilsonville recycle distillate. For the coal treated by incipient wetness, 100% of the Fe was retained in the agglomerates. For the ion-exchanged coal,

71% of the Fe was retained. These results indicate that agglomeration can integrate well with catalyst incorporation as coal pretreatment steps for liquefaction.

We received two samples of Black Thunder Mine coal which were impregnated with Fe by incipient wetness at CAER. These will be used in the Integrated Simulation Test.

TASK 2.4.2 SOLIDS SEPARATION (CONSOL)

In response to an action item from a quarterly review meeting, additional analyses of the Wilsonville 263J V-107 ash concentrate were obtained. The relatively high volatile matter content (25%, MF) and heating value (9333 Btu/lb, MF) indicate that the ash concentrate may be a good coker feed. The ash concentrate was agglomerated with heavy distillate in one run, but there was no significant physical ash rejection or ash dissolution. Additional steps which may improve ash rejection are being considered.

TASK 3.2 ECONOMIC EVALUATION (CONSOL)

At our request, LDP Associates will determine the economic benefits to the liquefaction process of low (≈ 2) pH agglomeration treatment, which results in the highest ash rejection from Black Thunder subbituminous coal. Potential benefits include: enhanced coal reactivity; extended supported catalyst life through decreased concentration of catalyst poisons such as Na; increased reactor throughput/decreased deasher size; decreased solids buildup; and improved dewatering.

TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP ASSOCIATES)

The Bechtel Baseline Design Report was reviewed. The baseline case developed in this program was adjusted to account for the lower demand for sulfiding agent for the iron catalyst. The estimated quantity of H_2S that will be produced exceeds by 24% the amount needed for sulfiding the added iron. Revised prices of iron oxide (12¢/lb) and molybdenum (\$2.70/lb) were obtained from suppliers. An assessment was begun on a hypothetical case of the effect on product price of reducing the hydrocarbon gas make by 50% as discussed in the last quarterly report. The economics of solvent dewaxing was completed.

SECTION ONE

**Center for Applied Energy Research
University of Kentucky**

WORK PERFORMED

Process Simulation Testing Plan

The overall program has been regularly reviewed as work progressed. Earlier reviews pointed out areas of promising leads that led to work that has been on-going. Several of the approaches that were evaluated were abandoned either because of unfavorable results or an obvious inability to generate sufficient data that would ultimately lead to a solid economic evaluation within the time constraint of the program. At the November quarterly review meeting, specific program areas were reviewed in detail and from this review specific approaches to be evaluated in the Process Simulation Testing Phase were selected. Subsequent to that review a detailed plan for evaluating these approaches was formulated by all the participants in this program.

This phase of the program will determine the effect of integrating various individual steps on the overall process performance. Because of the presence of significant concentrations of molybdenum in the ashy resid in the base case containing Wilsonville Run 262E solvent, which had been selected as the process solvent for evaluation earlier in the program, it was desired that comparisons be made in both Mo-containing and Mo-free full range V-131B process solvent. Therefore, the solvents that were selected for this study were the full-range reconstituted Mo-containing V-131B from Run 262E and a Mo-free V131B made up of 1050 °F⁺ bottoms from Run 258K V-131B and V-1074 distillate from Run 262E in which Mo was used.

The individual steps involved in this evaluation are:

- Dewaxing of the distillate recycle solvent stream to remove the paraffinic fraction by treating either the entire distillate recycle stream (100% case) or a portion of the stream (25% slipstream case).
- Preparing the 25% slipstream distillate by blending 37.5 wt% V-1074 from Run 262E and 62.5 wt% -5 °C acetone dewaxed V-1074 from Run 262E.

- Hydrotreating the 25% slipstream and 100% dewaxed distillate streams in a downflow fixed bed reactor.
- Agglomerating the coal using both the 25% and 100% dewaxed-hydrotreated distillate streams.
- Liquefying the as-received coal and the agglomerated coal using two different Mo-promoted hematite particulate catalysts.
- Liquefying two different Mo-Fe impregnated coals.
- Liquefying two oil-agglomerated, Mo-Fe impregnated coals.

A series of experiments was planned to address these factors. These experiments are summarized in Table 1. The first series of experiments will be conducted in a simulated full-range Mo-free ashy-resid solvent as described below, using 1050 °F⁺ bottoms prepared from Run 258K V-131B.

1. Liquefaction will be performed on as-received Black Thunder coal in a solvent comprising Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms.
2. Liquefaction will be performed on as-received Black Thunder coal in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms.
3. In this experiment, as-received Black Thunder coal, that will be oil-agglomerated using hydrotreated dewaxed Run 262E V-1074 distillate, will be liquefied in hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms.
4. Liquefaction will be performed on as-received Black Thunder coal in a solvent

Table 1. Summary of Process Simulation Testing Plan

Sample No.	Solvent^a	Coal^b	Oil Agglomerated^c	Resid^d	Catalyst^e
1	V	AR	N	FM	N
2	D	AR	N	FM	N
3	D	AR	Y	FM	N
4	D	AR	N	FM	P1
5	V	AR	N	FM	P2
6	S	AR	N	FM	P2
7	D	AR	N	FM	P2
8	D	AR	Y	FM	P2
9	V	IW-1	N	FM	N
10	D	IW-1	N	FM	N
11	V	IW-1	Y	FM	N
12	S	IW-1	Y	FM	N
13	D	IW-1	Y	FM	N
14	D	IW-2	Y	FM	N
15	V	AR	N	M	P2
16	D	AR	N	M	P2
17	D	IW-1	Y	M	N
18	V	AR	N	M	B
19	D	AR	N	M	B

a. Distillate solvent: V =Run 262E V-1074; D =hydrotreated 100% dewaxed V; S = hydrotreated 25% slipstream dewaxed V.

b. Coal: Wyodak Black Thunder coal used throughout; AR =as received; IW-1 =AR impregnated with 500 ppmw Mo/0.77 wt% Fe (dry basis); IW-2 =AR impregnated with 250 ppmw Mo/0.77 wt% Fe (dry basis).

c. Oil Agglomerated: Used specified distillate solvent; Y =yes; N =no.

d. Resid: M =1050 °F⁺ fraction of Run 262E V-131B; FM =1050 °F⁺ fraction of Run 258K V-131B.

e. Catalyst: N =none; P1 =particulate 1 wt% Mo/1 wt% Ni on sulfated-hematite catalyst added at a concentration of 1.0 wt% Fe₂O₃ on dry coal; P2 =particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe₂O₃ on dry coal; B =1.0 wt% Wilsonville iron oxide and 100 ppmw Mo as Molyvan L on dry coal.

comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms with a particulate 1 wt% Mo/1 wt% Ni on sulfated-hematite catalyst added at a concentration of 1.0 wt% Fe₂O₃ on dry coal.

5. In this experiment, liquefaction will be performed on as-received Black Thunder coal in a solvent comprising Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms to which will be added a particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe₂O₃ on dry coal.

6. This experiment will be performed on as-received Black Thunder coal in the 25% slipstream distillate and Run 258K V-131B 1050 °F⁺ bottoms to which will be added a particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe₂O₃ on dry coal.

7. In this experiment, as-received Black Thunder coal will be liquefied in a solvent comprising a hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms to which will be added a particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe₂O₃ on dry coal.

8. In this experiment, as-received Black Thunder coal that will be oil-agglomerated using hydrotreated dewaxed Run 262E V-1074 distillate will be liquefied in hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms to which will be added a particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe₂O₃ on dry coal.

9. In this experiment, an as-received coal impregnated with 500 ppm Mo/0.77 wt% Fe (dry basis) and dried to 5.4 wt% moisture will be liquefied in a solvent comprising Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms.

10. In this experiment, an as-received coal impregnated with 500 ppm Mo/0.77

wt% Fe (dry basis) and dried to 5.4 wt% moisture will be liquefied in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms.

11. An oil agglomerated coal, prepared by agglomerating undried as-received coal, that was impregnated with 500 ppm Mo and 0.77 wt% Fe (dry basis), in Run 262E V-1074 distillate oil, will be liquefied in a solvent comprising Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms.

12. An oil agglomerated coal prepared by agglomerating undried as-received coal, that was impregnated with 500 ppm Mo and 0.77 wt% Fe (dry basis), in an oil comprising a hydrotreated 25% dewaxed slipstream distillate, will be liquefied in a hydrotreated 25% dewaxed slipstream distillate and Run 258K V-131B 1050 °F⁺ bottoms.

13. An oil agglomerated coal prepared by agglomerating undried as-received coal, that was impregnated with 500 ppm Mo and 0.77 wt% Fe (dry basis), in a hydrotreated dewaxed Run 262E V-1074 distillate oil, will be liquefied in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms.

14. An oil agglomerated coal prepared by agglomerating undried as-received coal, that was impregnated with 250 ppm Mo and 0.77 wt% Fe (dry basis), in a hydrotreated dewaxed Run 262E V-1074 distillate oil, will be liquefied in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F⁺ bottoms.

The following experiments will be conducted in a simulated full-range solvent with Mo-containing ashy-resid using 1050 °F⁺ bottoms from Run 262E.

15. In this experiment liquefaction will be performed on as-received Black Thunder coal in a solvent comprising Run 262E V-1074 distillate and Run 262E V-131B 1050 °F⁺ bottoms to which will be added a particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe₂O₃ on dry coal.

16. In this experiment as-received Black Thunder coal will be liquefied in a solvent comprising a hydrotreated dewaxed Run 262E V-1074 distillate and Run 262E V-131B 1050 °F⁺ bottoms to which will be added a particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe₂O₃ on dry coal.

17. An oil agglomerated coal prepared by agglomerating undried as-received coal, that was impregnated with 500 ppm Mo/0.77 wt% Fe (dry basis), in a hydrotreated dewaxed Run 262E V-1074 distillate oil, will be liquefied in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 262E V-131B 1050 °F⁺ bottoms.

18. In this experiment liquefaction will be performed on as-received Black Thunder coal in a solvent comprising Run 262E V-1074 distillate and Run 262E V-131B 1050 °F⁺ bottoms to which will be added 100 ppm wt% Mo as Molyvan L and 1.0 wt% Fe₂O₃ as Wilsonville Iron Oxide (dry coal basis).

19. Liquefaction will be performed on as-received Black Thunder coal in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 262E V-131B 1050 °F⁺ bottoms to which will be added 100 ppm wt% Mo as Molyvan L and 1.0 wt% Fe₂O₃ as Wilsonville Iron Oxide (dry coal basis).

The liquefaction tests will be performed at 440 °C in tubing bombs for periods of 5 minutes and 22 minutes. Products will be analyzed by a workup procedure involving vacuum distillation to determine resid conversion to distillate product. A technique to distill the products from microautoclaves under the required conditions of temperature and pressure

to make a 1050 °F⁺ product split has been developed and will be employed to determine resid conversion.

TASK 2.1.1 CO PRETREATMENT

Summary

In previous reports, we have concentrated our effort on demonstrating the effect of CO-pretreatment by evaluating the chemical and structural changes that occur within the coal structure and the potential beneficial impact of coal pretreatment on the liquefaction performance under various reaction conditions. The water-gas-shift (WGS) conversion results of some of these reactions have been previously reported, although they were not extensively discussed. These results of the effect on CO conversion were consistently high because of a systematic error in the sampling protocol. Consequently, considerable effort and time was spent in the last quarter on re-checking equipment, volume capacities, analysis technique and on construction of a new gas sampling system. A precise gas balance is required to ensure success in determining the CO_x gas make from the coal reaction in subsequent work with ¹⁴C tracers. Test runs have been performed on the new system and the results have indicated a complete recovery and balance of gaseous products. Thus, the old results were re-evaluated and checked against results obtained from corresponding experiments in the newly installed gas sampling system. The revised CO conversion results from earlier experiments, calculated as a function of the recovery of total gas products, are in full agreement with the results from corresponding experiments obtained from the newly installed system. It is important to note that the revised numbers did not change the general trend and conclusions of the study. In this report, we present the results of the water-gas-shift (WGS) reaction and its implication on coal pretreatment.

The Water-Gas-Shift Reaction in Absence of Coal

The WGS reaction was studied in the absence of coal, with and without NaOH, over the temperature range 250-350 °C for an hour in 25 ml microautoclaves. All CO conversion values are calculated from product recoveries, i.e., CO, CO₂ and H₂. The revised results are presented in Table 2 and the uncertainty in these calculations is on the order of ± 5 %.

The CO_x recoveries are typically between 98-100%. Hydrogen recoveries are quantitative within experimental error. However, in the presence of coal, hydrogen recoveries are poor this will be discussed later in the context of the pretreatment reaction.

Table 2. Effect of Temperature on the WGS Reaction

Temperature, °C	350	320	320	300	300	300	250	250
CO press, psig	800	800	800	800	800	800	800	800
NaOH Conc, mol/L	0.33	0.33	NIL	0.33	0.33	NIL	0.33	NIL
Reaction Time, min	60	60	60	120	60	60	60	60
CO _x recoveries, mol%	102	100	100	91	96	97	97	98
CO Conv mole %	34	27	1	19	15	1	5	1

The WGS reaction has been shown to follow first order reversible kinetics with respect to CO concentration, as reported by Amestica and Wolf,¹ with the equilibrium constant for the forward reaction as shown in the following equation:

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

where K_{eq} is large, i.e., at 250 °C and 300 °C, K_{eq} is 67 and 49, respectively. The reaction should theoretically be complete. However, the experimental results shown in Table 2 and Figure 1 indicate that the WGS reaction is far from complete, although it not thermodynamically limited. In the presence of base, CO conversion increases with temperature. CO conversion approached 35% after an hour at 350 °C. In the absence of a base, the effect of the reactor wall on the WGS reaction under the conditions studied is very small, although NaOH has been reported to be highly active in promoting

Fig. 1 CO conversion Vs. Temperature

△ 6 ml. H₂O
○ 6 ml. 0.33M NaOH

the shift reaction in other studies.² The reason for this observation is unclear.

A preliminary study in this laboratory has shown that the WGS reaction can be accelerated with a well known shift catalyst, CoMo/S, leading to a 51% CO conversion after an hour reaction time at 300 °C. However, the addition of CoMo/S did not shift the reaction to equilibrium. This result is surprising since Amestica and Wolf reported a 90% CO conversion with this catalyst after an hour reaction time at 240 °C. This result is currently under further investigation.

In light of the good correlation between the WGS reaction and the coal pretreatment reaction, as discussed below, further investigation of methods of enhancing the WGS reaction by adding a suitable WGS catalyst and the coal reaction is continuing.

Relationship Between Product Solubility and CO Conversion

Although the chemistry of the WGS reaction is still subject to debate, the kinetics of the reaction, to a large extent, has been well studied. It has been a major objective of this pretreatment work to establish whether there is a correlation between the WGS reaction and the coal pretreatment reaction. Moreover, we seek to understand the influence of the reaction conditions on the reaction kinetics so that the overall process can be improved or optimized. Product solubility in THF, as a first approximation, has been a good indicator of the "level" of coal reaction in the pretreatment study. Therefore, it is logical to determine if a correlation exists between the THF solubility of the recovered products and the WGS reaction as measured by the level of CO conversion. The products recovered, including water-insoluble and humic acid material (if any is formed), is plotted against the amount of CO consumed/converted (mmol) during the reaction (Figure 2). The data points on the plot constitute reactions carried out at temperatures ranging from 250-300 °C, CO pressures from 300-800 psig and 6 ml. of NaOH solution at concentrations of 0.02-0.33 moles/L. The results presented in Figure 2 show a strong correlation between product solubility and CO conversion during pretreatment of the Black Thunder coal. It is interesting to note that the intercept of

**Fig. 2 THF solubility of Recovered Products vs
CO conversion from the Pretreatment of BT coal**

Legend

- A 300 psig CO, 6 ml. (0.02M) NaOH solution, 250 °C, 1h.
- B 800 psig CO, 6 ml. (0.02M) NaOH solution, 250 °C, 1h.
- C 300 psig CO, 6 ml. (0.02M) NaOH solution, 300 °C, 1h.
- D 300 psig CO, 6 ml. (0.33M) NaOH solution, 250 °C, 1h.
- E 550 psig CO, 6 ml. (0.16M) NaOH solution, 275 °C, 1h.
- F 800 psig CO, 6 ml. (0.02M) NaOH solution, 300 °C, 1h.
- G 800 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 30 min.
- H 800 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 1h.
- I 800 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 90 min.
- J 800 psig CO, 6 ml. (0.33M) NaOH solution, 320 °C, 1h.

this plot is very close to the origin, where the THF solubility of BT coal is experimentally determined to be ~ 1 wt% (maf coal basis). The efficiency of the pretreatment reaction is underscored by the relatively small amount of CO conversion during the reaction. This is between 15-20% of the CO charge at 800 psig initial CO pressure and 35-40% at 200 psig CO pressure. It is estimated that up to 85% of the hydrogen generated from the WGS reaction is taken up by the coal. Figure 3 shows a plot of the THF solubility of the products recovered from BT coal reaction versus hydrogen that was missing in the product from the WGS reaction. Although there is some scatter in the data, it is clear that there is a strong correlation between hydrogen "uptake " and THF solubility of the recovered pretreated material.

Similarly, Wyodak coal from the Clovis Point mine (Figure 4) shows the same trend for product THF solubility and CO conversion in spite of the relatively larger scatter of points. The larger scatter is attributed to earlier experimental procedures in the process of development. Some of these data points will be repeated. The reactions for this set of experiments were carried out with CO pressures varying from 200-800 psig and water loading at 2-6 ml at a constant temperature of 300 °C for an hour. The plot of THF solubility and missing hydrogen presented in Figure 5 show a much better correlation and is consistent with the results observed for the BT coal.

Effect of Temperature on the Pretreatment of BT Coal

The effect of temperature on the THF solubility of the recovered products from pretreatment of BT coal can be seen in Figure 6. The reactions were performed at 250-320 °C with 6 ml of solution at either 0.02 or 0.33 moles/L NaOH concentration and 800 psig CO for 1 hour. The results showed a strong correlation between THF solubility of the products and temperature. Similarly, the intercept of this plot comes very close to the origin. The CO conversion and the amount of hydrogen missing from the shift reaction is directionally consistent with the THF solubility trend. It has been our observation that although there is little material converted to THF solubles or water soluble organic acids at 250 °C , there appears to be a significant "loss" of approximately

**Fig. 3 THF conversion vs missing Hydrogen
in the Pretreatment of BT coal**

Legend

- A 300 psig CO, 6 ml. (0.02M) NaOH solution, 250 °C, 1h.
- B 800 psig CO, 6 ml. (0.02M) NaOH solution, 250 °C, 1h.
- C 300 psig CO, 6 ml. (0.02M) NaOH solution, 300 °C, 1h.
- D 300 psig CO, 6 ml. (0.33M) NaOH solution, 250 °C, 1h.
- E 550 psig CO, 6 ml. (0.16M) NaOH solution, 275 °C, 1h.
- F 800 psig CO, 6 ml. (0.02M) NaOH solution, 300 °C, 1h.
- G 800 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 30 min.
- H 800 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 1h.
- I 800 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 90 min.
- J 800 psig CO, 6 ml. (0.33M) NaOH solution, 320 °C, 1h.

Fig.4 THF solubility of Recovered Products vs CO conversion from the pretreatment of CP coal

Legend

- A 200 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 1h.
- B 200 psig CO, 2 ml. (0.33M) NaOH solution, 300 °C, 1h.
- C 400 psig CO, 4 ml. (0.33M) NaOH solution, 300 °C, 1h.
- D 800 psig CO, 6 ml. H₂O, no NaOH, 300 °C, 1h.
- E 800 psig CO, 2 ml. (0.33M) NaOH solution, 300 °C, 1h.
- F 800 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 1h.
- G 800 psig CO, 6 ml. (0.33M) NaOH solution, 300 °C, 120 min

- A 200 psig CO₂, 6 ml. (0.33M) NaOH solution, 300 °C, 1h.
 B 200 psig CO₂, 2 ml. (0.33M) NaOH solution, 300 °C, 1h.
 C 400 psig CO₂, 4 ml. (0.33M) NaOH solution, 300 °C, 1h.
 D 800 psig CO₂, 6 ml. H₂O, no NaOH, 300 °C, 1h.
 E 800 psig CO₂, 2 ml. (0.33M) NaOH solution, 300 °C, 1h.
 F 800 psig CO₂, 6 ml. (0.33M) NaOH solution, 300 °C, 1h.
 G 800 psig CO₂, 6 ml. (0.33M) NaOH solution, 300 °C, 120 min

Legend

Fig. 5 THF solubility of Recovered Products vs missing Hydrogen from the pretreatment of CP coal.

Fig.6 The Effect of Temperature on THF solubility of BT pretreated coal products.

17% oxygen from the coal. It is uncertain at this stage whether this loss in oxygen is attributable to CO_x evolution, leaching of mineral/inorganic matter or simply analytical error. Solomon et al.³ have shown that decarboxylation occurs at 200°C for low-rank coals. It is possible that oxygen containing mineral and inorganic matter may be leached from the coal during the reaction although CONSOL has recently shown that there is very little ash rejection from BT coal in their oil agglomeration study. It is observed that the oxygen loss increased from 17% at 250°C to 32% at 300 °C and to 64% at 320 °C. It is difficult to correlate the primary oxygen loss with either formation of water or CO_x evolution from these data. However, we are currently investigating the CO_x removal aspect of the reaction as a means of oxygen rejection from the coal using a series of ^{14}C tracers.

Effect of Reaction Time on Coal Pretreatment

The effect of reaction time on THF solubility of recovered products is currently under study. Preliminary data show that the THF solubility of the products follows the CO conversion and relates to the amount of missing hydrogen. For CP coal, the CO conversion and THF solubility of the water-insoluble product for the 120 min experiment is 37 wt% versus 20 wt% for the 60 min run. The H/C ratio is also higher after 120 min, being 0.97 for the 120 min run and 0.92 for 60 min reaction. Preliminary analysis of the water-insoluble product obtained from BT coal after a reaction time of 120 min indicated a 46% oxygen removal compared with ~30% oxygen removal after an hour reaction.

Conclusions

We have shown that there is also a strong correlation between the WGS reaction and coal solubilization in THF. In addition, both the coal and WGS reactions have a strong dependence on the reaction temperature. The results suggests that varying the reaction conditions may influence the kinetics of the WGS reaction such that the coal reaction may be further enhanced. A good correlation was found between THF solubility of the recovered products, CO conversion and hydrogen missing from the WGS reaction.

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS

Particulate Catalyst Synthesis and Characterization for Integrated Simulation Testing Introduction

The results of the screening reactions utilizing the promoted sulfated hematite catalysts, which were reported previously, were discussed extensively at the quarterly review meeting. Based on these discussions, two catalyst compositions were chosen for further investigation. The significant increase in catalyst activity at relatively low promoter metal loading reported for the 0.7 wt% Ni, 0.9 wt% Mo on α -Fe₂O₃ (SH-25C) generated considerable interest. Also, the maximum conversion and selectivity to oils obtained using the 10 wt% Mo on α -Fe₂O₃ (SH-37C) seemed suitable for further investigation. These two catalyst compositions were therefore chosen for scale up and use in the integrated simulation testing phase of the project.

Catalyst Synthesis

The larger batches of particulate catalysts were synthesized by the same aqueous precipitation technique previously reported. In this process iron alum (ferric ammonium sulfate hydrate) and urea were mixed in a beaker containing distilled deionized water. The solution was stirred and heated to ~95°C for ~ 2-3 hours. During this period the pH of the solution increased from ~2 to ~7 indicating completion of the reaction. The precipitate was separated by vacuum filtration, washed to remove unbound sulfate groups, and dried in an air flow in an oven at 100 °C overnight. The particles were then vacuum dried at 70 °C for 2 hrs. A muffle furnace was used to calcine the catalyst at 475 °C for ~45-60 minutes. Longer calcination times were necessary with the larger batch size, presumably due to mass transfer limitations .

The promoted sulfated hematites were produced by addition of a metal-containing compound to the iron alum / urea solution. Molybdenum was added as ammonium molybdate. Similarly, the use of ammonium nickel sulfate allowed the incorporation of nickel into the catalyst.

The scale up of the synthesis process involved increasing the volume of water and proportionally increasing the quantities of each of the ions present. The process resulted in an increased amount of all components by a factor of between 5 and 7.5 and yielded approximately 15-25 g of catalyst. The concentrations of the components in solution were calculated to be the same as those of the small batch catalysts.

Catalyst P-1 was prepared by adding 131.25 g of iron alum (ferric ammonium sulfate hydrate), 1.4672 g ammonium nickel sulfate hexahydrate, 0.4035 g ammonium molybdate tetrahydrate, and 187.65 g of urea to 3 L of distilled deionized water. This represents a scaling factor of 7.5 as compared to the SH-25C catalyst preparation. The solution was stirred and heated to $\sim 95^{\circ}\text{C}$ and maintained at temperature for ~ 2 hrs. During this time, the pH of the solution rose from ~ 2 to 7 indicating completion of the reaction. The particles were removed from solution by vacuum filtration and processed as described previously.

Catalyst P-2 was prepared using a scaling factor of 5 as compared to the SH-37C catalyst preparation. In this synthesis, 87.5 g of iron alum, 2.6650 g ammonium molybdate tetrahydrate, and 125.0 g of urea were mixed in 2 L of distilled deionized water. The remainder of the preparation method was as previously described.

Screening Reactions

The catalytic activity of these particles for the liquefaction of the Black Thunder subbituminous coal in tetralin was determined using 50 ml horizontal microautoclave reactors. In these experiments, the microautoclave reactors were loaded with 3 g of as-received coal, 5 g tetralin and 0.07 g dimethyldisulfide (DMDS), which was added as a sulfiding agent. The catalyst was added at an iron loading of 1 wt% with respect to maf coal. The reactors were sealed and pressurized to 1000 psig (cold) with hydrogen, then agitated in a heated fluidized sand bath at 400 cycles/minute. The reactions were carried out at 415°C for 60 minutes, after which the reactors were quenched in a cool sand bath. The use of this system allowed rapid heating and cooling of the reactor to

reduce errors associated with prolonged heat-up and cool-down times.

The total conversion was defined by THF solubility and the THF soluble, pentane insoluble product was defined as preasphaltenes + asphaltenes (PA&A). The THF insoluble product was defined as IOM and the pentane soluble fraction as oils. The total conversion and PA&A yield were determined by weight, and the oil yield was determined by difference. The gas yield was determined directly by gas chromatography. All conversions are reported on a maf coal basis.

In order to determine the activity of the catalysts in a larger scale process, liquefaction runs were carried out in a recycle solvent obtained from the Wilsonville facility. These experiments were carried out in horizontal microautoclave reactors with 3.0 g coal and 5.4 g V-131B solvent from Wilsonville Run 258K, which contained no background Mo. The catalysts were added at 0.7 wt% iron on maf coal and sulfur was added as dimethyldisulfide. The reactors were purged and pressurized to 1000 psig (cold) with hydrogen. Reactions were carried out at 440 °C for 22 minutes to approximate the resid conversions obtained at Wilsonville in run 262E.

The total conversion was determined by THF solubility in a Soxhlet extraction apparatus. The resid conversion was determined by vacuum distillation of the THF soluble portion to an atmospheric equivalent cut point of 1050 °F. The distillate yield was defined as the 1050 °F⁻ fraction while the 1050 °F⁺ fraction was defined as resid. The conversions were reported on an maf SO₃-free coal basis.

The results of the screening runs utilizing tetralin as the donor solvent are shown in Figure 7. As shown, the activity of the P-1 and P-2 catalysts are considerably lower than those of the earlier catalysts. The use of the P-1 catalyst resulted in a decrease in total conversion and oil yield of 3.7% and 6.8%, respectively, as compared to the results obtained with the use of SH-25C. Similarly, the use of P-2 resulted in a decrease of 4.5% and 5.4% in the total conversion and oil yield, respectively, as compared to the

Figure 7. Activity of catalyst for liquefaction of Black Thunder coal in tetralin at 415 °C for 60 minutes.

Figure 8. Activity of catalyst for liquefaction of Black Thunder coal in V-131B at 440 °C for 22 minutes.

results obtained using SH-37C. While the use of both P-1 and P-2 resulted in significant increases in oil yield compared to the use of the unpromoted sulfated hematite, the catalytic activity was lower than expected.

Similarly, the results of runs using the Run 258K V-131B solvent indicated a similar trend in catalyst activities. As shown in Figure 8, the use of the P-1 catalyst resulted in no significant difference in resid conversion or distillate yield compared to the unpromoted sulfated hematite, indicating an apparent loss of promoter effect in P-1. The use of P-2 resulted in a significant increase in resid conversion and distillate yield compared to the unpromoted sulfated hematite, although still slightly lower than that obtained using SH-37C.

Characterization

There are several possible explanations for the lower activity of the large batch catalysts. The scale-up of the catalyst synthesis technique should have had no effect on the concentration of the species involved in the reaction. However, the results of elemental analysis of the catalysts, shown in Table 3, indicate some significant differences.

Elemental analysis of P-1 confirms only a slight 11% increase in molybdenum concentration but a significant increase of 43% in nickel concentration and a 30% decrease in sulfur concentration over the SH-25C. It has been previously reported that the increase in nickel concentration exhibited a negative effect on the selectivity of the molybdenum and nickel promoted sulfated hematites. The decrease in oil yield with the increase in nickel concentration reported for the P-1 fits well with the other data on other nickel molybdenum catalysts that were tested, as demonstrated in Figure 9.

A comparison of the XRD spectra of the SH-25C and P-1 catalysts indicate that the particle phase and average diameter were nearly identical. However, the P-2 particles exhibited a weak spectrum indicating poor crystallinity. The phase of the particles for both catalysts was confirmed as α -Fe₂O₃, although estimations of particles size from this spectrum were dubious. The small particle size estimated for the P-2 appears to be

confirmed by BET nitrogen measurements which indicate a surface area of $\sim 150 \text{ m}^2/\text{g}$. Therefore, the cause for the reduced activity for both catalysts cannot be attributed to surface area. The analysis of P-2 showed a 22% increase in the molybdenum concentration and a 55% increase in sulfur concentration as compared to the SH-37C. Since it had previously been shown that the catalyst activity increases with increasing molybdenum concentration, this should have resulted in higher catalytic activity for P-2. The reason for the lower activity is still under investigation.

Table 3. Elemental Concentrations

	SH-25C	P-1	SH-37C	P-2
Molybdenum	0.9	1.0	8.0	9.7
Nickel	0.7	1.0	0.0	0.0
Sulfur	3.2	2.1	1.1	1.7

Catalyst Aging

In order to determine the effect of aging on catalyst activity, runs were repeated using the aged SH-25C and SH-37C catalysts. As shown in Figure 10, both catalysts showed significant loss of activity of $\sim 3.9\%$. More importantly, a reduction in oil yield of 6.4% and 8.1% were determined for the SH-25C and SH-37C, respectively. This appears to indicate that the associated with these catalysts decreases with age. The catalysts were stored in air and no efforts were made to exclude moisture. It may be possible to regenerate the catalyst to near its original activity by recalcining prior to reaction to remove any moisture. The effectiveness of this technique will be investigated.

Conclusions

Two catalyst compositions were chosen for further study in the integrated simulation testing process. Large batches of these catalysts, designated P-1 and P-2, were synthesized during the reporting period. Results of the screening reactions in tetralin

Figure 9. Effect of nickel and molybdenum concentrations on oil yield from Black Thunder coal in tetralin at 415 °C for 60 minutes.

Figure 10. Effect of aging on catalyst activity for the liquefaction of Black Thunder coal in tetralin at 415 °C for 60 minutes.

indicated that, although higher in activity than the unpromoted sulfated hematite, both of the catalysts exhibited lower catalytic activity than expected. In reactions utilizing Run 258K V-131B as the reaction solvent, the P-2 catalyst showed only slightly lower resid conversion than expected, but the P-1 exhibited no promoter effect. The loss in activity for the P-1 catalyst may be related to the increased nickel content of the particles compared to the SH-25C particles. Based on the favorable results of the P-2 catalyst, this sample will be used in the integrated simulation testing process. However, work is continuing to improve the activity of the P-1 catalyst.

Catalyst Impregnation on Coal

Summary

Experiments were conducted to compare the positive effect on liquefaction of impregnating ferrous sulfate on as-received coal using the incipient wetness technique, relative to the thermal conversion of coal or to either the addition of solid ferrous sulfate or an aqueous solution of ferrous sulfate. These experiments were done with tetralin as the hydrogen donor solvent in microautoclaves. Liquefaction results among the latter two, reported as total THF conversion, were within one standard deviation of each other, and were slightly better than the thermal case, indicating that adding ferrous sulfate in either a solid or dissolved form results in only a slight improvement in the conversion of coal. The yield of oil was not statistically different between the three. However, liquefaction was obviously enhanced for the samples where the ferrous sulfate was impregnated on the coal.

Further, a series of experiments was performed to compare the effect of impregnating ferrous sulfate onto a portion of the coal feed, including feed coal fractions of 10, 50 and 90%. The THF conversions of the mixed feed coals were very similar to the samples which were entirely impregnated with ferrous sulfate, implying that the impregnation of the iron on only a portion of the coal does not hinder the performance of the coal in tetralin solvent.

Introduction

We reported previously that good liquefaction results could be obtained by dispersing iron oxide on the coal surface. A number of samples were prepared using an incipient wetness technique for dispersing nitrate and sulfate salts on the coal. In some cases, these impregnated coals were treated with an ammonium hydroxide to precipitate the iron as FeOOH . This was confirmed by XPS which showed that the iron was highly dispersed regardless of whether the impregnated coals were treated with base or not. More recently, a series of experiments were conducted to see if impregnating a portion of each coal would achieve the same level of conversion as dispersing the metal on all of the coal sample. Since it had been determined earlier that ferrous sulfate is probably the cheapest form of soluble iron that is available, this work was performed exclusively with this salt.

The reasons for examining this approach were:

1. If an impregnation technique were to be used on a commercial scale, the reduced cost of handling only a fraction of the coal would be substantial.
2. If the metal added in this way were active, other more robust and/or active substrates might be considered as the catalyst carrier.

In earlier work using molybdenum, Bockrath⁴ reported that molybdenum sulfide present in THF extracted liquefaction residues retained its catalytic activity when mixed with fresh coal slurry. In later experiments, avoiding the THF extraction and other laboratory work-up steps that might affect the catalyst, 20,000 ppm molybdenum was impregnated onto coal which was then exposed to liquefaction conditions in a microautoclave. The liquefaction product was subsequently mixed with 20 times as much fresh coal to yield 1000 ppm Mo for reaction in a 0.5 liter stirred autoclave, and was found to be active even in the initial stages of liquefaction. In that study, a powdered ammonium molybdate added directly to the microautoclave performed only marginally better than coal without added catalyst.

In our work, liquefaction experiments were carried out using 3.0 g as-received Black Thunder coal in 5.4 g tetralin. The 50 ml microautoclaves were pressurized to 6.89 MPa with hydrogen, sealed, and shaken in an air-fluidized sand bath at 415 °C for 30 minutes. Whenever an iron catalyst precursor was added to the reaction mixture, sulfur, as DMDS, was added in excess at a minimum ratio of 1.5 mol S/mol Fe in order to insure the production of pyrrhotite as the final form of the catalyst. The products of the reaction were removed from the reactor with THF and extracted in a Soxhlet apparatus with THF. The soluble material was separated into pentane soluble (oil) and pentane insoluble (PA+A) fractions. In a comparison run, the activity of non-impregnated ferrous sulfate was determined by adding the solid to the reactor with the coal, tetralin, DMDS and hydrogen.

In a set of experiments shown in Table 4, the positive effect of impregnating ferrous sulfate on as-received coal is shown relative to either the thermal conversion of coal or the addition of either solid ferrous sulfate or an aqueous solution of ferrous sulfate. Data in the first column establish reference or baseline data for the liquefaction of coal at the conditions that were chosen for this study. These results show total THF conversion of 76.4% and an oil yield of 33.2% were obtained with standard deviations for these two measurements of 0.6% and 5.0%, respectively. In the next column data from direct addition of ferrous sulfate to the microautoclave are presented. Powdered ferrous sulfate was added to give 0.79 wt% added Fe on a dry coal basis. DMDS was also added at the same sulfide to iron atomic ratio that was used in the other experiments. These data show that total THF conversion of the coal increased slightly to 78.3%, while the oil yield dropped one point to 32.2%. In the next column, in Table 4, the effect of adding the ferrous sulfate in an aqueous solution is presented. This solution, which contained the equivalent of 0.78 wt% added Fe as ferrous sulfate used only about 1/10th of the water used to impregnate the coals by the incipient wetness method that is discussed below. This solution was added directly to the reactor along with coal, DMDS, tetralin and hydrogen. The results from this run were very close to those from the thermal and solid-addition runs shown in Table 4, which lead to the

conclusions that adding ferrous sulfate in either a solid or dissolved form results in only slight improvement in the conversion of coal, and no statistically significant effect on the yield of oil.

The results from liquefaction of the coal resulting from impregnating the ferrous sulfate onto the coal followed by subsequent base treatment, which will be discussed below, are shown in the last column of Table 4. These data show that impregnating the iron salt onto the coal obviously improved the THF conversion relative to the direct addition of the solid or the ferrous sulfate solution to the reactor. The increase in THF conversion to 84.7% is statistically significant relative to the other runs. The increase in oil yield to 34.3% is not, however, statistically different from the other runs. Earlier data that indicated a significant increase in oil yield by coals having similar concentrations of impregnated Fe were obtained in 60 minute runs; the data here which were obtained at 30 minutes.⁵

A series of experiments were performed to compare the effect of impregnating ferrous sulfate onto only a portion of the total feed coal. Although some of our studies have been done on samples that were not treated with base, all of the samples in the work reported here were subjected to base treatment. As we showed earlier, base treatment of Fe-impregnated samples results in formation of FeOOH. In this discussion, the fraction of the starting coal that was impregnated with the iron is termed the "vector coal". Vector coal fractions of 10, 50, and 90% were evaluated in this study.

Preparation of the Vector Coals- The vector coal samples were prepared using the incipient wetness technique. The weight of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ equivalent to 0.78 wt% Fe on total feed coal (dry basis) was dissolved in a volume of water equivalent to 0.76 g H_2O /g vector coal (dry basis). This solution was added dropwise while stirring the dry coal. Following complete addition of the aqueous Fe solution, the coal was allowed to stand for ¼ hour. Then an ammonium hydroxide solution, which had been prepared from concentrated ammonium hydroxide that had been diluted 10:1 with distilled water, was

Table 4. Liquefaction of Black Thunder coal in tetralin. ^a								
Catalyst Added	none		Powdered ferrous sulfate		Aqueous ferrous sulfate		Impregnated ferrous sulfate	
		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$
Coal moisture, wt% Coal	20.7	1.6	22.4	0.5	21.5	n/a	35.2	5.1
Added Fe, wt% mf Coal	0	n/a	0.79	0.01	0.78	0.00	0.78	0.00
S/Added Fe m/m	0	n/a	1.5	0.1	1.5	0.0	2.7	0.2
Products, wt% maf Coal								
HC Gases	0.7	0.0	0.8	0.0	0.9	n/a	1.1	0.1
CO+CO ₂	4.7	0.6	5.3	0.5	4.8	n/a	5.8	0.7
Oils	33.2	5.0	32.2	1.6	31.5	1.1	34.3	3.3
PA+A	37.9	4.7	40.0	2.7	40.0	0.0	43.6	0.4
IOM	23.6	0.6	21.7	0.7	22.9	1.1	15.3	2.1
THF Conv	76.4	0.6	78.3	0.7	77.2	1.1	84.7	2.1
Run numbers	2154-1 3291-3 3341-1		3252-1 4003-1		4025-1 4025-2		3267-1 3253-1	
a. 3.0 g Black Thunder coal in 5.4 g tetralin at 415 °C for 30 minutes, using 6.89 MPa H ₂ (cold). Ash corrected for SO ₃ content.								

added to a mole ratio of 138 mol NH₃/mol Fe. The resulting coal slurry was vacuum filtered to removed the base solution and washed with distilled water (25 cc/g coal) until the odor of ammonia was absent. The sample was then dried to approximately 20% moisture in flowing N₂ at 25 °C for 20 hours.

The ammonium hydroxide filtrate and the washwater were combined and analyzed for iron content. The efficiency of iron deposition onto the coal was calculated based upon the Fe found in the filtrates as shown in the following equation and presented in Table 5.

$$Efficiency = (1 - Fe_{lost} / Fe_{original}) * 100$$

Recovery of Fe in the impregnation step was high, ranging from a low of 97.8% up to 99.8 wt%. The lower number was observed when deposition was made from the most concentrated Fe solution onto the smallest amount of coal. When impregnating larger amounts of coal with solutions having lower concentrations of Fe, the recovery increased to 99.8%.

Also shown in this table is the range of salt (as wt% FeOOH) on the wet vector coal mixture, which is of interest when considering the physical character of the vector coal. This value ranged from a high of 10.3% for the 10% laden fraction (CB-24), to a low of 0.8% for the sample where all the coal was loaded with iron (CB-16).

The liquefaction results using the impregnated vector coals are shown in Table 6. The THF conversion of the mixed feed coal are very similar, ranging from a low of 82.7% using 90% vector coal, to a high of 85.1% using 10% vector coal. Statistically, these conversions are essentially the same. The oil yields also appeared to be about the same with a slight advantage for the 10% case. A corresponding relationship was observed with the PA+A with the 10% case being somewhat lower. Overall, the results using the vector coals from 10% to 100% of the total feed coal are very similar, suggesting that

impregnation of the iron on a portion of the coal does not hinder the performance of the coal. Not only does this impact on the overall understanding of the mechanism operating in this case but it also significantly impacts on the process possibilities of using this technique of injecting the catalyst into the reactor.

Table 5. Efficiency of iron addition to the vector coals.				
Vector coal fraction of total feed coal, wt%	10	50	90	100
Amount of vector coal prepared, g AR coal	4	20	20	22
Combined base filtrate and washwater solution, ml	487	887	729	775
Fe concentration in combined solution, ppmw	11.1	0.73	0.35	0.29
Fe recovered in vector coal, wt%	97.8	99.7	99.8	99.8
Added Fe, wt% mf vector coal (salt-free basis)	7.59	1.55	0.87	0.78
Added Fe as FeOOH, wt% of wet vector coal mixture	10.3	2.0	1.1	0.8
Vector coal sample number	CB-24	CB-22	CB-15	CB-16

Table 6. Effect of Vector Coals on Liquefaction of Black Thunder coal								
Vector Coal/total coal, wt%	10		50		90		100	
	±σ		±σ		±σ		±σ	
Coal moisture, wt% total Coal	20.6	0.0	21.0	0.5	19.2	0.0	35.2	5.1
Added Fe, wt% mf total Coal	0.81	0.00	0.78	0.00	0.78	0.00	0.78	0.00
S/Added Fe mol/mol	2.1	0.4	2.0	0.3	1.7	0.3	2.7	0.2
Products, wt% maf total Coal								
HC Gases	1.0	0.1	1.0	0.0	0.8	0.0	1.1	0.1
CO+CO2	4.8	0.1	4.9	0.1	4.7	0.4	5.8	0.7
Oils	38.2	0.4	33.3	0.4	32.6	1.5	34.3	3.3
PA+A	41.1	0.6	44.0	1.1	44.6	1.5	43.6	0.4
IOM	14.9	0.4	16.8	0.8	17.4	0.5	15.3	2.1
THF Conv	85.1	0.4	83.2	0.8	82.7	0.5	84.7	2.1
Run numbers	3322-1 3322-2		3316-2 3320-1		3246-3 3258-1		3267-1 3253-1	

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SECTION TWO

CONSOL Inc.

**QUARTERLY PROGRESS REPORT
FOR THE PERIOD OCTOBER 1 THROUGH DECEMBER 31, 1993
SUBCONTRACT No. UKRF-4-25582-92-76**

TASK 1.2 - LABORATORY SUPPORT (CONSOL)

Summary

Two dewaxed oil samples were prepared and sent to Sandia for hydrotreatment in preparation for the Integrated Simulation Tests, IST.

Basic nitrogen contents of two slack waxes were determined by the National Institute for Petroleum and Energy Research. These results were forwarded to Burns and Roe Services Corp. to help them to refine their predictions concerning FCC yields from slack wax feedstock.

Revised analyses are reported for the Martin Lake lignite previously shipped to program participants.

Float/sink fractions of Black Thunder coal, Martin Lake lignite, and Burning Star 2 coal produced by CONSOL were provided to CAER for examination by petrography to investigate maceral segregation effects.

Discussion

Two dewaxed oil samples, ~1 L each, were prepared and were shipped to Sandia for hydrotreatment. These consisted of -5 °C acetone dewaxed V-1074 from Wilsonville Run 262E and a simulation of oil that would be produced by dewaxing a 25% slipstream of the total distillate at -5 °C in acetone. Preparation of these materials is discussed under Task 2.1.2.1. These hydrotreated dewaxed oils will be used in the Integrated Simulation Testing (IST) phase of the contract.

Basic nitrogen contents of two slack waxes, produced by dewaxing Run 262E V-1074 with acetone at -35 °C and -5 °C, were determined by the National Institute for Petroleum and Energy Research. These were 0.0419 wt % for the -35 °C wax and 0.0203 wt % for the -5 °C wax. These results were forwarded to Burns and Roe Services Corp. to help them to refine their predictions concerning FCC yields from slack wax feedstock.

Analysis results are given in Table 1 for the valid current Martin Lake lignite sample (Bag 9); these results replace previous analyses reported in the June 1993 status report and in the Technical Progress Report for the second quarter 1993, which were obtained from the anomalous Bag 1 sample (see discussion in the second quarter 1993 report and in the status reports for June, July, and August 1993). The current sample (Bag 9) contains more ash, more SiO_2 and Al_2O_3 in the ash, less Fe_2O_3 and SO_3 in the ash, less fixed carbon, less carbon, and it has a lower heating value than the anomalous sample. The current sample also has a larger mean particle size than the anomalous sample. The size difference suggests that some size segregation, perhaps from inadequate riffing, may have caused the Bag 1 sample to be anomalous.

Geoff Kimber at CAER informed us that petrography showed that the Black Thunder coal we are using is contaminated by 1% bituminous coal. Contamination like this has been previously observed in coals ground at Empire Coke Co., a facility used by both Wilsonville and HRI. Float/sink fractions of Black Thunder coal, Martin Lake lignite, and Burning Star 2 coal produced by CONSOL were provided to CAER for petrographic examination. CAER will explore maceral segregation effects in these materials.

Task 2.1.2.1 - Pretreatment Work at CONSOL - Dewaxing

Summary

Approximately 2.6 kg of V-1074 heavy distillate from Wilsonville Run 262E was dewaxed in acetone at -5 °C for use in integrated testing. Over 2 kg of dewaxed oil was recovered. Samples (~1 kg each) of the dewaxed oil and of a simulation of oil that would be produced by dewaxing a 25% slipstream of the total distillate were shipped to Sandia for hydrotreatment.

Examination of the ^1H -NMR proton distributions as a function of the degree of dewaxing suggests that there may be a peak in the hydroaromatic proton content at about 20 wt % wax removal. Coupled with solvent quality studies which showed that intermediately dewaxed (-5 °C in acetone) distillate is a better donor solvent than either shallower dewaxed (-35 °C in acetone/MEK) or deeper dewaxed (-35 °C in acetone) distillate, the NMR data suggest that ~20 wt % wax removal is optimum for producing the best donor solvent from the Wilsonville Run 262E distillate.

Analyses of dewaxed distillate samples hydrotreated at different space velocities showed that increasing the space velocity from 0.79 to 1.44 hr⁻¹ resulted in a material with a greater concentration of aromatic protons (less hydrogenated) but with similar donor solvent properties (by microautoclave testing).

Use of Mo-free resid from Wilsonville Run 258K in microautoclave tests results in about 15 wt % lower coal conversions than when Mo-containing ashy resid from Run 262E is used.

Duplicate base case microautoclave tests (5-min, 824 °F, 1500 psig H₂, 1.5 S/C and Wilsonville Run 262E solvent blend) were run that suggest that some sample deterioration may have occurred over the past several months. Resid conversion when SC1 was used as the distillate in the base case test was 12.2 wt % compared with 6.5 wt % when V-1074 was used. A new aliquot of the Black Thunder coal sample was prepared for use in future microautoclave tests. Tests with this new coal aliquot will help determine if the observed decreases in coal conversion over time were due to deterioration of the coal sample.

A systematic error was found in the coal conversions, IOM conversions and total resid conversions reported for all microautoclave tests with Black Thunder coal. Correction of this error lowers the calculated coal conversions by 1.0 to 2.3 wt %, it lowers the calculated IOM conversions by 0.8 to 2.5 wt % and it lowers the calculated total resid conversions by 0.3 to 3.5 wt %. The corrections do not alter any conclusions drawn from these data.

Comparison of TGA-simulated distillations with microdistillations of THF soluble resids from earlier microautoclave tests was continued. TGA repeatability is excellent and data for samples containing 55 to 70 wt % resid fall close to the parity line. TGA data for samples that contain less than 55 wt % resid or more than 70 wt % resid appear to be biased low.

Discussion

Preparation of Dewaxed Distillates for Integrated Simulation Tests

A large batch (2584 g) of V-1074 distillate from Wilsonville Run 262E was dewaxed in seventeen 150 g batches at -5 °C in acetone for use in the integrated simulation testing (IST) phase of this contract. The dewaxing conditions were

chosen, based on our prior studies, to produce dewaxed distillate with the highest possible solvent quality (as defined by conversion of Black Thunder coal to THF solubles in 5-min microautoclave tests). The method used to dewax the distillate in 150 g batches was described previously.¹ The yields, chemical analyses, proton distributions and phenolic -OH contents of the dewaxed oil and wax fractions from this dewaxing are shown in Table 2. The ¹H-NMR analysis of the Wilsonville Run 262E V-1074 distillate shown on this table is the mean of three recent determinations. This analysis differs from the single measurement value, determined in July 1992, that was used until this re-determination. The most significant differences in these analyses are the alkyl beta proton content (31.5% presently vs 34.6%) and in the gamma proton content (17.9% vs 12.3%). The NMR instrument currently is being repaired, and the analysis of the V-1074 will be repeated upon completion of these repairs. A total of 2.2 g of THF insoluble material (0.1 wt %) also was recovered. The dewaxed oil yield from these experiments is higher than that obtained in the preparation of the previous large batch of -5 °C acetone dewaxed distillate, 80.2 wt % compared with 75.0 wt %.²

A 1000 g portion of this dewaxed oil (No. 1621-22-5I) was shipped to Sandia. A second ~1100 g batch of material was prepared by mixing the -5 °C dewaxed oil with the original V-1074 to simulate the distillate product that would be obtained by dewaxing a 25% slipstream of the total distillate. The blend ratio of 37.5 wt % V-1074 and 62.5 wt % -5 °C acetone dewaxed distillate was calculated from the LDP estimate² of the alkyl beta proton content (25.6%) of such a distillate and from the hydrogen contents and ¹H-NMR spectra of the dewaxed distillate and those of the V-1074 (Table 2). The ¹H-NMR proton distributions and phenolic -OH content in this blend are also reported in Table 2. A 1000 g aliquot of this mixed material (No. 1621-22-5K) also was shipped to Sandia.

Proton Distribution vs Degree of Dewaxing

¹H-NMR proton distributions of most of the dewaxed oils produced under this contract are plotted as a function of degree of dewaxing in Figure 1. Second order polynomial regression fits to the data are plotted on the figure as guides to help visualize the data trends. The aromatic proton contents (condensed and uncondensed) and the alpha proton contents (cyclic and alkyl) increase with the degree of dewaxing. The alkyl beta and gamma proton contents (paraffinic protons) decrease with dewaxing. There appears to be a broad peak in the cyclic

beta proton concentration (one group of hydroaromatic protons) with a maximum at about 20 to 25 wt % wax removal. This apparent maximum in the hydroaromatic content coincides with an observed peak in solvent performance when the distillate portion of the solvent is dewaxed to an intermediate degree. In 5-min microautoclave tests, more Black Thunder coal was converted to THF solubles when simulated Wilsonville Run 262E recycle solvent with -5 °C acetone dewaxed V-1074 used as the distillate component (91.3 wt %) than when either the shallower dewaxed (-35 °C acetone/MEK) or deeper dewaxed (-35 °C acetone) V-1074 was used as the distillate component (89.9 and 89.1 wt %, respectively).³ However, these differences in coal conversion may not be significant. The reproducibility (one standard deviation) based on four repeat runs at 880 °F was 2.9 wt %; the present runs were at 824 °F.

Effect of Space Velocity of Hydrotreatment on Solvent Reactivity

Two hydrotreated samples were received from Sandia. These are -35 °C acetone dewaxed V-1074 samples that were hydrotreated over Shell 324 catalyst in the trickle-bed reactor at 360 °C and ~1300 psig H₂ pressure at different space velocities. Sandia #90303 is dewaxed V-1074 distillate that was hydrotreated at a WHSV of 0.79 hr⁻¹ and #90307 was the same dewaxed V-1074 distillate hydrotreated at a WHSV of 1.44 hr⁻¹. Proton distributions (¹H-NMR) for these samples are shown in Table 3. Both samples have significantly reduced aromatic proton contents (more hydrogenated) compared with the feed dewaxed oil. Higher space velocity, as expected, results in less hydrogenation of the dewaxed distillate.

Microautoclave tests (5 min., 824 °F, 1.5 S/C, 1500 psig H₂), Runs 88 and 89, Table 4, were made with Sandia #90303 and #90307 used as the distillate part of the recycle solvent. Black Thunder coal conversions with these two distillates were nearly the same (86.5 and 86.2 wt % respectively). The resid conversions determined by microdistillation these two runs were 15.4 wt % for 90303 and 12.5 for 90307.

Mo-free Resid Studies

Microautoclave tests (5 min, 824 °F, 1.5 S/C, 1500 psig H₂) were made with the Mo-free resid, obtained by distillation (320 °C, 2 torr) of the recycle solvent (V-131B) from Wilsonville Run 258K, (no Run 262E resid was used in these tests

to completely eliminate the Mo catalyst). The results of these tests are given in Table 4. The Mo-free resid from Run 258K was substituted for the total resid (V-130 + V-1082) in the simulated Wilsonville Run 262E solvent blend. Separate tests were made with Wilsonville Run 262E V-1074 (Run 80), -35 °C acetone/MEK (55/45 vol%) dewaxed Run 262E V-1074 (Run 81) and Sandia SC1 (hydrotreated -5 °C acetone dewaxed Run 262E V-1074) (Runs 82 and 85) used as the distillate portion of the recycle solvent blend. The coal conversions measured with the untreated V-1074 and the -35 °C dewaxed V-1074 were similar to each other (71.2 and 70.4 wt %, respectively); however, the initially measured coal conversion for the SC1 case was significantly lower, 62.2 wt % (Run 82). This was an unexpected result based on all prior work with the Sandia SC1 hydrotreated dewaxed distillate; therefore, the run was repeated. The repeat microautoclave determination of coal conversion with the Mo-free resid from Wilsonville Run 258K and Sandia SC1 hydrotreated -5 °C dewaxed V-1074 (Run 85) resulted in 74.9 wt % conversion of Black Thunder coal to THF solubles. This conversion is higher than the 71.2 and 70.4 wt % conversions, respectively, determined when the untreated V-1074 and the -35 °C dewaxed V-1074 were used as the distillate portion of the recycle solvent blend.

The Black Thunder coal conversions determined in these tests with no Mo catalyst present are similar to those reported earlier when Wilsonville Run 262E V-130 deashed resid (53 ppm Mo) was used with the V-131B-derived resid from Run 258K.⁴ In the earlier tests, coal conversion was 72.0 wt % with V-1074, 73.2 wt % with the -35 °C acetone/MEK dewaxed V-1074 and 76.0 wt % with SC1. The presence of Mo catalyst in the ashy resid results in about a 15 wt % increase in coal conversion for each solvent tested.

The THF solubles from Run 80 (V-1074 in the recycle solvent) were lost during microdistillation. Resid conversions determined from distillation of the THF soluble material from Runs 81 and 82 were -0.5 wt % for the case where -35 °C acetone dewaxed V-1074 was used as the distillate in the solvent blend (Run 81) and 5.6 wt % when SC1 was used (Run 82). Resid conversion determination for the repeat run with SC1 distillate (Run 85) was 11.2 wt %. In the previous tests with Mo-free V-131B-derived resid from Wilsonville Run 258K and deashed resid from Wilsonville Run 262E (with 53 ppm Mo), the total resid conversions determined when V-1074 was used as the distillate and when -35 °C acetone dewaxed

V-1074 was used as the distillate were 0.0 and -3.8 wt %, respectively. Use of the hydrotreated dewaxed distillate, SC1, appears to significantly improve the total resid conversion in the absence of Mo catalyst (from -0.5 wt % with dewaxed V-1074 to 11.2 wt % with SC1).

Base Case Studies

Determination of resid conversions did not begin until we were well into our program to determine Black Thunder coal conversions in the 5-min, 824 °F microautoclave test. By the time microdistillation of the THF solubles was begun to determine resid conversions (Run 35 in the CONSOL program), samples from the early runs had been either discarded or sitting on the shelves for a prolonged period. Therefore, the two base case runs (5-min, 824 °F, 1500 psig H₂, 1.5 S/C and Wilsonville Run 262E solvent blend) with V-1074 and SC1 used as the distillate in the solvent blend were repeated. Run 86 with V-1074 was a repeat of Run 14 and Run 87 with SC1 was a repeat of Run 18. The results of the repeat tests and the original tests are shown in Table 4. In both cases, the coal conversion in the repeat run is about 2 wt % lower than it was in the initial run. These differences are within the range of repeatability for consecutively run tests;⁵ however, the fact that both repeats are lower than the originals suggests that one or more of the feed components may have deteriorated during storage. Gradual degradation of one or more of the solvent mix components cannot be ruled out. The components are stored in closed jars and vials when not in use, but the distillates must be warmed for sampling prior to each microautoclave test. The Black Thunder coal sample that was stored in a 16 oz jar with a screw cap during this period, however, is more likely to have deteriorated than the distillate or resid samples. For this reason, a new aliquot of the Black Thunder coal sample was prepared for use in future microautoclave tests. Tests with this new Black Thunder coal aliquot will help determine if the decreases in coal conversion that were discussed earlier were a result of degradation of the coal sample. A 20 lb bag of Black Thunder coal from Wilsonville Run 262E (sample No. 1621-22-1) was opened and riffled into several smaller sized aliquots, including five 100 g aliquots that will be used in future microautoclave tests. One of the 100 g aliquots was stored in a jar for immediate use and the rest of the aliquots were re-sealed in triple-layer bags, under vacuum. An aliquot of the Black Thunder coal in the jar was analyzed. The results of this analysis are shown in

Table 5. The analysis of the previous sample of Black Thunder coal is also shown in this table, for comparison.

Resid conversion, determined by microdistillation of the THF solubles, is significantly higher in the case where SC1 was used as the distillate, Run 87, than when untreated V-1074 was used, Run 86, (11.7 wt % vs. 6.1 wt %). Higher resid conversions were also observed when SC1 was substituted for V-1074 in microautoclave runs to test the effect of distillate/resid ratio on conversion (solvent containing SC1 gave coal conversions ~2 wt % higher than those with V-1074 at a distillate/resid ratio of 1 and ~6 wt % higher than those with V-1074 at a D/R ratio of 0.5)⁴. When the -5 °C acetone dewaxed V-1074 distillate from which the SC1 was derived was tested, both the coal conversion and the resid conversion were higher than in the case of the SC1 (91.3 wt % vs. 87.3 wt % coal conversion and 14.4 wt % vs. 11.7 wt % resid conversion).³ As discussed previously,^{3,5} the -5 °C acetone dewaxed V-1074 appears to represent an optimum degree of dewaxing (~20 to 25 wt % wax removal), as defined by solvent quality for microautoclave coal conversion (i.e., the -5 °C dewaxed oil performs better as the distillate portion of the recycle solvent in microautoclave conversion of Black Thunder coal than either the more highly dewaxed -35 °C acetone dewaxed V-1074 or the less-dewaxed -35 °C acetone/MEK dewaxed V-1074). The present data suggest that this optimum dewaxing degree may also apply to resid conversion.

Correction of Microautoclave Data from Runs with Black Thunder Coal

An error was discovered in the calculations of the conversions in all microautoclave tests made with Black Thunder coal. All microautoclave conversion data that have been reported were corrected to reflect this calculation error. The originally reported values and corrected values of the conversions affected by this error (coal conversion, IOM conversion and total resid conversion) are given in Table 6. The run numbers shown in this table correspond to those reported in all previous reports. Correction of this error lowers the calculated coal conversions by 1.0 to 2.3 wt %, it lowers the calculated IOM conversions by 0.8 to 2.5 wt % and it lowers the calculated total resid conversions by 0.3 to 3.5 wt %. The corrections do not alter any conclusions drawn from these data.

TGA Determination of Resid Conversion

The previously described TGA method^{5,6} was used to simulate distillations on 39 samples (13 of these were duplicates). The results of these determinations are compared with the microdistillation results in Figure 2. Duplicate TGA determinations are shown by different symbols in the figure. The TGA repeatability appears to be excellent. The data in the middle of the plot (~55 to 70 wt %) fall close to the parity line; however, there may be a bias at both high and low resid contents. This work is continuing; approximately half of the available samples have been run on the TGA. Duplicate samples were sent to Sandia for similar TGA tests. When the TGA trials are completed, it will be determined if the TGA method is a viable technique for resid conversion determination.

Task 2.1.2.2 - Pretreatment Work at CONSOL - Agglomeration

Summary

We applied an ash-SO₃ correction to agglomeration results from an early low-pH run with Black Thunder coal. Corrected ash rejection including dissolution was 31.2%. The product ash content was 3.9%; the feed coal ash content was 5.54% MF.

The results from two previous agglomeration runs (Run A45 with Burning Star 2 coal and Run A47 with Kemmerer coal) were revised, based on re-analysis of the products. Relative to the values reported last quarter, the product ash contents were higher, dissolved plus physical ash rejections were lower, and the ash balances were improved. The revisions were significant for the Burning Star 2 case, but were minor for the Kemmerer case. In both runs, physical ash rejection and organic recovery were unaffected.

Discussion

Ash-SO₃ Correction and Revision of Selected Agglomeration Runs

We obtained ash sulfur analyses and used them to obtain ash-SO₃ corrected agglomeration results for Run A12, an early low-pH run with Black Thunder coal. Run A12 (Table 7) gave a product ash content (SO₃- and oil-free MF basis) of 3.9% (3.7 and 4.0% in two samples), with a feed coal ash content of 5.54% MF. Since the ash samples contained only 2 to 5% SO₃, the product ash contents are only slightly lower than the uncorrected value of 4.0%. Corrected ash rejection

including dissolution was 31.2%. The small quantity of filter cake ash was assumed to be SO_3 -free.

Product agglomerates from two previously-reported runs were re-analyzed because of suspiciously low ash contents. Re-analysis resulted in higher values for the ash contents (MF, oil-included basis) of both agglomerates. The ash content of the agglomerated Burning Star 2 coal (Run A45) was increased from 4.93 to 5.75 wt % ash (MF, oil included). The ash content of the agglomerated Kemmerer coal (Run A47) was increased from 1.42 to 1.58 wt % ash (MF, oil included). This difference was significant for the Burning Star 2 coal run, and consequently new results are reported to replace the previous results (Table 7). For the Kemmerer coal run, the ash difference was small, but new results are reported (Table 7) so that the more-conservative, higher-ash results can be used. The product ash results, presented in the table and described below, are on an oil-free basis; they are calculated from the oil-included ash results given above.

In Run A45 with Burning Star 2 coal (Table 7), the product ash content was increased from 6.6 to 7.7 wt % MF (oil-free), dissolved plus physical ash rejection was decreased from 46.0 to 37.0 wt %, and the ash balance was increased from 86.9 to 95.9 wt %. In Run A47 with Kemmerer coal (Table 7), the product ash content was increased from 1.7 to 1.9 wt % MF (oil-free), dissolved plus physical ash rejection was decreased from 54.7 to 49.6 wt %, and the ash balance was increased from 75.0 to 80.1 wt %. In both runs, physical ash rejection and organic recovery were unaffected.

Miscellaneous

Aspects of our agglomeration and related work, especially in regard to resid deashing and ash concentrate recovery/upgrading, were discussed with B. Utz of PETC. We are considering several suggestions that he made concerning possible experimental work.

Task 2.3.2 - Catalyst Studies (CONSOL)

Summary

High organic recoveries were obtained when two forms of Fe-impregnated Black Thunder coal were agglomerated with Wilsonville recycle distillate. For the coal treated by incipient wetness, 100% of the Fe was retained in the agglomerates.

For the ion-exchanged coal, 71% of the Fe was retained. These results indicate that agglomeration can integrate well with catalyst incorporation as coal pretreatment steps for liquefaction.

We received two samples of Black Thunder Mine coal which were impregnated with Fe by incipient wetness at CAER. These will be used in the Integrated Simulation Test.

Discussion

Two Fe catalyst-impregnated Black Thunder coals provided by CAER were agglomerated with heavy recycle distillate from Wilsonville (Table 7). Elemental analyses and Fe and ash balances were obtained (Table 8). Organic recoveries were 99.3 % and higher (Table 7). The coal treated by incipient wetness was reduced in ash content from 6.5 to 5.6 wt % MF ash (SO_3 -free), giving an ash rejection of 7.2% (physical), and 12.2% (including dissolution). The agglomerated coal retained 100.1 % of the feed coal iron (3.4% was rejected, Fe balance was 103.5), indicating retention of essentially all of the added catalyst (Table 8). The coal treated by ion exchange was reduced in ash content from 8.3 to 6.2 wt % MF ash (SO_3 -free), giving an ash rejection of 15.6% (physical), and 26.7% (including dissolution). The agglomerated coal retained 71.2% of the feed coal iron (22.2% was rejected, Fe balance was 93.4%), indicating retention of most of the added catalyst. Although some iron is rejected along with the overall ash, the product ash is very similar in elemental composition to the feed ash (Table 8). These results indicate that agglomeration can integrate well with catalyst incorporation as steps in coal pretreatment.

We received two samples of Black Thunder Mine coal which were impregnated with Fe by incipient wetness at CAER. These will be used in the Integrated Simulation Test.

Task 2.4.2 - Solids Separation (CONSOL)

Summary

In response to an action item from a quarterly review meeting, additional analyses of the Wilsonville 263J V-107 ash concentrate were obtained. The relatively high volatile matter content (25%, MF) and heating value (9333 Btu/lb, MF) indicate that the ash concentrate may be a good coker feed. The ash

concentrate was agglomerated with heavy distillate in one run, but there was no significant physical ash rejection or ash dissolution. Additional steps which may improve ash rejection are being considered.

Discussion

In response to an action item from the June 29-30, 1993 quarterly review meeting, additional analyses of the Wilsonville 263J V-107 ash concentrate were obtained. These are presented in Table 9, along with a subset of the ash concentrate analyses previously presented in the report for the second quarter 1993 and in the May 1993 status report. The volatile matter content was determined to be 25% (dry, SO₃-free ash basis). This is higher than expected, based on the sample's 10% solubility in THF as previously measured in our laboratory by pressure filtration (Soxhlet extraction gave about 30% extractables) (presented in the June 1993 status report and second quarter 1993 report). The measured dry heating value of 9,333 Btu/lb is close to the value of $\approx 9,200$ Btu/lb we previously calculated from the ultimate analysis (May 1993 status report and second quarter 1993 report). The as-received heating value is much higher than that of the Black Thunder feed coal, which is 7,939 Btu/lb (reported in the third quarter 1992 report). The relatively high volatile matter content and heating value indicate that the ash concentrate may be a good coker feed. Other alternatives for recovery or use of the ash concentrate are being explored or considered. The ash concentrate was agglomerated with heavy distillate in one run (Run B36, Table 7). In spite of physical agglomeration, there was no significant physical ash rejection (0.02%), or ash dissolution. The feed was prepared by screening to 100 mesh and then grinding the oversize material to -100 mesh. Other steps, such as additional grinding, surfactant addition, etc. are being considered to improve ash rejection.

Task 2.6.2 - Coker Overhead Characterization (CONSOL)

No work was performed on this task.

Task 3.2 - Economic Evaluation (CONSOL)

Summary

At our request, LDP Associates will determine the economic benefits to the liquefaction process of low (≈ 2) pH agglomeration treatment, which results in the highest ash rejection from Black Thunder subbituminous coal. Potential benefits

include: enhanced coal reactivity; extended supported catalyst life through decreased concentration of catalyst poisons such as Na; increased reactor throughput/decreased deasher size; decreased solids buildup; and improved dewatering.

Discussion

Because the highest ash rejection from Black Thunder coal occurs when it is agglomerated at low pH (≈ 2 to 3 pH) through ash dissolution, LDP Associates will determine the economic benefits of the low pH agglomeration treatment. Potential benefits include: enhanced coal reactivity; extended supported catalyst life through decreased concentration of catalyst poisons such as Na; increased reactor throughput/decreased deasher size; decreased solids build-up; and improved dewatering. We sent a few papers on the impact of ion-exchange on liquefaction of low-rank coals for M. Peluso's reference. Our estimates indicate that reagent cost for such treatment are small ($< \$0.50/T$ coal), but that water treatment costs could be several dollars per ton of coal.

References

1. CONSOL Inc., Project Technical Progress Report for July through September 1992, Subcontract No. UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040, November 1992.
2. Peluso, M., Personal Communication to F. P. Burke, November 15, 1993.
3. CONSOL Inc., Project Technical Progress Report for July through September 1993, Subcontract No. UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040, November 1993.
4. CONSOL Inc., Project Status Report for August 1993, Subcontract No. UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040, October 1993.
5. CONSOL Inc., Project Status Report for September 1993, Subcontract No. UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040, September 1993.
6. CONSOL Inc., Project Status Report for July 1993, Subcontract No. UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040, September 1993.

TABLE 1
REVISED ANALYSIS OF MARTIN LAKE LIGNITE

	Original Sample (Bag 1)	Valid Sample (Bag 9)
Moisture, wt % As-Determined	25.85	25.08
Ash, wt % MF, Including SO ₃	10.88	13.76
Proximate, wt % MF, SO ₃ -Free Ash Basis		
Ash, SO ₃ -Free	8.39	11.16
Volatile Matter	46.57	46.46
Fixed Carbon	45.04	42.38
Ultimate, wt % MF, SO ₃ -Free Ash Basis		
Carbon	66.10	63.76
Hydrogen	4.89	4.84
Nitrogen	1.23	1.15
Sulfur	1.36	1.41
Chlorine	0.040	0.019
Oxygen (by Diff.)	17.99	17.66
Ash, SO ₃ -Free	8.39	11.16
Sulfur Forms, wt % (MF)		
Pyritic	0.28	0.37
Sulfate	0.02	0.03
Organic (by Diff.)	1.06	1.01
Ash Elementals, Oxide Wt % of Ash		
Na ₂ O	1.13	0.98
K ₂ O	0.31	0.50
CaO	18.61	16.06
MgO	4.29	3.76
Fe ₂ O ₃	6.56	6.53
TiO ₂	0.94	1.17
P ₂ O ₅	<0.019	<0.020
SiO ₂	31.13	38.73
Al ₂ O ₃	12.02	13.63
SO ₃	22.85	18.89
Total	97.86	100.25
HHV, Btu/lb (MF)	11,305	11,067
Particle Size by Laser Diffraction, Vol %		
D ₁₀	8.4 μm	9.3 μm
D ₅₀	43.6 μm	64.1 μm
D ₉₀	125.0 μm	139.1 μm

Analyses were performed by CONSOL R&D.

TABLE 2
ANALYSES OF DISTILLATES PREPARED FOR INTEGRATED TESTING

	V-1074	-5 °C Acetone Dewaxed Oil	-5 °C Acetone Dewaxed Wax	Simulated 25% Slipstream DW
Sample Number	1621-22-5	1621-22-5I	1621-22-5J	1621-22-5K
wt, g	2583.8	2071.8	511.6	1100
Yield, wt %	100	80.2	19.8	N/A (a)
Ultimate, wt % dry				
Carbon	88.86	89.50	85.91	89.54
Hydrogen	9.91	8.80	13.87	9.22
Nitrogen	0.44	0.53	0.13	0.54
Sulfur	<0.03	0.04	<0.03	0.04
Oxygen (diff)	0.79	1.13	0.09	0.70
¹H-NMR Proton Distributions, %				
Condensed Aromatic	9.9	13.6	0.3	12.2
Uncondensed Aromatic	5.0	7.5	0.3	6.4
Cyclic Alpha	13.1	16.5	2.6	15.0
Alkyl Alpha	7.6	9.7	2.8	9.0
Cyclic Beta	15.1	17.1	9.6	16.0
Alkyl Beta	31.5	21.6	62.2	25.4
Gamma	17.9	14.1	22.1	16.0
Phenolic -OH Conc., meq/g	0.44	0.50	<0.05	0.46

(a) Produced by blending 37.5 wt % V-1074 and 62.5 wt % -5 °C acetone dewaxed V-1074.

TABLE 3

¹H-NMR PROTON DISTRIBUTIONS OF HYDROTREATED DEWAXED V-1074 DISTILLATE

Sample	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
-35 °C ADW (a)	17.3	6.2	20.0	10.3	17.1	17.9	11.2
90303 (b)	9.9	7.4	17.5	10.8	19.2	19.7	15.4
90307 (c)	12.0	7.2	19.1	10.8	18.6	19.2	13.2

(a) 100% acetone dewaxed.

(b) hydrotreated at 0.79 hr⁻¹ space velocity, 360 °C, 1300 psig H₂, Shell 324 catalyst.

(c) hydrotreated at 1.44 hr⁻¹ space velocity, 360 °C, 1300 psig H₂, Shell 324 catalyst.

TABLE 4

MICROAUTOCLAVE TESTS FOR OCTOBER - DECEMBER 1993

Run No.	Distillate	Resid	SO ₂ -free Conversion, wt %				Comments
			Soluble Resid	Total Resid	Coal	IOM	
88	Sandia #90303	V-130+V-1082	-76.7	15.4	86.5	73.7	-35 °C ADW ^a Hydrotreated at WHSV = 0.79 hr ⁻¹
89	Sandia #90307	V-130+V-1082	-83.7	12.5	86.2	73.4	-35 °C ADW ^a Hydrotreated at WHSV = 1.44 hr ⁻¹
80	V-1074	V-131B ¹	Sample lost		71.2	61.4	Test of Mo-free Resid with V-1074
81	-35 °C A/M-DW ²	V-131B ¹	-96.5	-0.5	70.4	60.8	Test of Mo-free Resid with Dewaxed V-1074
82	Sandia SC1	V-131B ¹	-69.3	5.6	62.2	53.6	Test of Mo-free Resid with Hydrotreated Dewaxed V-1074. Results appear to be spurious.
85	Sandia SC1	V-131B ¹	-72.6	11.2	74.9	64.6	Test of Mo-free Resid with Hydrotreated Dewaxed V-1074
14	V-1074	V-130+V-1082			86.0	73.2	Std. 5-min. test with V-1074
86	V-1074	V-130+V-1082	-96.5	6.1	83.5	71.1	Std. 5-min. test with V-1074
18	Sandia SC1	V-130+V-1082			90.7	77.2	Std. 5-min. test with Sandia SC1
87	Sandia SC1	V-130+V-1082	-87.1	11.7	87.3	74.3	Std. 5-min. test with Sandia SC1

(a) Mo-free ashy resid from distillation of V-131B sample from Wilsonville Run 258K

(b) 55/45 (vol %) acetone/MEK dewaxed V-1074 from Wilsonville Run 262E

(c) Dewaxed in 100% acetone.

TABLE 5
ANALYSIS OF BLACK THUNDER COAL

	New Aliquot	Old Aliquot
Moisture, wt % (as received)	19.71	22.4
Ash, wt % (as Received)	5.12	5.19
Ash, wt % (MF)	6.38	6.69
SO₃, wt % in ash	11.25	17.26
Ash, wt % (as received, SO₃-free)	4.55	4.3

TABLE 6
CONVERSION CORRECTIONS - BLACK THUNDER COAL

Run No.	COAL and IOM CONVERSIONS wt % (SO ₂ -free basis)				TOTAL RESID CONVERSION wt % (SO ₂ -free basis)	
	ORIGINAL		CORRECTED		Original	Corrected
	Coal	Total IOM	Coal	Total IOM		
5	108.5	88.7	108.2	88.5		
6	108.0	88.3	107.7	88.0		
7	108.8	88.2	107.8	88.0		
8	108.5	88.3	108.1	87.0		
9	104.4	88.1	108.1	87.8		
10	81.4	81.4	78.8	78.8		
11	108.4	84.2	105.1	83.0		
12	88.8	70.3	87.4	68.9		
13	80.5	80.5	88.0	88.0		
14	87.5	74.8	88.0	73.2		
15	88.7	71.1	88.2	68.7		
16	88.0	78.0	87.5	74.5		
17	88.1	78.7	88.6	77.4		
18	82.1	78.6	80.7	77.2	2.3	0.9
19	71.8	64.1	70.0	62.5		
20	78.8	68.4	74.9	68.8		
21	78.7	71.2	78.0	69.6		
22	82.7	73.9	81.1	72.4		
23	78.0	69.7	78.3	68.1		
24	82.6	82.6	80.8	80.8		
26	71.8	71.8	70.0	70.0		
27	93.6	74.1	82.2	72.8		
29	87.0	54.4	85.2	52.9		
30	88.8	74.5	84.6	72.1		
31	84.0	72.1	81.7	68.6		
32	87.8	75.2	85.8	72.9		
33	88.4	78.7	87.5	74.5		
35	88.3	84.4	88.8	82.5	11.8	8.5
36	84.0	80.7	82.3	78.6	7.8	4.4
37	91.0	78.1	88.1	75.9	15.9	12.7
38	84.0	80.6	82.3	78.6	20.1	17.0
40	88.8	78.9	87.7	74.7	25.3	22.3
41	84.9	81.4	83.2	79.4		
42	88.8	82.9	85.1	81.0	27.7	24.8
43	88.0	82.4	84.4	80.4	27.7	24.8
44	91.8	78.8	80.0	78.7	23.9	20.9
45	84.9	81.5	83.3	79.5	28.8	23.9
46	47.4	40.3	48.4	38.5	13.8	13.4
47	83.7	79.8	82.4	78.7	30.9	30.4
48	88.2	84.4	87.9	83.4	31.3	30.8
49	77.9	68.3	76.7	65.3	8.6	6.2
57	75.5	64.2	74.3	63.3	12.1	11.7
58	87.8	78.1	88.5	75.1	11.9	11.5
60	82.2	79.9	80.8	78.9	14.1	13.7
61	80.1	74.9	88.8	73.9	12.7	12.3
62	83.1	77.4	81.7	78.4	18.6	18.2
63	73.2	64.1	72.0	63.1	0.3	0.0
64	77.2	67.6	78.0	68.6		
65	74.4	65.1	73.2	64.1	-3.4	-3.8
66	74.2	63.1	73.0	62.1	35.3	35.0
67	80.4	78.9	80.1	75.9	5.3	4.9
68	91.8	77.9	90.3	78.9	7.4	7.0
69	88.8	58.8	87.7	57.6		
70	88.8	78.2	88.3	75.2	14.0	13.6
71	88.3	78.0	88.0	74.9		
72	80.8	77.1	88.3	78.0	19.4	19.0
73	80.4	78.9	80.0	75.8	18.4	15.9
74	80.4	78.9	80.1	75.9	4.2	3.8
75	88.1	75.0	88.8	73.9	17.3	16.8
76	80.2	78.8	88.9	75.7	13.7	13.3
77	88.1	58.8	87.9	57.9	3.6	3.3
78	82.8	78.8	81.3	77.8	14.8	14.4
79	81.3	77.8	88.9	78.6	11.9	11.5
80	72.4	62.4	71.2	61.4		
81	71.8	61.7	70.4	60.8	-0.1	-0.5
82	83.3	54.8	82.2	53.8	6.0	5.8
83	81.7	78.0	80.4	77.0	8.5	8.1
84	80.5	77.0	88.2	78.0	9.7	9.2
85	78.1	65.8	74.9	64.8	11.8	11.2
86	84.8	72.1	83.5	71.1	6.5	6.1
87	88.8	75.4	87.3	74.3	12.2	11.7
88	87.8	74.7	88.5	73.7	15.8	15.4
89	87.5	74.4	88.2	73.4	12.9	12.5

TABLE 7

FOURTH QUARTER 1993 AGGLOMERATION RESULTS

Run (a)	Coal	Oil	Oil Dosage, wt % MF Coal	pH, Agent	Temp., °C	Product Ash, wt % Oil-Free	Organic Recovery, wt %	Ash Rejection (b) (Dissolved and Physical), wt %	Physical Ash Rejection (c), wt %	Ash Balance (d), wt %
B36	AC	C1	24.0	6.5, None	50	35.40	99.9	-3.4	0.02	103.5
A12(e)	BT	P1	12.9	2.5, H ₂ SO ₄	50	3.98	99.2	42.2	4.33	62.2
B34	BTIW	C1	38.4	7.2, None	50	5.75	99.3	19.4	6.51	87.1
B35	BTIE	C1	39.7	3.0, None	50	6.22	99.6	26.6	15.64	89.1
SO ₂ -Free Ash Basis										
A12(f)	BT	P1	12.9	2.5, H ₂ SO ₄	50	3.88	99.2	31.2	5.23	74.1
B34	BTIW	C1	38.4	7.2, None	50	5.62	99.3	12.2	7.22	95.0
B35	BTIE	C1	39.7	3.0, None	50	6.20	99.6	26.7	15.56	88.9
Results Previously Reported (Third Quarter 1993)										
A45	BS2	P1	24.8	8.0, NaOH	54	6.64	96.7	46.0	32.69	86.9
A47	KM	P3	51.1	8.0, NaOH	27	1.70	97.9	54.7	29.77	75.0
Revised Results										
A45	BS2	P1	24.8	8.0, NaOH	54	7.66	96.7	37.0	32.69	95.9
A47	KM	P3	51.1	8.0, NaOH	27	1.89	97.9	49.6	29.77	80.1

Coals: AC = Wilsonville 263J ash concentrate from Black Thunder coal (ash content 34.63% MF, including SO₂); BT = Black Thunder (ash content 6.69% MF, including SO₂; 5.54% MF, excluding SO₂); BTIW = Black Thunder coal impregnated with Fe by incipient wetness (ash content 7.04 % MF, including SO₂; 6.35 % MF, excluding SO₂); BTIE = Black Thunder coal impregnated with Fe by ion exchange (ash content 8.28 % MF, with no detectable SO₂); BS2 = Burning Star 2 (new sample); KM = Kemmerer (old sample).

Oils: C1 = Run 262 V-1074; P1 = No. 6 fuel oil; P3 = No. 2 diesel fuel.

- (a) Run numbers with prefix A were made in the large vessel, those with prefix B were made in the small vessel.
 (b) Based on feed ash which was not recovered in the product.
 (c) Based on feed ash which was recovered in the solid reject (filter cake).
 (d) Ash balance does not include dissolved ash.
 (e) Results reported previously in the Technical Progress Report for the Third Quarter 1992 (Third Quarterly Report).
 (f) Based on average of two product ash content determinations.
 Note: Results are reported without SO₂ ash correction, except as otherwise noted.

TABLE 8

ANALYSES AND ASH AND Fe BALANCES OF Fe-IMPREGNATED BLACK THUNDER COAL AGGLOMERATION SAMPLES

Run	Run B34, BTIW Feed			Run B35, BTIE Feed		
Sample	Feed	Product Agglomerate	Reject (Filter Cake)	Feed	Product Agglomerate	Reject (Filter Cake)
Weight, g	30.27	25.11	0.2385	30.43	27.88	0.3482
Ash Balance, SO ₃ -Free Basis						
Ash wt, g	1.0665	0.9354	0.0770	1.5891	1.1634	0.2476
Ash, wt % of Feed Ash	100.0	87.7	7.2	100.0	73.2	15.6
Total Ash = Sum of Product and Reject, wt % of Feed Coal Ash	94.9			88.8		
Fe Balance						
Fe ₂ O ₃ wt, g	0.2741	0.2744	0.0094	0.9266	0.6595	3.2060
Fe, wt % of Feed Coal Fe	100.0	100.1	3.4	100.0	71.2	22.2
Total Fe = Sum of Product and Reject, wt % of Feed Coal Fe	103.5			93.4		
Moisture, wt % As-Determined	44.54	13.56	0.00	36.93	8.00	0.00
Ash, wt % MF, Including SO ₃	7.04	4.39	32.28	8.28	4.55	71.37
Ash, wt % MF, SO ₃ -Free	6.35	4.31	32.28(a)	8.28(a)	4.54	71.11
Ash Elementals, Oxide Wt % of Ash						
Na ₂ O	0.19	0.19	0.14	0.96	<0.011	<0.007
K ₂ O	0.36	0.21	0.72	0.99	0.31	<0.053
CaO	19.63	23.07	1.95	1.92	1.96	0.12
MgO	4.08	4.79	0.44	0.25	0.26	0.05
Fe ₂ O ₃	23.19	28.80	12.26	58.31	56.51	82.91
TiO ₂	1.02	1.20	0.36	0.85	1.13	0.08
P ₂ O ₅	0.94	1.09	0.59	0.78	1.02	0.15
SiO ₂	26.33	23.38	67.79	23.12	24.46	16.59
Al ₂ O ₃	13.49	14.88	14.02	10.73	13.98	0.83
SO ₃	9.76	1.83	<0.109	<0.225	0.31	0.36
Total	98.99	99.44	98.27	97.91	99.94	101.09

(a) Ash SO₃ content of 0 wt % was assumed.
Analyses were performed by CONSOL R&D.

TABLE 9
ADDITIONAL ANALYSES OF WILSONVILLE PERIOD 263J V-107 ASH CONCENTRATE

	Ash Concentrate Analysis	
	Previously Reported (2nd Qtr 1993)	This Report
Moisture, wt % As-Determined Ash, wt % MF, Including SO ₃	0.40 37.99	0.69 39.00
Proximate, wt % MF, SO ₃ -Free Ash Basis Ash, SO ₃ -Free Volatile Matter Fixed Carbon	32.03 - -	33.97 25.36 40.67
SO ₃ , Wt % of Ash	15.70	12.89
HHV, Btu/lb (MF)	-	9,333

Analyses were performed by CONSOL R&D.

Figure 1. Proton Distribution vs Dewaxed Oil Yield.

Figure 1 (Cont'd). Proton Distribution vs Dewaxed Oil Yield.

Figure 2. Parity Plot of Resid Contents Determined by TGA and Microdistillation.

(Symbols: Diamonds = First Test; Triangles and Stars = Replicates)

SECTION THREE

SANDIA NATIONAL LABORATORY

ADVANCED DIRECT LIQUEFACTION CONCEPTS for PETC GENERIC UNITS QUARTERLY PROGRESS REPORT for OCTOBER 1993 through DECEMBER 1993

SANDIA NATIONAL LABORATORIES

Introduction

Experiments performed this quarter have been used to evaluate the effects of solvent hydrotreating parameters on yield of hydroaromatic components in the hydrotreated product. Several operating parameters, such as hydrotreating temperature, liquid space velocities, and hydrogen gas treat rates were investigated. A trickle-bed hydrotreater packed with a supported nickel / molybdenum on alumina catalyst was used to hydrotreat Wilsonville Run 262E V1074 heavy distillate and dewaxed V1074 distillate. The hydrotreated distillate was analyzed for hydrogen content and hydrogen distribution using elemental analysis and proton NMR spectroscopy. A catalytic dehydrogenation test was also used to quantify the amount of donor hydrogen in hydrotreated distillate samples.

Additionally, distillations were performed on the V131B recycle stream from Wilsonville Run 258K. These distillations were performed as part of the laboratory support subtask, to produce a 1050°F- feed material for subsequent testing in the trickle-bed reactor.

Subtask 1.3 Laboratory Support

Distillation of V131B from Run 258K

A series of four distillations were performed on the V131B from Wilsonville run 258K to prepare enough 1050°F- heavy distillate for future solvent hydrogenation tests with this material. Experiments with run 258K distillate are not part of the Integrated Simulation Tests that will use run 262 heavy distillate samples.

A one gallon sample of the V131B was sent to Sandia from CAER in November. The average yield of 1050°F- distillate from the four distillations was 41.7%. The samples from the distillations were combined and a subsample was diluted for analysis with a high resolution gas chromatograph. Figure 1 shows a high resolution gas chromatogram of the V131B distillate. For comparison purposes, Figure 2 shows a high resolution gas chromatogram of Run 262E V1074 (sample 1621-22-5). As can be seen in the chromatograms, the distillate from the 258K sample has peaks that elute earlier owing to more material boiling at lower temperatures than the V1074 sample from 262E. The run 258K heavy distillate is substantially lighter than the heavy distillate material from run 262E. Also the heavy distillate from run 258K has a higher concentration of pyrene, a hydrogen donor precursor, than the run 262E sample. Proton NMR results from CONSOL (April-June 1993 Quarterly report) indicate that aromaticity (% of protons as measured by NMR) of the run 258K distillate (850°F-) was 19.7% compared to 15.0% for the run 262E distillate.

Subtask 2.1.3 Solvent Pretreatment

Analysis of Hydrotreating Run Using -35°C Dewaxed V1074

Proton NMR spectroscopy was used to evaluate heavy distillate samples which were hydrotreated during September (see July-Sept 1993 quarterly report). The samples were hydrotreated at 360°C with the trickle-bed reactor packed with Shell 324 catalyst. Table 1 presents the results from proton NMR spectroscopy along with analytical and process data from the run. The samples were hydrotreated at different liquid hourly space velocities (LHSV) to evaluate the effects of increasing flow on the degree of hydrogenation. Increasing liquid flow would allow the process to utilize smaller or fewer hydrotreating reactors for the proposed solvent hydrogenation step in the Advanced Concepts Program.

The trickle-bed reactor system pressure was maintained at 1300-1400 psig during the reaction; liquid samples were taken at one hour intervals. Results of proton NMR analyses, displayed in Table 1, show that the level of paraffinic hydrogen (alkyl α , alkyl β and γ) was higher at the lower space velocities (44.6% at LHSV=0.7 hr⁻¹, 41.7% at LHSV=1.1 hr⁻¹). This could be due to hydrocracking of solvent at the lower liquid hourly space velocity. The level of hydroaromatic hydrogen was relatively unchanged when the LHSV was increased to 1.1 hr⁻¹ from 0.7 hr⁻¹. This indicates that there appears to be no penalty to increasing space velocity from ~0.7 hr⁻¹ to 1.1 hr⁻¹ under these conditions (360°C, 1300 psig), at least as far as the proton distributions are concerned. Samples produced at the higher liquid hourly space velocity also have a somewhat lower overall hydrogen content. Re-analysis of two samples (90303 and 90307) indicate that hydrogen content increased 1.2% and 0.9%, respectively, for these two samples. Overall these hydrogenated samples were very effectively hydrogenated at 360°C. Samples 90303 and 90307 were sent to CONSOL for microautoclave testing.

Gas Analyses of Test Using -35°C Dewaxed V1074

Hydrogenation at 360°C is favored thermodynamically over hydrogenation at 400°C since higher equilibrium concentrations of hydroaromatic compounds are favored at the lower temperature for any given hydrogen pressure. Another reason for using milder hydrogenation temperatures is to avoid temperatures at which the solvent can be hydrocracked. Previous hydrotreating tests with the trickle-bed reactor did not include gas measurement of the effluent gases. Such analyses would indicate the amount of hydrocarbon gases produced during the reaction and also help to estimate hydrogen consumption by gas forming reactions. Hydrogenation testing at 320°C and 360°C was reported in July-September quarterly report, and gas analyses were performed on the effluent gases from the tests. Table 2 presents the results from those analyses.

The hydrogen treatment rate for these experiments was 330 sccm H₂/cm³ liquid (1850 scf/Bbl). Hydrocarbon gases account for less than 0.3 vol% of the gases in the effluent at 360°C and less than 0.1 vol% at 320°C. Therefore hydrogen consumption due to hydrocarbon gas formation is approximately 0.4% of the feed hydrogen (total hydrocarbon hydrogen/feed hydrogen) at 360°C.

The hydrogen flow rate at 360°C was measured to be 165 sccm in the feed and 137 sccm in the product gases. The difference in measured gas flow rate indicates a hydrogen consumption of 28 sccm, or 1.25 millimoles of hydrogen per minute (2.52mg H/min). This gas measurement was

made when the liquid flow rate was 0.5g/min. The hydrogen consumption therefore, was 28sccm/0.45cm³ of feed or 62 sccm/cm³ (460 scf/Bbl), which is approximately 0.5 wt% hydrogen on a liquid feed basis. The liquid elemental analyses showed approximately 0.6 wt% increase in hydrogen for this period. The gas data are in general agreement with the liquid analyses.

Analysis of Hydrotreating Run Using V1074

In preparation for the solvent hydrotreating experiments with the dewaxed materials in the Integrated Simulation Tests (IST), a test run was made with run 262E V1074 heavy distillate (sample 1621-22-5). The IST is designed to use the most favorable process improvements from the Advanced Concepts Program and integrate them in an experimental plan which will use the products from one operation as feed for a subsequent step. A larger-scale dewaxing (1000g) test will produce feed for hydrotreating experiments at Sandia. The products from the hydrotreating step will be used for the oil agglomeration and coal liquefaction testing at CAER and CONSOL.

Shell 324 catalyst was used for these tests. Table 3 displays the hydrotreating conditions and product analyses for the V1074 hydrotreating experiments. Two temperatures were used for these experiments, 367°C and 384°C. In general the aromatic hydrogen content decreases and the percentage of γ protons increases with hydrotreating. Sample 122307, taken at 384°C shows a significant increase in cyclic α protons and a marked decrease in alkyl β protons. It is possible that hydrocracking reactions at 384°C are contributing to this. The test used a higher hydrogen gas treatment rate than the previous tests. Previous tests with heavy distillate samples used hydrogen treatment rates of 330 sccm H₂/cm³ liquid (1850 scf/Bbl). These tests used hydrogen treatment rates of 600 sccm/cm³ liquid (3350 scf/Bbl). Overall, the hydrotreated samples showed extensive hydrogenation and indicate that a nominal starting point for the IST could be the following :

LHSV = 1 hr⁻¹, temperature $\approx$ 365°C, hydrogen pressure $\approx$ 1400 psig and a hydrogen gas treatment rate > 3000 scf/Bbl.

Gas Analyses of Test Using V1074

Table 4 shows the gas analysis of the effluent stream from the trickle-bed reactor. As was noted for the previous hydrotreating run, very little hydrocarbon gas make takes place at these conditions. Approximately 0.2% of the feed hydrogen was consumed to form hydrocarbon gas. The hydrogen flow rate was 332 sccm in the feed and 288 sccm and 305 sccm in the effluent at 367°C and 384°C respectively. The hydrogen consumption measured at 367°C was 44 sccm at a liquid flow rate of 0.41 cm³/min or 107 sccm/cm³ (605 scf/Bbl). The hydrogen consumption for the 384°C test was 27sccm at a liquid flow rate of 0.51 cm³/min or 53 sccm/cm³ (297 scf/Bbl). The rather large differences in hydrogen consumption are caused in part by catalyst deactivation (the catalyst for 367°C test was on stream for approximately 3 hours compared to the 384°C test that had been on stream approximately 12 hours). In addition hydrogen consumption at 384°C (sample 122307) was lower, because the liquid space velocity was higher for this sample and the equilibrium constant for aromatic hydrogenation is smaller at higher temperatures.

Trickle Bed Catalyst Analyses

Table 5 shows the nitrogen content of the used catalyst from the V1074 hydrogenation experiments. The nitrogen content increases from 2630 ppm at the feed end of the reactor to 3320 ppm at the effluent end of the reactor. This trend was noticed before (July-September 1993 quarterly report). One would expect a higher deposition of nitrogen at the feed end of the reactor since the catalyst bed would be expected to adsorb the nitrogen containing compounds as they enter the reactor, however the trend has reproduced itself in the past two flow reactor experiments.

Dehydrogenation Test for Donor Solvent Hydrogen

During this project proton NMR and coal liquefaction tests have been used to evaluate the solvent quality of hydrotreated distillate samples from Sandia. Proton NMR data have been used to estimate the distribution of hydrogen, and combustion-elemental analysis has been used to determine the amount of hydrogen in the distillates. Coal liquefaction tests including the "modified equilibrium" test developed by CONSOL have been performed to measure solvent quality. Other measurements of donor solvent potential for model compounds and process-derived distillates have been reported in the literature [1-5]. Model compounds have been used as hydrogen acceptors to evaluate the hydrogen donation potential of various solvents. Dibenzyl [1], fluorenone [2], and benzyl phenyl ether [3] have been used to evaluate the amount of donor hydrogen in selected donor solvents. Hydrogen donors have also been evaluated with a combination of a model compound acceptor (stilbene) and catalytic dehydrogenation using a palladium catalyst [4]. Still others have used a palladium catalyst alone to dehydrogenate the donor compound in a nonreducing atmosphere [5] to measure donor hydrogen content of donor solvents.

This quarter we modified a catalytic dehydrogenation test using a supported palladium catalyst in our batch microautoclaves. Our test consists of heating a model compound or heavy distillate sample with a powdered palladium on alumina catalyst (0.5% Pd). The method was tested at 300°C for one hour and also at 400°C for one hour with a model hydroaromatic compound (1,2,3,6,7,8 hexahdropyrene-H₆Py). After reaction the amount of dehydrogenation was measured by high resolution gas chromatography. At 300°C for one hour the H₆Py was only 59% dehydrogenated; at 400°C for one hour the H₆Py was 95% dehydrogenated. When distillate samples were substituted for pyrene, hydrocarbon gases were produced in the one hour, 400°C tests. It was found that hydrocarbon gas formation could be minimized while still maintaining a high degree of dehydrogenation if the test were shortened from one hour to 20 minutes. Optimum conditions for the test were selected as 400°C for 20 minutes (92% H₆Py dehydrogenated). Table 6 presents the data from dehydrogenation tests using this method with a series of model compounds and heavy distillate solvents. The amount of hydrogen lost from the material was determined by elemental analysis and gives a relative indication of the hydrogen donor content of the sample. Table 6 also has a column listing the proton NMR results (% of total protons) for cyclic α and β protons. The V1074 heavy distillate lost only 0.1 wt% hydrogen and had the lowest amount of hydroaromatic hydrogen (30.5 % cyclic α and β hydrogen), while the H₆Py, which had the most hydroaromatic hydrogen (55.2%), lost the most hydrogen during dehydrogenation at 2.6 wt %. hydrogen. Thus a correlation exists between the weight % hydrogen lost due to dehydrogenation and hydroaromatic proton concentration.

The method was evaluated for selective dehydrogenation of hydroaromatic compounds by testing a variety of model compounds. Hexahydroanthracene (1,4,5,8,9,10 H₆ An) was chosen as one test compound because it has no hydroaromatic hydrogen (only olefinic and saturated hydrogen). Table 7 presents the results of catalytic dehydrogenation tests with H₆An and a few other compounds known to be hydrogen donors. As can be seen in Table 7, all of the compounds with the exception of the H₆An are extensively dehydrogenated with the test.

The catalytic dehydrogenation test is relatively easy to use and gives supplementary evidence about donor hydrogen content of the hydrotreated distillates. This test will be used in the future to evaluate hydrogen donor content along with the other tests (proton NMR and coal liquefaction).

Additional Business

An Advanced Concepts Quarterly Meeting was held on November 9 and 10, at CAER. The last quarter's work was reviewed and an experimental plan for the Integrated Testing was agreed upon.

We have received 43 samples from CONSOL for use in standardizing the TGA for tests to measure resid conversion. The samples are THF soluble extracts from various coal liquefaction tests at CONSOL. We have also received a one gallon sample of Wilsonville Run 258K V131B, recycle oil from CAER. The V131B sample was heated and subsampled at Sandia for future distillation and testing. Sandia shipped a sample of hydrogenated dewaxed V1074 heavy distillate to CAER for preliminary coal liquefaction testing prior to receiving samples of hydrotreated distillate for the matrix of tests that were agreed on at the quarterly meeting.

Two samples were received from CONSOL for the Integrated Simulation Tests. The samples are described below.

Sample 1621-22-5-I -5°C acetone dewaxed.

Sample 1621-22-5-K Blend of the above sample and untreated V1074 to simulate (based on alkyl beta proton contents) the distillate that would be obtained by dewaxing a 25% slipstream of the distillate. The blend was 37.5 wt% V1074 and 62.5 wt% 1621-22-5-I.

Reactor Modifications

Experiments in May and June indicated that Sandia's microautoclave experiments showed lower conversions than those performed at CONSOL or CAER at similar conditions. At that time we thought that our microautoclave design may have some gas liquid mass transfer limitations. To address this concern we built a new microautoclave shaker similar to the designs of CONSOL and CAER. The new apparatus was installed this month. Tests with this shaker will begin next month. In addition a new high flow rate (20L/min) gas flow controller was installed on the trickle-bed reactor. This new flow controller and additionally installed pressure transducers will allow us to more carefully control operating conditions and gas treatment rates in the trickle-bed hydrotreating reactor.

References

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- 3) Oviawe, A.P. , Nicole, D. , Fringant, J.L. , FUEL, 1993, 72, 65.
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- 5) Curtis, C.W. , Guin, J.A. , Hale, M.A. , Smith, N.L. , Proceedings International Conference on Coal Science, 1983, Pittsburgh, PA, 164.

Figure 1. High Resolution Gas Chromatogram of 1050°F- Distillate Run 258K

Figure 2. High Resolution Gas Chromatogram of V1074 from Run 262E (Sample 1622-22-5)

Table 1. Proton NMR Results for Heavy Distillate Hydrotreated with NiMo Catalyst at 360°C

Sample	LHSV* (hr ⁻¹)	% H	Cond Arom	Uncond Arom	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
V1074	NA	9.9	11.3	3.6	14.7	7.6	15.8	34.6	12.3
Dewaxed V1074**	NA	8.1	17.3	6.2	20	10.3	17.1	17.9	11.2
90303	0.7	9.3 (8.8)	9.9	6.8	17.2	9.7	21.5	20.6	14.3
90304	0.9	ND	8.3	5.7	17.0	10.0	20.4	23.0	15.5
90307	1.1	9.0 (8.5)	12.8	5.0	18.8	10.1	21.7	19.6	12.0
90308	1.1	ND	11.9	6.9	18.4	10.6	21.0	18.9	12.2

ND = Not Determined. * Assume density : packed catalyst = 0.86 g/cm³; feed = 1.10 g/cm³.

** Dewaxed at -35°C with acetone. Numbers in parentheses are results presented previously, newer results were generated with more replication and with closer control of combustion conditions on the hydrogen analyzer.

Table 2. Gas Analyses of Trickle-Bed Hydrogenation Reactor Products for Hydrotreating -35°C Acetone Dewaxed V1074 (Effluent Stream)

	H ₂ **	CH ₄	C ₂ H ₆	C ₃ H ₈
Temp 320°C				
Volume %	99.90	0.059	0.025	0.014
sccm*	NA	0.081	0.034	0.019
Temp 360°C				
Volume %	99.71	0.163	0.080	0.050
sccm*	137	0.222	0.110	0.068

* Hydrogen feed to the reactor was 165 sccm (GHSV= 430 hr⁻¹ assuming 23cm³ reactor volume). NA means not analyzed for the 320°C case.

**Hydrogen by difference.

Table 3. Proton NMR Results for V1074 Heavy Distillate Hydrotreated with NiMo Catalyst

Sample	LHSV* (hr ⁻¹)	Temp** (°C)	Cond Arom	Uncond Arom	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
V1074	NA	NA	11.3	3.6	14.7	7.6	15.8	34.6	12.3
122205	1.2	367	3.2	2.4	15.6	7.8	17.6	36.1	17.4
122303	1.3	367	3.8	0.8	13.5	7.4	17.3	38.9	18.3
122307	1.4	384	2.9	3.8	20.0	8.5	16.9	30.7	17.2

*Assume density : packed catalyst = 0.86 g/cm³; feed = 1.0 g/cm³.

** Hydrotreating Temperature.

Table 4. Gas Analyses of Trickle-Bed Hydrogenation Reactor Products for Hydrotreating V1074 Heavy Distillate (Effluent Stream)

	H ₂ **	CH ₄	C ₂ H ₆	C ₃ H ₈
Temp 367°C				
Volume %	99.87	0.068	0.037	0.025
sccm*	288	0.185	0.100	0.068
Temp 384°C				
Volume %	99.77	0.115	0.070	0.049
sccm*	305	0.351	0.214	0.149

* Hydrogen feed to the reactor was 332 sccm (GHSV= 860 hr⁻¹ assuming 23cm³ reactor volume). ** Hydrogen by difference.

Table 5. Post Reaction Catalyst Analysis

Catalyst	Bed Position	Nitrogen (ppm)
NiMo (Shell)	1(top)	2630
NiMo (Shell)	2	2900
NiMo (Shell)	3	2580
NiMo (Shell)	4	2930
NiMo (Shell)	5	3220
NiMo (Shell)	6(bottom)	3320

Table 6. Dehydrogenation Test Results Using Pd on Alumina, 400°C, 20 min.

Sample	Cyclic $\alpha+\beta$ (% of hydrogen)	% hydrogen initial	% hydrogen final	% hydrogen difference
V1074 Heavy Distillate (1621-22-5)	30.5	9.9	9.8	0.1
-35°C Dewaxed with acetone (1621-22-5A) V1074	37.1	8.1	7.9	0.2
Hydrogenated -35°C dewaxed 90303	39.7	9.3	8.4	0.9
Hydrogenated -35°C dewaxed 90307	40.5	9.0	8.4	0.6
1,2,3,6,7,8 Hexahdropyrene	55.2	7.7	5.1	2.6

**Table 7. Dehydrogenation Test Results Using Model Compounds.
Pd on Alumina 400°C, 20 min.**

Compound	% Dehydrogenated
1,2,3,6,7,8 Hexahdropyrene	92
9,10 Dihydrophenanthrene	92
1,2,3,10b Tetrahydrofluoranthene	93
1,2,3,4 Tetrahydrocarbazole	96
1,2,3,4 Tetrahydroquinoline	98
1,2,3,4 Tetrahydronaphthalene	88
1,4,5,8,9,10 Hexahydroanthracene	12

SECTION FOUR

LDP ASSOCIATES

LDP ASSOCIATES

**Michael Peluso, Proprietor
609-737-7121**

**1581 Reed Rd.
Trenton, N.J. 08628**

**February 24, 1994
Revised : April 5, 1994**

**Dr. Ed Givens
Center for Applied Energy Research
3572 Iron Works Pike
Lexington, Kentucky 40511-8433**

Dear Ed:

Subject: QUARTERLY PROGRESS REPORT FOR OCT. THRU DEC. 1993

For the quarter ending December 31, 1993 the following subcontract services (UKRF-4-25582-92-75) were performed in support of the DOE Advanced Concepts Program (DE-AC22-91PC91040):

BASELINE ECONOMIC ASSESSMENT

A partial review of the eight volume Bechtel's Baseline Design Report (Illinois #6 coal) of March 1993 was made. The basis for the ebullated-bed reactor design used in our Base Case differs from that supplied by HRI for the Bechtel report. The extent to which such differences in bases will affect our comparative results will have to be determined.

In the course of reviewing Bechtel's report it was noted that overall product yield differences existed between their Baseline Case and their Improved Baseline Case. It was determined that the differences in overall yields were almost entirely due to differing yield structures in the Gas Oil Hydrotreating Units (GOHT). Since the feedstock to the GOHT is essentially the same in both cases, it seems highly doubtful that a significant variation in GOHT yields would result. Because the overall yield difference significantly affects the relative economics of the two cases, Ed Klunder of PETC was notified of this finding.

Bailey Engineers in Alabama was contacted with regard to the iron oxide which they supplied to Wilsonville for Run# 263. They estimated a price of 12¢/lb. for very large quantities for their ground (95% thru 325 mesh) iron oxide. The cost of the sulfiding agent, H₂S, was also reassessed. The estimated quantity of H₂S produced in the commercial plant exceeds (by 24%) the quantity of H₂S required for sulfiding. Given the adequacy of internal supply the per unit H₂S operating cost was lowered by 25% from the value previously used. The total Base Case operating costs were revised accordingly as shown in Table 14A.

Climax Molybdenum Company was contacted to ascertain the price of the moly precursor material (Ammonium Octamolybdate) being considered for use in certain portions of CAER's dispersed catalyst development work. A price of \$4.45/lb. was indicated for quantities greater than 10 tons. Since the precursor contains approximately 61 % molybdenum, its price per pound of moly is only about 20% of that of the Molyvan L used at Wilsonville during Runs# 262 & 263. If this water-soluble moly precursor could be utilized, significant cost savings could be achieved.

ALTERNATE ECONOMIC ASSESSMENT

A series of topical process alternatives developed by G. Kimber at CAER was briefly reviewed. As a result, installed reactor cost data for our Base Case was isolated and a study of the change in these costs associated with increasing reactor volume was begun.

An assessment was begun of the impact on product price of a 50% reduction in the yield of light hydrocarbon gas make (C₁ to C₃) and a corresponding increase in distillate yield, while holding all other parameters constant. As shown in Table 2, the hydrogen consumption per unit of coal feed decreases by almost 8%, while distillate production per unit of coal feed would increase by 6% under these assumptions.

The hydrogen and fuel gas balances for this hypothetical case are shown in comparison to the Base Case in Table 8. At the assumed constant product rate, liquefaction system hydrogen consumption decreases by approximately 13%. Because of the lower availability of hydrocarbon fuel gases, less hydrogen is produced and less fuel gas is required in Steam Reforming. Additional coal is gasified to close the hydrogen balance. However, overall coal consumption for this alternate case is 2.2% less than for the Base Case.

ECONOMIC ASSESSMENT OF DEWAXING

A first pass assessment of the economics of solvent dewaxing was completed and presented at the Quarterly Review Meeting in Lexington (see Attachment #1). Summary data on the 25% and 100% Dewaxing Unit (DWU) feed cases is shown in Table 6 of the above referenced presentation. Results are indicated for 100% of byproduct sales as fully refined paraffin wax (FRPW) and for FRPW sales at a 10% penetration of the U.S. wax market.

If 100% of byproduct sales are as FRPW, the cost of solvent dewaxing is exactly offset by the value of the FRPW sales for the 100% feed case. An even more favorable result occurs for the 25% feed case under the same assumptions. In this case, FRPW sales exceed DWU costs by approximately 52¢/Bbl. of gasoline. However, in a five plant scenario, the amount of FRPW sold would be 76% of the total U.S. wax market for the

25% feed case and 121% of the U.S. market for the 100% feed case.

At the conservatively low wax market penetration of 10%, DWU costs exceed byproduct revenues by \$1.16/Bbl. of gasoline for the 25% feed case and by \$3.27/Bbl. of gasoline for the 100% feed case.

The above results range from a decrease in gasoline product cost of 52¢/Bbl. for the 25% feed-100% wax sales case to an increase of \$3.27/Bbl. for the 100% feed-10% wax market penetration case. These results indicate the extremely significant effect DWU feedrate and byproduct disposition have on dewaxing economics.

The benefit to the liquefaction system of using the better dewaxed distillate solvent has not been rigorously determined due to a lack of definitive experimental data up to now. Instead, guesstimated benefits of \$1.00/Bbl. of gasoline were assigned to the 25% feed case and \$1.50/Bbl. for the 100% feed case. The difference between the two solvents is the degree of removal of paraffinic components. The dewaxed distillate solvent for the 25% feed case contains 25.5% alkyl beta protons, while the dewaxed distillate for the 100% feed case contains 21.4% alkyl beta protons. If the guesstimated liquefaction benefits prove to be valid, then the 25% and 100% feed cases are a standoff at the 100% FRPW sales assumption (both lower gasoline product price by \$1.50/Bbl.), while the 25% feed case is clearly superior, though uneconomical, for the 10% wax market penetration level. Under such circumstances catalytic dewaxing may be a more viable alternative. However, these preliminary results can be markedly different if the assumed liquefaction system benefits differ significantly from their guesstimated values.

DEWAXED OIL HYDROTREATING

As a follow-up to September's recommendation, the implications of the preliminary results from the higher space velocity tests were discussed with R. Kottenstette along with his plan for additional tests.

DEWAXING UNIT FEED NMR

It was noted that a recent CONSOL proton NMR distribution (Lancet to SANDIA, 12/9/93) for the V-1074 Dewaxing Unit feed stream indicated significant differences in the alkyl beta and gamma proton concentrations from those of an earlier NMR (31.5% vs 34.6% and 17.9% vs 12.3%). CONSOL was asked to ascertain the reason for these differences.

FLUID COKING

Exxon fluid coking experimental data and economic data from Bechtel's recently completed Illinois #6 coal study were used to evaluate the use of fluid coking in place of the ROSE unit. As shown in Table 1 of Attachment #2 "Assessment of Fluid Coking", the fluid coking option recovers about 18% less heavy liquid for recycle compared to the ROSE unit. As shown in Tables 40.3 and 45.2 of Bechtel's study, the fluid coking option has a capital cost almost four times that of the ROSE unit. Therefore, fluid coking isn't an attractive option for replacing the ROSE unit since the above significant disadvantages would outweigh any potential advantage of obtaining a somewhat improved solvent. A presentation on the above was made at the Quarterly Review Meeting in November.

Very truly yours,

Michael Peluso
LDP Associates

cc: F. Derbyshire @ CAER
G. Kimber @ CAER
R. Winschel @ CONSOL
R. Kottenstette @ SANDIA

TABLE 14A
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
BASE CASE ANNUAL OPERATING COSTS

	<u>COST (\$ / Bbl. of Gasoline)</u>
TOTAL MF COAL: 16,545 T/D @ \$10/T	3.31
PURCHASED ELECTRICAL POWER, 248 MW @ 4¢/ Kw-hr.	4.76
LIQUEFACTION SYSTEM ADDITIVES :	
- Iron Oxide @ 12¢/lb. & H ₂ S @ 7.5¢/lb.	0.80
- Dispersed @ \$3.20/ lb.	2.02
- Supported @ \$3/lb.	2.37
UPGRADING UNITS CATALYSTS & CHEM.	0.75
OTHER CATALYSTS & CHEMICALS	1.33
OPERATING LABOR	1.02
MAINTENANCE @ 2% of TPC + ICC	5.11
INSURANCE & LOCAL TAXES @ 1.5% of TPC + ICC	3.83
ADMINISTRATION & OPERATIONS SUPPORT	<u>0.76</u>
Total =	26.06

TABLE 2
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
LIQUEFACTION SYSTEM YIELDS

INPUTS:

• MF COAL	100.000	
• DISPERSED MOLY CATALYST	0.120	(Molyvan L)
• IRON OXIDE	1.000	
• SULFIDING AGENT (H ₂ S)	0.430	
• MAKEUP DAS	0.489	
• HYDROGEN	<u>5.906</u>	[5.457]
Total = 107.945		[107.496]

OUTPUTS:

• WATER	12.450	[12.375]
• HYDROGEN SULFIDE	0.310	[0.304]
• AMMONIA	0.630	[0.608]
• CARBON MONOXIDE	0.970	
• CARBON DIOXIDE	5.150	
• C1 to C3 GASES	7.830	[3.920]
• C4+ DISTILLATE	59.545	[63.109]
• ASH CONCENTRATE	<u>21.060</u>	
Total = 107.945		[107.496]

[] = 50% Lower C₁ to C₃ Gas Make

TABLE 8
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
HYDROGEN AND FUEL GAS BALANCES

HYDROGEN BALANCE (MMSCFD):

• CONSUMPTION		
- LIQUEFACTION UNIT	308.8	[269.2]
- UPGRADING	<u>144.2</u>	
Total =	453.0	[413.4]
• PRODUCTION		
- GASIFICATION OF ASH CONC.	108.0	[101.9]
- GASIFICATION OF COAL	196.7	[218.7]
- PRODUCED IN CAT. REFORMING	71.1	
- STEAM REFORMING OF HC GASES	<u>77.2</u>	[21.7]
Total =	453.0	[413.4]

FUEL BALANCE (Millions of Btu { LHV}/ Hr.):

• CONSUMPTION		
- SLURRY PREHEATER	971	[887]
- STEAM REFORMER	611	[172]
- CAT. REFORMER	661	
- DISTILLATE HYDROPROCESSING	217	
- VACUUM UNIT	149	[231]
- GASIFICATION COAL, DRYING	148	[165]
- ROSE UNIT	97	[92]
- SULFUR RECOVERY UNIT & MISC.	<u>20</u>	
Total =	2,874	[2,445]
• PRODUCTION		
- LIQUEFACTION OFF GAS	2,010	[1,045]
- DISTILLATE HYDRO. OFF GAS	1,553	
- CAT. REFORMING OFF GAS	<u>57</u>	
Sub-Total =	3,620	[2,655]
- STEAM REFORMING FEED	<u>- 746</u>	[- 210]
Total =	2,874	[2,445]

[] = ~~50%~~ Lower C₁ to C₃ Gas Make

Attachment #1

**ECONOMIC ASSESSMENT OF
SOLVENT DEWAXING
THE DISTILLATE RECYCLE SOLVENT
IN THE LIQUEFACTION OF SUB-BITUMINOUS COAL**

**BY LDP ASSOCIATES
PRESENTATION @ NOVEMBER 1993 PROJECT REVIEW MEETING
ADVANCED DIRECT LIQUEFACTION CONCEPTS
DOE CONTRACT DE-AC22-91PC91040**

TABLE 1
DISTILLATE PROCESS SOLVENT (V-1074) PROPERTIES
WILSONVILLE RUN # 263J
BLACK THUNDER COAL, HYBRID MODE OPERATION

WEIGHT RATIO TO MF COAL : 0.858

ESTIMATED SPECIFIC GRAVITY : 1.04 (4.6°API)

ESTIMATED ELEMENTAL ANALYSIS , Wt. %

- Carbon	89.28
- Hydrogen	9.49
- Oxygen	0.76
- Nitrogen	0.44
- Sulfur	0.03

BOILING RANGE, °F : 650 to 1,000

ESTIMATED WATSON "K" FACTOR : 10.5

PROTON NMR DISTRIB'N (CONSOL), %:

- Condensed Aromatics	13.9
- Uncondensed Aromatics	4.4
- Cyclic Alpha	14.3
- Alkyl Alpha	8.2
- Cyclic Beta	14.5
- Alkyl Beta	32.9
- Gamma	11.8

SOLVENT QUALITY* (CONSOL): 70.9

* 1.5/1 SOLVENT-TO-COAL, INDIANA V COAL, 750 F, 30 MINUTES.

FIGURE 1
SIMPLIFIED BLOCK FLOW DIAGRAM
DEWAXING & HYDROTREATING of DISTILLATE RECYCLE SOLVENT

FIGURE 2
CONSOL MICROAUTOCLAVE DATA
EFFECT OF DEWAXING & HYDROTREATING
ON THE CONVERSION OF BLACK THUNDER COAL

TEXACO DEVELOPMENT CORPORATION

TWO STAGE SOLVENT DEWAXING UNIT WITH INCREMENTAL DILUTION

FIGURE 2A

AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

301/587-8202

2 of 2

TEXACO DEVELOPMENT CORPORATION

THREE STAGE SOLVENT DEWAXING-WAX FRACTIONATION UNIT WITH INCREMENTAL DILUTION AND WARM UP DEOILING

FIGURE 2B

TABLE 2
DEWAXING & HYDROTREATING
OF DISTILLATE PORTION OF PROCESS SOLVENT
TYPICAL PROPERTIES OF FULLY REFINED PARAFFIN WAX*

ESTIMATED SPECIFIC GRAVITY : 0.92

ELEMENTAL ANALYSIS, Wt. % :

- Carbon	85.0
- Hydrogen	14.8
- Nitrogen	0.1
- Sulfur	< 0.03

PROTON NMR DISTRIBUTION,% :

- Condensed Aromatics	0.0
- Uncondensed Aromatics	0.0
- Cyclic Alpha	0.8
- Alkyl Alpha	0.7
- Cyclic Beta	5.8
- Alkyl Beta	79.0
- Gamma	13.7

* PROPERTIES SHOWN ARE FOR "PARASEAL" WAX

FIGURE 3
EFFECT OF DEWAXING UNIT BYPASS

TABLE 3
DEWAXING & HYDROTREATING
OF DISTILLATE RECYCLE SOLVENT
DEWAXING UNIT OPTIONS

% FED TO DEWAXING UNIT:	None	25	50	100
DEWAXING UNIT FEED				
- Feedrate, Lb/100lb MF Coal	None	24.37	46.95	91.09
- % Alkyl Beta Protons	-----	26.80	25.06	23.62
- Wt.% Hydrogen	-----	9.36	9.22	9.10
SLACK WAX YIELD				
- Wt.% of Feed	-----	11.06	7.64	4.81
- lb/100lb MF Coal	-----	2.70	3.59	4.38
SLACK WAX PROPERTIES				
- % Alkyl Beta Protons	-----	67.66	67.19	66.80
- Wt.% Hydrogen	-----	14.60	14.35	14.15
- Watson 'K' Factor	-----	12.05	12.04	12.02
DEWAXED OIL PROPERTIES				
- % Alkyl Beta Protons	-----	21.72	21.57	21.44
- Wt.% Hydrogen	-----	8.71	8.79	8.84
DISTILLATE TO HYDROTREATING				
- % Alkyl Beta Protons	32.90	25.53	23.31	21.44
- Wt.% Hydrogen	9.49	9.20	8.95	8.84

TABLE 4
DEWAXING & HYDROTREATING
OF DISTILLATE PORTION OF PROCESS SOLVENT
FACTS ON THE U. S. WAX MARKET

• **PRODUCTS**

1. Fully Refined Paraffin Wax

- LESS THAN 0.5% OIL
- USED IN PAPER, CONTAINER & CUP COATINGS
- ESTIMATED CURRENT DEMAND : 550,000 TON/Yr.
- ESTIMATED GROWTH RATE : 1.0 to 1.2 %/Yr.
- CURRENT MARKET PRICE : 25 to 37 ¢/Lb

2. Slack Wax

- NORMALLY 15% OIL
- MAIN GROWTH AREA IS AS MOISTURE BARRIER
IN PARTICLE & HARDBOARDS
- ESTIMATED CURRENT DEMAND : 375,000 TON/Yr.
- ESTIMATED GROWTH RATE : 6 to 7 %/Yr.
- CURRENT MARKET PRICE : 12 to 17 ¢/Lb.

• **IMPORT / EXPORT BALANCE**

- U. S. MARKET ALMOST SELF-SUFFICIENT
- 25,000 TON/Yr. of IMPORTS NEEDED to MEET DEMAND
- BUT POTENTIAL IMPORT SUPPLY MUCH HIGHER
(e. g. 100,000 T/Yr. of Wax from Shell's F-T Plant in Malaysia)

TABLE 5
DEWAXING & HYDROTREATING
OF DISTILLATE PORTION OF PROCESS SOLVENT
KEY FACTORS IN ECONOMIC EVALUATION

- ABILITY of U.S. WAX MARKET to ABSORB WAX PRODUCTION
in MULTI-PLANT SCENARIO
- SENSITIVITY of COSTS vs % FED to DEWAXING UNIT
- SENSITIVITY OF BENEFITS vs % FED to DEWAXING UNIT

TABLE 6
BLACK THUNDER LIQUEFACTION STUDY
DEWAXING OF DISTILLATE PORTION OF PROCESS SOLVENT
FIRST PASS ECONOMIC EVALUATION

• **BASIS**

- Liquefaction : Five Plants @ 50,000 BPSD of Gasoline Each
- Wax Yield : 4% of MAF Coal
- Wax Cracking Rate : 22% of Wax Circulating
- Crude Oil Price : \$ 30/ Bbl.
- Gasoline Price : \$ 40 / Bbl.
- Wax Value : 34.3 ¢ / lb.
- Slack Wax Value : 18.8 ¢ / lb.
- FCC Feed Value : 11.5 ¢ / lb.

• **TOTAL PRODUCTION DATA**

	All Wax		Wax = 10% of Market	
	25%	100%	25%	100%
- Product Distribution				
- % of Feed to DWU				
- Fully Refined Wax, T/Yr.	462,000	737,500	60,700	60,700
- Slack Wax, T/Yr.	None	None	67,200	67,200
- FCC Feed, T/Yr.	None	None	415,600	729,000

• **ECONOMIC DATA / PLANT**

- Est'd DWU Capital Cost, \$ MM	236	463	180	410
- Capital Savings in Upgrading	- 24	- 39	- 30	- 64
- Net Capital Cost	212	424	150	346
- DWU Product Revenue, \$ MM/Yr.	63.4	101.2	32.5	46.9
- Decreased Gasoline Revenue	- 23.6	- 37.6	- 27.8	- 43.8
- Net Revenue	39.8	63.6	4.7	3.1
- Net Annualized Δ in Cap. Cost*	31.8	63.6	22.5	51.9
- Net Δ in Gasoline Cost, \$ MM/Yr.	- 8.0	None	+ 17.8	+ 48.8
- " " " " " " , \$ / Bbl.	- 0.52	None	+ 1.16	+ 3.27
- Guessed Liq' n Benefit, \$ / Bbl.**	- 1.00	- 1.50	- 1.00	- 1.50
- Total Δ in Gasoline Cost, \$ / Bbl.**	- 1.52	- 1.50	+ 0.16	+ 1.77

* ASSUMING 15% CAPITAL CHARGE FACTOR

** NOT INCLUDING HYDROTREATING COST

TABLE 7
DEWAXING & HYDROTREATING
OF DISTILLATE PORTION OF PROCESS SOLVENT
PLAN OF FUTURE WORK

- FIRM UP DEWAXING UNIT ECONOMICS
- ESTIMATE HYDROTREATER UNIT
CAPITAL & OPERATING COSTS
- QUANTIFY LIQUEFACTION SYSTEM BENEFITS vs
DEGREE OF SOLVENT QUALITY IMPROVEMENT
- INVESTIGATE TECHNICAL & ECONOMIC FEASIBILITY OF
USING CATALYTIC DEWAXING AND THERMAL CRACKING
TO CONTROL WAX CONCENTRATION

Attachment #2

**ASSESSMENT OF FLUID COKING
IN THE LIQUEFACTION OF SUB-BITUMINOUS COAL**

**BY LDP ASSOCIATES
PRESENTATION @ NOVEMBER 1993 PROJECT REVIEW MEETING
ADVANCED DIRECT LIQUEFACTION CONCEPTS
DOE CONTRACT DE-AC22-91PC91040**

FIGURE 1A SIMPLIFIED RESID, IOM & ASH BALANCE
REVISED BASE CASE (SO₃- Free ash basis, WR#263J)

FIGURE 6.1

PROCESS FLOW DIAGRAM OF FLUID COKER

Original Source: Bechtel DOE Study

March 1993

TABLE 1
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
FLUID COKING Vs ROSE UNIT
PERFORMANCE COMPARISON

VACUUM BOTTOMS FEEDSTOCK

	Wt. % of Feed
• Distillate	3.20
• Resid	60.10
• IOM	19.63
• Ash	<u>17.07</u>
Total	= 100.00

ESTIMATED* YIELDS

• Gas	2.50	
• Distillate	3.20	[3.2]
• Heavy Liquid for Recycle	35.40	[43.0]
• Coke to Gasification	<u>58.90</u>	[53.8]
Total	= 100.00	

CLEAN RESID RECOVERY, %	58.9	[71.6]
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ORGANICS REJECTION. % of MF Coal	17.1	[14.5]
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[] = ROSE UNIT DATA

* BASED ON EXXON EXPERIMENTAL DATA ON H-COAL VACUUM BOTTOMS

LDP ASSOCIATES 11/8/93

FIGURE 1A SIMPLIFIED RESID, IOM & ASH BALANCE
REVISED BASE CASE (SO₃-Free ash basis, WR#263J)

TABLE 2
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
CONCLUSION RE: FLUID COKING OPTION

FLUID COKING ISN'T AN ATTRACTIVE OPTION
COMPARED TO THE ROSE UNIT BECAUSE OF ITS
LOWER RECOVERY OF HEAVY LIQUID FOR RECYCLE
AND ITS SUBSTANTIALLY HIGHER INVESTMENT COST.

THESE SIGNIFICANT DISADVANTAGES WOULD OUTWEIGH
THE POTENTIAL ADVANTAGE OF OBTAINING A SOMEWHAT
IMPROVED SOLVENT VIA THE USE OF FLUID COKING.

Table 40.3

ISBL Installed Plant Costs

BECHTEL BASELINE CASE

CAPITAL COST FOR THE COMPLEX BASE LINE FOR THE NTH PLANT					
Plant #	Number of Operating Train	Total Number of Train	ISBL Plant Field Costs 1000\$	ISBL Plant Adj. With OSBL Costs 1000\$	Installed Plant Costs 1000\$
1	5	5	91000	131000	160800
1.4	10	10	87500	126000	154600
2	5	5	932200	1343000	1647800
3	1	1	25300	36400	44700
4	1	1	15600	22500	27600
5	1	1	74000	106500	130700
6	1	1	152600	220000	269800
8	1	1	42200	60800	74600
9	5	5	263700	380000	465900
10	5	5	191000	275000	337700
11	4	4	46700	67200	82500
38	1	1	40100	57800	71000
39	1	1	13300	19200	23500
TOTAL			1975200	2845400	3491200

ROSE
UNIT

Table 45.2

BECHTEL Study Option 5 - FLUID COKING

CAPITAL COST FOR THE COMPLEX OPTION 5 FOR THE NTH PLANT					
Plant #	Number of Operating Train	Total Number of Train	ISBL Plant Field Costs 1000\$	ISBL Plant Adj. With OSBL Costs 1000\$	Installed Plant Costs 1000\$
1	5	5	80000	109900	134800
1.4	10	10	87500	120100	147300
2	5	5	932200	1279700	1570100
3	1	1	21100	28900	35500
4	1	1	12900	17700	21700
5	1	1	61700	84800	104000
6	1	1	134400	184500	226400
8	1	1	161100	221100	271300
9	5	5	217800	299000	366800
10	5	5	164900	226400	277800
11	4	4	39500	54200	66500
38	1	1	37800	51900	63700
39	1	1	13100	18000	22100
TOTAL			1964000	2696200	3308000

FLUID COKING UNIT

DATE

FILMED

7/28/94

END