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

**Quarterly Technical Progress Report
for Period January 1993 through March 1993**

by

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

Sandia National Laboratories

CONSOL Inc.

LDP Associates

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MASTER

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870

INDEX

INDEX	ii
SUMMARY	1
SECTION ONE	6d
WORK PERFORMED	6e
TASK 1.1 LABORATORY SUPPORT (UK/CAER)	6e
Method for Measurement of 1050°F	6e
Baseline Test	15
Catalyst Testing	20
TASK 1.3 LABORATORY SUPPORT - (Sandia)	28
TASK 2.1.1 CO PRETREATMENT (UK/CAER)	29
Liquefaction of CO Pretreated Coals	33
TASK 2.1.3 SOLVENT PRETREATMENT (Sandia)	36
Coated NiMo HTO Catalyst Tests	36
Bulk NiMo HTO Tests	37
TASK 2.2.3 MODIFIED REACTOR CONCEPTS (Sandia)	38
Nitrogen gas phase tests	40
Hydrogen gas phase tests	40
Proton NMR Studies of Liquefaction Product Oils	41
Nitrogen Overpressure Tests	41
Hydrogen Overpressure Tests	42
Conclusions	43
Solvent Upgrading Using In Situ WGS Reaction	43
TASK 2.3.1 IRON BASED DISPERSED CATALYSTS (UK/CAER)	45
Iron Impregnated Coal by Incipient Wetness	45
Moisture Content of Coal	45
Chemical Cost	47
Liquefaction of IW Impregnated Coals	49
Effect of Moisture Content	56

Effect of Final Dry	60
Effect of NH_4^+ /Fe Ratio	61
Impregnation Compound	63
 TASK 2.3.3 CATALYST STUDIES (SANDIA)	 67
TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP Assoc)	67
Assessment of Improved Coal Conversion Case	68
Upgrading of Dewaxed Oil	69
REFERENCES	79
 SECTION TWO	 80
TASK 1.2 LABORATORY SUPPORT AT CONSOL	1
Summary	1
Discussion	1
TASK 2.1.2.1 PRETREATMENT WORK AT CONSOL - DEWAXING	3
Summary	3
Discussion	4
Production of Acetone/MEK Dewaxed Oil	4
Wax Yields	4
Wax Properties	5
Calculated Solvent Qualities	5
Development of Microautoclave Test for Composite Recycle	
Solvent Quality	6
TASK 2.1.2.2 PRETREATMENT WORK - AGGLOMERATION	10
Summary	11
Discussion	12
CO-Pretreated Coal	12
Alternative Feedstocks	13
Dewatering - Beulah-Zap Lignite	13

Dewatering - Black Thunder Coal	14
Black Thunder Coal Cleanability	14
TASK 2.4.2 SOLIDS SEPARATION AT CONSOL	15
Summary	15
Discussion	15
Low-Temperature Approach	15
High-Temperature Approach	16
Liberation of Ashy Resid Materials	16
Miscellaneous	17
TASK 2.6.2 COKER OVERHEAD CHARACTERIZATION AT CONSOL	17
Summary	17
Discussion	18
REFERENCES	22
APPENDIX 1	37
APPENDIX 2	44
APPENDIX 3	51

SUMMARY

TASK 1.1 LABORATORY SUPPORT (UK/CAER)

The base case developed by M. Peluso defines the baseline conditions for relating catalyst performance with Wilsonville Run 263J. The key performance factors are coal conversion of 93.6% and conversion of coal+resid+IOM+MAF of 24.6% which corresponds to a 1050°F⁺ resid conversion across the first stage of the Wilsonville plant of 51 lbs per 100 lbs fresh dry coal feed. Work is progressing on determining 1050°F⁺ distillate. A discussion is included of previous work on relating pentane soluble product to the 1000°F⁺ product that was isolated by vacuum distillation. Work is progressing on distilling a sample of V131B from Wilsonville Run 258K and the composited WRO from Run 262 to develop a standard which will be used to develop a method to determine 1050°F⁺ resid in our products.

Several baseline testing runs were made with Black Thunder coal in WRO under the conditions laid out for the test. Runs were made over a time span from 7 minutes up to 30 minutes and the THF conversions and resid conversions were measured. These resid conversions are based upon solvent separation results making the assumption that the oils in the 1050°F⁺ fractions are unchanged by the process. Runs were made without added Fe or Mo, with 1% Fe₂O₃ and 100 ppm Mo in Molyvan L, but in the absence of any added sulfur, and with this same Fe and Mo concentration but with added DMDS. The THF conversion and resid conversion data overlap on a log plot showing a reasonable linear relationship. The target conversion of 90% coal is reached at about 11-12 minutes while the target resid conversion is reached at 22-23 minutes.

TASK 1.2 - LABORATORY SUPPORT (CONSOL)

Solvent qualities of four hydrotreated dewaxed distillate samples received this quarter from Sandia were higher than those of the respective feeds. Phenolic -OH determination by FTIR showed that hydrotreatment of the dewaxed distillate at

Sandia significantly reduced the concentration of phenolic -OH in the four samples.

Wilsonville personnel verified that no ash-SO₃ correction was applied to plant balances when low-rank coals were run. CONSOL will determine what ash-SO₃ adjustments are appropriate in the reported plant results from period 263J, which is used in the baseline economic assessment by LDP Associates.

Progress was made in obtaining samples for use as alternative feedstocks for this project. A sample of Illinois No. 6, Burning Star 2 coal received from HRI was prepared. However, the coal has an atypical analysis, and it will be replaced. We received the Martin Lake lignite sample we requested from TUMCO. We shipped deashed resid to Amoco in anticipated exchange for their supply of lignite oils from Wilsonville Run 255. We began determining the suitability of the Wilsonville Run 260 end-of-run inventory of V-1067 as a supply of Mo-free ashy recycle material for this project.

TASK 1.3 LABORATORY SUPPORT (SANDIA)

Laboratory support activities at Sandia included elemental carbon, hydrogen, nitrogen and sulfur determinations on solvent distillates which were hydrogenated with the combined water-gas shift reaction. Solvent characterization was also performed using proton NMR spectroscopy and microautoclave coal liquefaction experiments. Several sample exchanges took place this quarter.

TASK 2.1.1 CO PRETREATMENT (UK/CAER)

Since at low concentrations of NaOH the level of water-gas-shift reaction was comparable to that observed at higher base concentrations at both 250° and 300°C, the shift reaction apparently will proceed even after complete exhaustion of the NaOH in the reaction medium. Even as formation of the bicarbonate progresses during the course of the reaction as CO₂ is formed, the corresponding coal pretreatment reaction appears to continue

unabated. Experiments were run to test the activity of HCO_3^- , i.e., NaHCO_3 , relative to NaOH and Na_2CO_3 . At 0.33M NaHCO_3 , the level of THF conversion was the same as the Na_2CO_3 and slightly higher than for NaOH while the PA+A yields were all 30 ± 1 wt%. Also the WGS reaction and hydrogen consumption for these runs were about the same. This result suggests that the reaction can be run using the recycle stream obviating the need for large amounts of base.

The water insoluble products from the CO-pretreatment reaction were separated by pyridine extraction into soluble and insoluble materials. The pyridine solubles for the NaOH and Na_2CO_3 runs were 60 and 56 wt%, respectively. Elemental analysis indicated a significant decrease in the oxygen content of these fractions with more oxygen being present in the pyridine insolubles and more hydrogen being in the pyridine soluble fraction. The H/C ratios of the pyridine solubles were noticeably higher than for the insolubles. The H/C ratio of the pyridine soluble products are higher than for the coal while the reverse is true for the pyridine insoluble products.

TGA/MS analysis of the various water insoluble products were performed on the pretreated products. For the pretreated Black Thunder coal the magnitude of the volatile fractions was greater than for the raw coal based upon the total mass. The temperature of inflection in the weight loss curve, which corresponds to the temperature of maximum weight loss, was lower for the CO-pretreated Black Thunder coal than for the blank.

TASK 2.1.2.1 - PRETREATMENT WORK AT CONSOL - Dewaxing

Five hundred mL of oil produced by dewaxing V-1074 distillate at -35°C in 55/45 (vol %) acetone/MEK was sent to Sandia for hydrotreatment studies. A clean wax yield of 3.1 wt % MAF (slack wax yield of 3.5 to 4.0% MAF) was determined for the liquefaction of Black Thunder coal. Simulated distillation of the waxes separated from Wilsonville V-1074 oil at -5°C and -35°C in acetone gave an IBP of -350°C and a mid-point of -435°C .

Microautoclave tests were made in which Black Thunder coal was liquefied in simulated Wilsonville Run 262E recycle solvents containing dewaxed and hydrogenated-dewaxed V-1074 (the distillate recycle component). The purpose of these tests was to identify microautoclave conditions for evaluating solvent quality improvements. Conversions at 824 °F, 5 min, and 1.5:1 recycle:coal ratio are in the range of 90% MAF coal (SO₂-free ash basis). Therefore, these are suitable conditions to simulate Wilsonville coal conversion results. At these conditions, the combination of dewaxing and hydrogenation of the recycle distillate component results in a 4-5% increase in MAF coal conversion.

Task 2.1.2.2 - PRETREATMENT WORK AT CONSOL - Agglomeration

The objectives of oil agglomeration are to reject coal ash, to recover and dewater pretreated coal, to integrate agglomeration with CO-pretreatment, to disperse catalyst, and to reject resid ash within the framework of the liquefaction process.

The CO-pretreated coal received from CAER was agglomerated with Wilsonville recycle distillate in two runs made at 50 °C and 175 °C. The pretreated coal produced large agglomerates with a low oil dosage, but virtually no ash rejection took place. The products had 23 to 36 wt % moisture when surface-dried, but the moisture content decreased to 1 to 7 wt % after air drying overnight. We sent CAER the requested samples of agglomerate products and unused pretreated coal.

A new sample of Burning Star 2 coal (atypical, see Task 1.2), an existing sample of Martin Lake (Texas) lignite, and an existing sample of Spring Creek subbituminous coal were each agglomerated with No. 6 fuel oil at 50°C. Physical ash rejection was about 30 wt % with Burning Star 2 coal and about 25 wt % with Martin Lake lignite. Repeat runs will be made with replacement samples of both coals. Although we previously identified Spring Creek coal to be potentially cleanable by oil agglomeration, on the basis of its reported washability, results were poor. Large agglomerates were produced, but ash rejection was low, similar to that of Black Thunder coal.

Much of the work performed this quarter was focused on dewatering. We performed our part of a small cooperative project with Argonne National Laboratory to investigate dewatering effects of agglomeration of Beulah-Zap (North Dakota) lignite. Physical ash rejection with this coal ranged from 4 to 12 wt %, but ash rejection including dissolution was 71 to 77 wt % (tests at pH 1). Wet product agglomerates had moisture contents that ranged from 41.8 to 68.2 wt % moisture, but agglomerates air-dried overnight had 3.6 to 14.3 wt % moisture content, much lower than that of the feed coal (32.2 wt %). Three agglomeration runs were made with Black Thunder coal and No. 6 fuel oil to determine the degree of dewatering. No pore dewatering effect was evident, but coal moisture is not greatly increased by agglomeration, provided that surface moisture can readily drain away. Air-drying can reduce product moisture below that of the feed coal. A complete report is included as Appendix 2.

Column flotation tests were performed by Ames Lab on the Black Thunder coal. The coal showed poor cleanability, confirming our oil agglomeration experience. A report of their results is included as Appendix 3.

The reported particle size of the Black Thunder feed coal (95% -200 mesh) was confirmed by laboratory measurement using a laser diffraction method.

TASK 2.1.3 SOLVENT PRETREATMENT (SANDIA)

Solvent pretreatment work at Sandia involves the formation of hydrogen from an in situ water-gas shift reaction to concurrently hydrogenate a solvent in a trickle-bed reactor. Experiments conducted this quarter used dewaxed V1074 heavy distillate in the microflow reactor. The dewaxed distillate was prepared by CONSOL at -5°C using acetone as the dewaxing solvent. Experiments with a bulk NiMo hydrous titanium oxide (HTO) catalyst showed that hydrogen uptake by the distillate was equivalent to previous tests using NiMo/alumina supported catalysts. Samples taken after the reactor had lined-out showed that the hydrogenated solvent picked up approximately 0.5 wt% hydrogen and proton NMR analysis showed cyclic alpha and beta proton concentrations increasing from 36% to near 40% for most of the samples.

TASK 2.2.3 MODIFIED REACTOR CONCEPTS (SANDIA)

The goal of these experiments is to effectively manage solvent hydrogen in order to reduce first stage pressures during donor solvent initiated dissolution with an aim toward reducing first stage processing pressures. Several coal liquefaction tests were run this quarter using autogenic reaction conditions (300 psig nitrogen), and hydrogen pressurized conditions (800 psig hydrogen). These tests were used to evaluate the solvent quality of hydrotreated distillates produced with the in situ water-gas shift reaction. Wyodak subbituminous coal from the Argonne Premium Coal Sample Program was used. Several types of catalysts were tested in the hydrogen overpressure experiments. In general hydrogen overpressure enhanced coal conversions. Liquefaction experiments using hydrogenated distillates showed significantly improved coal conversions and oil yields.

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS (UK/CAER)

Since the level of drying can affect the structural features of a coal and result in an impact on the coal's performance in liquefaction, the overall preparation scheme of iron incipient wetness (IW) impregnated coals has been expanded to examine the effect of moisture. The variables that are being examined are the impregnating salt, the use of as-received coal and coal predried at 110°C/10 Torr/20 hours, the use of $\text{NH}_4\text{OH}/\text{Fe}$ ratios of 31 to 138, the final water washing of the coal, and final drying at 40°C/10 Torr/20 hours, 100°/10 Torr/20 hours, or in flowing N_2 at 40°C/20 hours. Both Fe^{+3} and Fe^{+2} salts in which the anion was varied between nitrate and sulfate were examined. Two samples also included Mo that was impregnated first with ammonium molybdate solution followed by impregnation with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution.

Results show that predrying the coal prior to impregnating the iron increased the surface iron concentration relative to the impregnated as-received coals. Likewise, predrying in nitrogen had a detrimental effect on reactivity of coal impregnated with 0.77 wt% iron. Final drying performed at 40°C at 10 Torr was the mildest form evaluated thus far. However, based upon processing

costs, air drying or drying at atmospheric pressure in an inert gas will be more feasible. Those studies are in progress.

The surface compositions of these various coals were evaluated by XPS. The concentration of Ca, Al, and Si, on the surface of the coal without any added Fe exceeded the bulk composition. This is related to grinding where the fracturing of the particle occurs along mineral rich planes. Typically as added iron increased in the IW-samples, the oxygen concentration on the surface increased while carbon decreased. In all cases the surface concentration of the iron exceeded the bulk concentrations. These highest Fe surface concentration (12.5%) was observed on one of the samples to which 1 wt% Fe had been added. Analysis of the bonding types on the surface for the $\text{Fe}_{2p\ 3/2}$ and the O_{1s} peaks indicate a major contribution from the FeOOH structure.

Liquefaction results are certainly less than definitive in tetralin in evaluating the effect of drying. Conversion appears to reach a conversion plateau of ~90%. The oil yields were most affected by the iron concentration. No effect of using ferric versus ferrous sulfate salts was observed which suggests that the less expensive ferrous sulfate may be suitable for this type of preparation. Overall, the sulfate salts appeared to give higher oil yield than the nitrate salts at the same Fe loading.

Although adding Mo did not affect THF conversion, oil yield increased from 43.0 wt% for the Fe-only sample to 50.5 wt% for a 1000 ppm Mo sample. A 500 ppm Mo sample falls between the value for 1000 ppm Mo sample and the Fe only sample. Work is underway to determine if the extremely low moisture levels, i.e., less than 3 wt% dry coal, in these samples had a detrimental effect on liquefaction performance.

TASK 2.3.3 CATALYST STUDIES (SANDIA)

A bulk nickel molybdenum hydrous titanium oxide (HTO) catalyst was formulated for testing with the dewaxed distillate. The catalyst had 9.8% molybdenum and 3.2% nickel. Post reaction analysis of the

catalyst showed that it had carbon deposition amounts which were similar to those which occurred with Shell 324M catalyst under similar conditions. Hence, similar amounts of catalyst deactivation are suspected.

TASK 2.4.2 - SOLIDS SEPARATION - CONSOL

Two approaches are being taken to deashing liquefaction bottoms (resid) by agglomeration. These are: 1) to use the resid as the hydrophobic solid (instead of or along with coal); and 2) to use the ashy resid as the agglomerating oil, and use dilution and high temperature to reduce oil viscosity to the desired level. The first approach produced substantial ash dissolution and a small amount of physical ash rejection, when used at conditions of low pH and room temperature with an appropriate oil.

The second approach has not resulted in resid deashing. Three pressure agglomeration runs were made with Black Thunder coal and ashy resid diluted with distillate at natural pH, pH 1, and pH 13 using resid only (no coal), so that resid deashing would be easily detected. Results ranged from no phase separation to 8 wt % physical ash rejection.

The particle size of finely-ground (ball-milled) ashy resid was found to be quite small (volume % D_{50} of 9 μm), though the extent of ash liberation is unknown. Examination of a sample of the THF-insoluble fraction of the ashy resid by SEM/EDX showed that there is a significant fraction of liberated mineral matter (quartz, calcite, pyrrhotite, 10 to 20 μm) in the insolubles.

We located sufficient material and began exploring the possibility of selectively rejecting ash from an ash concentrate material from Wilsonville. Some process benefits may result if this can be done.

Task 2.6.2 - Coker Overhead Characterization (CONSOL)

Summary

CONSOL's role in the fluid coker aspect of this project is to characterize the coker overheads, to determine if the coker results are consistent with prior, related work, and to use our experience to evaluate the potential of using the coker overhead as a component of the liquefaction recycle oil.

CONSOL characterized four coker overheads produced by CAER from the V-1082 ashy resid. The overheads were all produced at a relatively low coking temperature of 500°C, but at steam/resid ratios varying from 4.4 to 13. Tentative overhead yields increased from 43% to 53% with increasing steam/resid ratio. Other than differing in solids content, the overheads differ from the feedstock in that they are somewhat more aromatic and less paraffinic and they have slightly elevated oxygen-by-difference contents. As received by CONSOL, the overheads were quite wet. They contain some form of silicon that is not removed by filtration. Perhaps this is silicone grease contamination; it yields about 1% of a pure silica ash. The relatively minor difference between the compositions of the overheads and that of the feedstock indicate that the overheads were produced primarily through steam distillation and entrainment, and not primarily through pyrolysis. The calculated solvent quality indexes of the overheads and feedstock are similar. The steam/resid ratio had only a minor effect on overhead composition.

The characteristics of the coker overheads are consistent with coker overheads produced previously from liquefaction resids in the Lummus-Crest, Inc. continuous stirred coking unit, if the lower coker temperature employed by CAER is considered. The CAER tests were conducted at a lower temperature, but at much higher steam/feed ratios than the Lummus tests.

The characteristics of the coker overheads indicate that they should be suitable components of the liquefaction recycle oil. The "soluble" silicon and high moisture contents of the samples examined were unexpected. It should be determined if these overhead components are contaminants introduced during sample collection and handling.

Solubility fractionation analyses were conducted on the four overheads and on the feedstock. Solubility fractionation analyses show that the coker overheads have lower concentrations of preasphaltenes than the soluble portion of the feedstock; i.e., similar to the ROSE process, coking selects for hexane-soluble oils and against preasphaltenes in the product.

TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP ASSOCIATES)

Preparation of the baseline economic assessment, based on Wilsonville Run #263J, was completed during this quarter. This baseline will serve as the reference against which the results of this program will be compared. Investment costs for the process units and offsite units were determined on a mid-1992, Wyoming plant site basis. The cost of the process units were split into three groups; 39.8% for liquefaction, 38.6% for makeup hydrogen production and 21.6% for upgrading of the liquefaction distillate to gasoline. Total plant cost, the total capital required, and the annual operating costs were also determined. A discounted cash flow (DCF) economic analysis indicated that the required gasoline selling price (RGSP) is a strong function of the assumed DCF real rate of return. For example, at a DCF of 2.5%, the RGSP is 61.8% of the corresponding value at a DCF of 10%.

An improved coal conversion case (ICC) was the first alternative case selected for comparison with the above base case. The ICC case assumed overall coal conversion of 96.8% as compared with 93.6% coal conversion in the base case. This case had a lower total plant cost (approximately \$75 million) and lower operating cost (approximately \$8 million/yr) than the base case. At a DCF real rate of return of 10%, the RGSP for the ICC case was \$1.32/bbl less than the RGSP for the base case.

AMOCO is unable to perform microscale selective cat cracking tests for upgrading our slack wax under their existing DOE contract.

SECTION ONE

WORK PERFORMED

TASK 1.1 LABORATORY SUPPORT (UK/CAER)

The base case developed by M. Peluso defines the baseline conversion conditions for relating catalyst performance with Wilsonville Run 263J. In that run Wilsonville operated with addition of 1% Fe_2O_3 and 100 ppm Mo, as Molyvan L, to the feed to the 1st stage liquefaction unit. The plant was operating at an effective temperature of 840°F and a H_2 partial pressure of 2185 psig with total pressure of 3200 psig. The key performance factors were coal conversion of 93.6% and conversion of coal+resid+IOM+MAF of 24.6%. This corresponds to a 1050°F⁺ resid conversion across the first stage of the Wilsonville plant of 51 lbs per 100 lbs fresh dry coal feed.

The method of analysis is key to making a comparison of dissolution and product yields that compare with this base case. Since the material balance methods used at Wilsonville vary from those used in our laboratory, relating the laboratory conversion values to the base case is required. On a macro scale several key differences between methods used in our laboratory are in measurement of IOM and the determination of distillate yields. The total dissolution values at Wilsonville were based upon mixed cresol solubilities, which may be slightly higher than the THF measurements made on our reaction products. Likewise, for runs made in microautoclaves, distillate yields are not directly measured, and correlating solubility classes to distillate yield is also not straightforward in that the oil yield is a calculated value and is not directly measured in our workup scheme. This value includes pentane solubles plus any non-recoverable fractions, such as water, and any errors in measurement.

Method for Measurement of 1050°F⁻ Fraction

Since the base case relates to conversion of 1050°F⁺ resid in the feed, relating conversions in microautoclaves that are based upon solvent separation techniques to distillate is necessary. Previous work had shown that pentane solubles could be related to 1050°F⁻ distillate when operating in a non-catalytic mode.¹ The amount of pentane soluble product was correlated directly to the 1000°F⁻ product that was isolated by vacuum distillation (see Table 1 and Figure

1). In that study the stated endpoint was somewhat arbitrarily chosen since the method actually specified a final pressure of 1 torr or less. Since the boiling point based upon ASTM 1160 is dependent on pressure, by specifying a final pressure of 1 torr or less can result in widely differing final boiling points (see **Figure 2**). We are, however, examining the distillation of V131B materials and the composited WRO to determine those distillate fractions from which a method will be developed to determine 1050°F⁺ resid in our products.

A TGA method for measuring 1050°F⁺ residual material in the products from the microautoclave studies is being developed using a programmable DuPont 2000 TGA Analyzer which measures the weight loss as temperature is increased. A temperature, time, treatment sequence similar to that described in **Table 2** is being evaluated. In this test, THF is volatilized off of the sample at which time a reading is made. The next reading made at 375°C measures the amount of water and distillable material equivalent to the 1050°F⁻ distillate. The next measurement provides the amount of organic residue in the sample with the remaining being equal to the inorganic ash component. The method depends on getting an accurate weight of the reactor product that is being analyzed.

Using as a sample of V131B from Run 258K at Wilsonville, this material was distilled in our lab following the Wilsonville method in which 46.6 wt% distillate was found. This material was then used in the TGA to standardize the various measurement times. Results from runs in this TGA method gave the composition shown in **Table 3**. Representative TGA curves showing weight loss versus both time and temperature are shown for V131B from Run 258K at Wilsonville (**Figure 3**). The TGA of the Wilsonville Run 258K 1050°F⁻ distillate is shown in **Figure 4** where the cut point was selected to give complete vaporization of the distillate with an additional line out of about 5 minutes. The TGA of the Wilsonville Run 258K 1050°F⁺ residue is shown in **Figure 5**. This scan shows that the selected cut point at 700°F is not perfectly lined out but is continuing to diminish in weight. At that point the bottoms still contains a sizable amount of vaporizable material, i.e., 11.9 wt%.

Table 1

Comparison of Distillate Yield (by Distillation I,
Column Heated) with Oil Yield (by Solvent Separation)

Sample	Oil yield (wt %)	Distillate yield (wt %)
23-169	72.00 ^a	72.2
32-15,37	68.1 ^b	69.1
32-87,101	63.9 ^b	65.4 ^b
32-125,139	70.0 ^b	69.4
33-21,28	66.5 ^b	66.9
33-94,101,108	72.3 ^b	71.6 ^b
33-137,151	68.9 ^b	66.2 ^b
33-173,180,187	69.2 ^a	68.5 ^a
36-15,30	72.6 ^b	69.5
36-56,63	71.9 ^b	71.2
36-85,92	67.1 ^b	63.6
36-110,117	68.4	65.0
36-136	67.8	64.1

^aAverage of three determinations.

^bAverage of two determinations.

Figure 1

Solvent-Separated Oil Yield vs. Distillation I
(Heated Column) Distillate Yield

Figure 2

D1160 Boiling Point Correction

Table 2. CAER TGA Analysis method for 1050°F ⁻ Distillate ^a		
	Duration min	Elapsed Time min
Isothermal to load pan 3-10 mg	-	-
25-100°C @ 40°C/min	1.9	1.9
Hold 100°C	10.6	12.5
Make Reading 100°C	0	12.5
100°C to 375°C@40°C/min [375°C=707°F]	6.9	19.4
Hold at 375°C	9.4	28.8
Make Reading 375°C=707°F	0	28.8
375°C to 732°C@30°C/min- in Ar	12.0	40.8
Make Reading 707°C	0	40.8
O ₂ turned on at 732°C	0	40.8
Hold at 732°C	3.3	44.2
Make Final Reading 732°C	0	44.2
a. DuPont 2000 TGA Analyzer		

Table 3. TGA Analysis of Wilsonville Solvents (wt%)			
	1050°F ⁻ Distillate	1050°F ⁺ Residue	Ash
Run 258K V-131B	48.5	42.7	8.8
Run 258K V-131B 1050°F ⁻ Distillate	100		
Run 258K V-131B 1050°F ⁺ Residue	11.9	71.7	16.4

Figure 3
TGA of Wilsonville V131B Run 258K

Sample: V131B
Size: 44.1950 mg
Method: HRI METHOD EDITED
Comment: V131B

TGA

File: C:\ED.005
Operator: GT
Run Date: 11-May-93 08:34

Sample: V131B Run 258K
Size: 44.1950 mg
Method: HRI METHOD EDITED
Comment: V131B

TGA

File: C:\ED.005
Operator: GT
Run Date: 11-May-93 08:34

Figure 4
TGA Wilsonville Run 258K 1050°F Distillate

Sample: -1050 RESID
Size: 29.8090 mg
Method: HRI METHOD EDITED
Comment: CAL SPL

TGA

File: C:ED.011
Operator: GT
Run Date: 7-May-93 11:51

Sample: -1050 RESID RUN 258K
Size: 29.8090 mg
Method: HRI METHOD EDITED
Comment: CAL SPL

TGA

File: C:ED.011
Operator: GT
Run Date: 7-May-93 11:51

Figure 5
TGA Wilsonville Run 258K 1050°F+ Residue

For comparison, the standard Run 262 material components in the Wilsonville Recycle Oil used throughout this program were run in the TGA test. Those scans are shown below on both time and temperature scales. The 1050°F heavy distillate (V-1074) TGA is shown in Figure 6. This scan is very similar to the V-131B heavy distillate shown above in Figure 4 in that the scan lines out at 700°F for about 5 minutes before the reading is taken. The ash and residue was found to be 2.74% which was not determined by Wilsonville as shown in Table 4. The TGA of Wilsonville Run 262 V-1082 Ashy Resid is shown in Figure 7 where the reading point at 700°F has not lined out but is continuing to show volatilization of the sample. The reading at this cut point is 22.1 wt% which is considerably higher than the reported 2.5% in Table 4. The TGA of the Wilsonville Run 262 V-130 Deashed Resid is shown in Figure 8. The volatility in the TGA test was 32.8% versus the reported value of 16.0% for the 1050°F⁻ fraction in Table 4. These data suggest that the present technique needs revision in order to measure the distillate fraction in distillation bottoms. However, these results do not preclude its use for measuring the 1050°F⁻ distillate in recycle solvents. Additional distillations are in progress on the Run 262 WRO to more fully investigate the results that we have reported above.

Baseline Test

Several initial catalyst evaluations were made relative to the general baseline criteria that were discussed above. Tests were made of Black Thunder coal in Wilsonville recycle oil (WRO) which contains the Fe and the Mo added at Wilsonville during Run 262. Runs were made over a time span from 7 minutes up to 30 minutes and the THF conversions and resid conversions were measured. These resid conversions are based upon solvent separation results in which the quantity of oils in the 1050°F⁺ fractions are assumed to be unchanged by the process. Whether this assumption will hold will depend upon data that will be developed subsequently in this program.

Three different sets of runs were made. In the first runs, no added Fe or Mo was used which provides a measure of the effect of those metals already in the feed. These runs are shown as

Figure 6

TGA of Wilsonville Run 262 V-1074 1050°F Distillate

Sample: HD2 LOT 1
Size: 17.9670 mg
Method: HRI METHOD EDITED

TGA

File: C:ED.002
Operator: GT
Run Date: 23-Feb-93 14:49

Sample: HD2 LOT 1 Run 262
Size: 17.9670 mg
Method: HRI METHOD EDITED

TGA

File: C:ED.002
Operator: GT
Run Date: 23-Feb-93 14:49

Figure 7
TGA of Wilsonville Run 262 V-1082 Ashy Resid

Sample: ASHY RESID
 Size: 26.2210 mg
 Method: HRI METHOD EDITED

TGA

File: C:\ED.004
 Operator: GT
 Run Date: 23-Feb-93 17:58

Sample: ASHY RESID Run 262
 Size: 26.2210 mg
 Method: HRI METHOD EDITED

TGA

File: C:\ED.004
 Operator: GT
 Run Date: 23-Feb-93 17:58

Table 4

ANALYSES OF PRIMARY OIL SAMPLES
WILSONVILLE RUN 262, 9/16/91

stream	V-1074 heavy distillate	V-130 deashed resid	V-1082 ashy resid	V-131B recycle solvent	calcu- lated V-131B
fraction of recycle solvent blend, wt%	42.7	6.6	50.7	100.0	100.0
Composition, wt%					
solvent (~1050°F dist.)	N.D. (assume 100.0)	16.0	2.5	43.8	45.0
soluble resid (diff.)	N.D. (assume 0.0)	83.9	58.8	36.6	35.3
cresol insoluble organics	N.D. (assume 0.0)	0.01	18.3	19.6	9.3
ash	N.D. (assume 0.0)	0.11	20.4		10.4
analysis, wt%					
C	89.6	90.5	72.4	80.8	80.9
H	10.0	7.4	5.5	7.5	7.5
N	0.45	1.1	1.0	0.8	0.8
O (diff)	-0.1	0.8	-1.5	N.D.	-0.7
S	0.04	0.1	2.2	N.D.	1.1
ash	N.D. (assume 0.0)	0.11	20.4	N.D.	10.4

Note: Data supplied by C. Cantrell, letter to G.A. Robbins, Feb.21, 1992. N.D.= not determined. Assumed and calculated values supplied by CONSOL.

Figure 8

TGA of Wilsonville Run 262 V-130 Deashed Resid

Sample: DEASHED RESID
Size: 25.7200 mg
Method: HRI METHOD EDITED

TGA

File: C:ED.003
Operator: GT
Run Date: 23-Feb-93 16:37

Sample: DEASHED RESID Run 262
Size: 25.7200 mg
Method: HRI METHOD EDITED

TGA

File: C:ED.003
Operator: GT
Run Date: 23-Feb-93 16:37

WRO. Then runs were made in which 1% Fe_2O_3 and 100 ppm Mo in Molyvan L were added in the absence of any added sulfur. These data are referred to in the figures as Fe/Mo-WRO. Finally, runs were made using the same feed stream but with added sulfur to convert the Fe and Mo to the pyrrhotite and molybdenum disulfide forms, respectively.

THF conversions are shown in **Figure 9** where the 110-THF Conversions are plotted versus reaction time. The scale is based upon the maximum conversion observed previously in this coal-solvent system.³ These data show a reasonably linear relationship with the line falling below both the intercept at zero time and below the data at 30 minutes. The extent of reaction has proceeded essentially to completion after 15 minutes which causes this plot to diverge from linearity. We might note that the 90% conversion level on this curve falls at about 13.5-14 minutes. However, using only the 7 and 15 minute data would suggest this time would more likely be 11-12 minutes.

The unconverted resid plots shown in **Figure 10** shows a linear plot of this data from runs made between 7 and 30 minutes. The data from these runs show no distinction when they are separately plotted. However, a composite fit to the data shows an equally good fit with each of the three different systems performing equally well. The absence of any distinguishable effect of the added iron and Mo will be compared with those effects observed with adding other catalysts that have been used in this program.

Catalyst Testing

Shorter reaction times were investigated for evaluating catalyst performance in WRO. Most of the earlier work at 60 minutes failed to give any clearcut distinction between individual iron catalysts. To determine whether shorter times would give clearer distinction, both 15 and 30 minute runs were made. The run conditions were still those based upon the Wilsonville operation that have been reported previously. Base thermal runs were made using Black Thunder coal against which the performance of Wilsonville iron oxide (WIO) and Mach I superfine iron oxide (SFIO) was determined. The data are shown in **Table 5** where THF conversions were observed to go over 100% due to reactivity of the IOM in the feed ashy resid.

Figure 9

THF Conversion

30% BT Coal in Wilsonville Run 262 WRO

Figure 10

Unconverted Resid vs Time 30% BT Coal in Wilsonville Run 262 WRO

Table 5. Liquefaction of Black Thunder Coal in Wilsonville Recycle Oil ^a											
Reaction Time, min	15	15	15	30	30	30	60	60	60	60	60
Catalyst Added	none	WIO	SFIO	none	WIO	SFIO	none	WIO	SFIO	WIO	SFIO
Added Fe, wt% Coal	0	1.1	1.0	0	1.1	1.0	0	1.1	1.0	1.1	1.0
Added S, wt% dry Coal	0	1.5	1.5	0	1.5	1.5	0	1.6	1.6	1.6	1.6
S/Added Fe m/m	N/A	2.4	2.6	N/A	2.4	2.6	N/A	2.5	2.7		
Products, wt% maf Coal											
HC Gases	0.5	1.1	1.2	1.1	1.6	1.7	1.9	2.1	1.2		
CO + CO ₂	4.5	4.4	4.1	5.0	4.8	4.9	5.0	4.8	5.0		
Oils	21.3	20.8	29.7	36.4	36.0	45.1	51.3	53.8	56.7		
PA + A	57.6	58.1	54.4	56.2	59.3	52.6	48.4	45.3	45.0		
IOM	16.1	15.6	10.6	1.3	-1.7	-4.3	-6.6	-6.0	-7.9		
THF Conv	83.9	84.4	89.4	98.7	101.7	104.3	106.6	106.0	107.9		
Run Number	2148-2	2176-1	3074-2	2167-2	2169-1	3074-1	2139-1 2167-1 2337-1	2189-1 2142-2	2272-1		
a. 415°C, 3 g Black Thunder as-received coal, 21 wt% moisture, 5.4 g Wilsonville recycle oil, 1000 psig H ₂ cold.											

Comparison of the 15, 30 and 60 minute data show that for the thermal case and each of the catalysts the oil yields and THF conversions steadily increases over the period (See **Figure 11**). The oil yield went from slightly greater than 20 wt% up to a high of almost 57% for the 60 minute SFIO case, which indicates a significantly greater reaction rate for THF conversion in SFIO than when using the larger particle IO (iron oxide) used at Wilsonville. The data in this figure indicate that THF conversion has leveled out. A non-normalized log plot of 110-THF conversion is shown in **Figure 12**, where the 110 value is the apparent upper limit of coal conversion in this reaction system of Black Thunder coal in Run 262 recycle solvent. The lines shown in this plot use only the 15 and 30 minute data which gives a reasonably linear fit for three different cases that are shown. The lack of fit of the 60 minute data is quite significant, even though there continues to be a spread of the conversion with SFIO versus the blank run and WIO. The higher reaction rate, represented by the slope of these lines, for THF conversion in the presence of SFIO is quite apparent in this figure.

The oil yields taken over this 60 minute interval range between 51.3 and 56.7 wt%. A plot of 100 - oil yield on a maf basis on a log scale is shown in **Figure 13**. Although this is not a rigorous kinetic treatment of the data, it indicates that all of this data fail to follow first order kinetics since the 60 minute data are significantly displaced from the pattern indicated by the 15 and 30 minute data. The shorter residence time data show greater slope indicating the rates of oil formation in the presence of SFIO is higher versus the blank coal and IO. This conclusively proves that increased activity can be attained by reducing particle size of the catalyst to the nanometer size material.

This kind of spread in the data between these systems appears to provide the best type of comparison of these catalysts. Future evaluations will be done at shorter residence time to get a better measure of the relative catalytic activities of these candidates. In addition, more rigorous kinetic evaluations are being developed.

Figure 11

Liquefaction in WRO

Figure 12

Rate of Coal Conversion in WRO 415 C

Figure 13

Rate of Oil Formation in WRO 415 C

Task 1.3 LABORATORY SUPPORT

Laboratory support activities at Sandia included elemental carbon, hydrogen, nitrogen and sulfur determinations on distillate solvents which were hydrogenated with the combined water-gas shift reactor. Solvent characterization was also performed using proton NMR spectroscopy and microautoclave coal liquefaction experiments. Several sample exchanges took place this quarter.

Sample Exchanges

- Four samples were shipped to CONSOL in January (shown in Table 6). Samples 111903, 111907, and 121603 were to be tested for solvent quality while the composite sample was to be used for oil agglomeration experiments.

Table 6

Feed	Sample No.	Temp (°C)	WHSV (hr ⁻¹)	Pressure (psig)
-5°C Dewax	111903	325	0.78	1000
-5°C Dewax	111907	325	0.74	333
-5°C Dewax	121603	325	0.46	1000
-5°C Dewax	Composite	NA	NA	1000

In addition, several other sample exchanges took place.

- A composite sample of hydrogenated V1074 was shipped to CAER. The sample had 10.5% hydrogen (up from 9.9% in the original V1074). This sample will be used for testing the effect of hydrotreating the heavy distillate without dewaxing.
- A composite sample of coker overhead tar was received from CAER for hydrotreating tests.
- A 500 gram sample of V1074 heavy distillate which had been dewaxed with acetone/MEK was received from CONSOL.

TASK 2.1.1 CO PRETREATMENT (UK/CAER)

In the previous quarterly report the effect of low concentrations of NaOH on the low-temperature CO-pretreatment of coal was reported. Concentrations of 0.021 to 0.33 M NaOH were found to produce structurally modified coals. At these low concentrations of base, the level of water-gas-shift reaction was comparable to that observed at higher base concentrations at both 250° and 300°C. At 300°C and 800 psig CO and a ratio of CO/NaOH as high as 446/1, the WGS reaction was 41% which gives a CO turnover number of 161/1. Either the intermediate formic acid or the CO₂ formed in the reaction would rapidly consume the NaOH to produce Na₂CO₃ or the corresponding NaHCO₃. It therefore would likely be exhausted early in the reaction sequence. Since the shift reaction apparently proceeds even after formation of the bicarbonate, presumably the corresponding reactions involved in the coal pretreatment would also continue under these conditions. To test this apparent reactivity of the HCO₃⁻, a run was made with NaHCO₃ at 0.33 M to test reactivity relative to NaOH and Na₂CO₃. Data are shown in Table 7.

The level of THF conversion was the same as for the Na₂CO₃ case and slightly higher than for the NaOH case while the PA+A yields were all 30±1 wt%. Also the WGS reaction and hydrogen consumption for these runs were about the same. This result suggests that the CO-pretreatment reaction can be run using spent aqueous media rather than adding fresh base. The use of the aqueous recycle stream would certainly simplify the process and reduce the cost for chemicals.

Additional data on the characterization of the water insoluble products from the CO-pretreatment reaction became available during this period. The products from the large autoclave runs were separated by pyridine extraction into soluble and insoluble materials as shown in Table 8. The pyridine soluble products for the NaOH and Na₂CO₃ runs were 60 and 56 wt%, respectively. Elemental analysis of the fractions from the treatment indicate a significant decrease in the oxygen content of these fractions with more oxygen being present in the pyridine insolubles and more hydrogen being in the pyridine soluble fraction. The

Table 7. Effect of Na Salt on CO-Pretreatment of Wyodak Coal ^a			
Catalyst	NaOH	Na ₂ CO ₃	NaHCO ₃
Coal ^b	BT	BT	CP
THF Conv.	32.0	37.2	36.0
Product Distribution, wt% maf coal			
PA+A	29.0	29.5	31.1
Oils+Gas+Water	3.0	5.7	4.9
WGS Reaction ^c	45	47	51
H ₂ Consump, g/g maf coal ^d	20	22	24
Pyridine Solubles ^e	60	56	n.a. ^f
a. Conditions: 800 psig CO with 5.5 ml of 0.33M Na salt solution, 300°C, 1 hr. b. BT is Black Thunder Wyodak coal; CP is Clovis Point Wyodak coal. c. $WGS\ Conv(\%) = ([CO_{in}] - [CO_{out}]) / [CO_{in}]$ d. $H_2\ Consump\ (mg/g\ maf\ coal) = [H_2(\text{from WGS})] - [H_2(\text{final})]$ e. Wt% of water-insoluble product. f. n.a. not available			

Table 8. Characterization of Water Insoluble Product from CO-Pretreated Coal ^a					
	Na ₂ CO ₃		NaOH		Coal
	Pyridine Insoluble	Pyridine Soluble	Pyridine Insoluble	Pyridine Soluble	
Yield	44	56	40	60	
Elemental Analysis					
Carbon	77.8	80.6	78.9	80.7	73.9
Hydrogen	5.0	5.7	5.2	6.0	5.2
Nitrogen	2.1	2.2	2.0	2.1	1.3
Sulfur	0.6	0.4	0.7	0.4	0.6
Oxygen	14.5	11.1	13.2	11.5	19.0
H/C mol ratio	0.77	0.85	0.78	0.89	0.84
a. Wt% maf coal					

H/C ratios of the pyridine solubles were noticeably higher than for the insolubles. The H/C ratio of the pyridine soluble products are higher than for the coal while the reverse is true for the pyridine insoluble products.

XPS analysis of the NaOH and Na₂CO₃ treated samples were compared with raw coal. Data are shown in Table 9. The XPS band positions of the pretreated coal samples are shown in Table 10. Surface oxygen for the pretreated coal samples is diminished compared to oxygen in the bulk samples (see Table 21). The surface concentrations of aluminum and silicon also decreased relative to the starting coal. Sodium, however, which was contained in the reaction system, increased in both of the products relative to starting coal. The presence of sodium suggests that additional analyses will be necessary to determine the actual amount of sodium being incorporated into the product.

TGA/MS analysis of the various water insoluble products were performed to determine the thermal characteristics of the materials and the composition of the lower molecular weight materials in the volatile fraction. These results are shown in Table 11. For the treated Black Thunder coal the magnitude of the volatile fraction was greater than for the raw coal. These numbers, based upon the dry coal, represent the volatility of the total mass including the ash content. To relate the numbers for the CO-pretreated coal back to the raw coal these values would be multiplied by a factor of about 1.2, which is equal to $1/[\text{yield water insoluble product} \times (1 - \text{wt fraction ash})]$. The temperature of inflection in the weight loss curve, which corresponds to the temperature of maximum weight loss, was lower for the CO-pretreated Black Thunder coal than for the blank. This was, however, not true for the Clovis Point coal where the numbers were close together.

The mass spectra of the materials that were emitted during the devolatilization were followed during the TGA scans. Water, hydrogen, CO, CO₂, and methane were the most prominent peaks. The maxima for methane appeared typically around 505-515°C for the CO-pretreated Black Thunder coal versus 521°C for the untreated coal. For Clovis Point

Table 9. XPS Analysis of CO-Pretreated Coal ^a			
	Black Thunder Coal	NaOH	Na ₂ CO ₃
Elemental Composition, at %			
Carbon	78.5	84.6	83.1
Oxygen	17.0	13.7	14.1
Nitrogen	1.2	0.9	1.0
Iron	0.1	-	-
Calcium	0.2	0.3	0.2
Aluminum	1.0	0.6	0.4
Silicon	1.9	1.0	0.9
Sulfur	0.1	0.3	0.1
Sodium	-	0.2	0.2
a. Pretreatment at 310°C, 1 hour, 800 psig CO.			

Table 10. XPS Band Positions of CO-Pretreated Coals			
	Sample Description		Comment
	NaOH (eV)	Na ₂ CO ₃ (eV)	
C _{1s}	286.8	286.7	$\Delta = 286.7 - 284.6 = 2.1 \text{ eV}$
O _{1s}	532.1	532.3	
N _{1s}	398.8	399.9	
Ca _{2p}	347.0 350.7	347.1 350.3	CaCO ₃
Al _{2p}	73.4	73.4	
Si _{2p}	102.3	102.4	
S _{2p}	163.3 167.8	163.4 167.9	
Na _{1s}	1071.5 ^a 1072.4	1071.8	
a. Predominant peak.			

coal methane appeared at 540°C for both treated and untreated coals. Carbon dioxide peaked around 450°C for both of these coals and the CO-treated water-insoluble coals. Although the sodium salts are isolated in the aqueous layer and not in the water-insoluble product, the CO₂ peak could not be due to decomposition of any residual Na₂CO₃ that might be in this product since it occurs at about 800°C. However, the corresponding statement cannot be made about the decomposition temperature for HCOONa, which was not determined at this point. At any rate, based on the high solubility of these sodium salts and the presumed partitioning into the aqueous phase, the loss of CO₂ and the corresponding loss in CO, was attributed to the organic function of the coal and not to the decomposition of any significant amount of Na₂CO₃, HCOONa, or NaHCO₃ present in the water insoluble product. The magnitude of the loss of CO+CO₂ has not been completely determined at this point.

Liquefaction of CO-Pretreated Coals

The results from liquefaction of CO-pretreated coals that were catalyzed by NaOH and Na₂CO₃ are shown in Table 12. Comparison is made with untreated as-received coal. The conversion of the pretreated coal at 400°C, 1:1 tetralin:coal, 1 hour at 800 psig H₂ (cold) is higher than for the untreated coal. Based upon the ~90 wt% yield of water insoluble product from pretreatment of the starting coal this increase in conversion would be further magnified. This would be an advantage of performing pretreatment on the starting coal.

The effect of catalysts on the liquefaction of the pretreated coal is shown in Table 13. Again the higher conversions indicated an advantage for the CO-pretreated material and, when calculated based upon the ~90 wt% yield of water insoluble product, the yields are even more notable. Oil yields are also significantly higher for the CO-pretreated material which, when considered in light of the lower oxygen content in the pretreated coal, should be richer in hydrocarbon product. Likewise the lower gas yield from the CO-pretreated coal indicates the sizable drop in the yield of CO+CO₂.

Table 11. Volatility of CO-Pretreated Coals^a

Coal	Base		°C	CO psig	Volatility		Run No.
	Conc, M	cc			wt%	Max °C	
Black Thunder							
Blank	-	-	-	-	42.7	440	-
2 g ^b	0.33M NaOH	6	250	800	47.0	442	J119
100 g	0.38M NaOH	200	310	800	49.1	431	Run 1&2
2 g	0.33M NaHCO ₃	6	300	800	44.1	432	J183
Clovis Point							
Blank	-	-	-	-	45.5	438	-
2 g	0.33M NaOH	6	300	200	44.0	445	J120
2 g	0.33M NaOH	6	300	800	43	439	J83/84
2 g	0.14 wt% Fe ^c	6	300	800	46.5	443	J137

a. TGA program: 25 to 120°C at 10°C/min, hold 15 min, 120 to 900°C at 10°C/min, hold 1 min. Volatility = $100 \times (\text{wt}_{25 \text{ min}} - \text{wt}_{103 \text{ min}}) / \text{wt}_{25 \text{ min}}$ which corresponds to a cutoff at 930°C.

b. Dry basis

c. Added iron by IW method.

Table 12. Liquefaction of Base Promoted CO-Pretreated Coal^a

	Na ₂ CO ₃	NaOH	Untreated
THF Conversion, wt% maf coal	80.4	82.6	74.7
Product Distribution, wt% maf coal			
PA+A	53.4	50.6	43.9
Oil+water	24.3	30.0	26.1
Gases	2.7	2.0	4.7
H ₂ Consump, mg/g maf coal	17.8	18.6	21.4
Total H ₂ Consump, mg/g maf coal ^b	27.3	27.1	34.2

a. 400°C, 2 g dry coal/2 g tetralin, 1 hr, 800 psig H₂ (cold), 25 ml reactor.

b. Includes hydrogen from tetralin solvent.

Table 13. Catalyzed Liquefaction of CO-Pretreated Coal				
	Pretreated Coal ^a		Untreated Coal	
	Shell 324 ^b	Nanocat ^c	Shell 324 ^b	Nanocat ^c
Added Fe, wt% dry coal	-	1.0	-	1.0
Added Mo, wt% dry coal	0.1	-	0.1	-
THF Conv, wt% maf coal	84	86	83	81
Product Distribution, wt% maf coal				
PA + A	43	52	49	50
Oils + Water	39	32	29	25
Gases	2	2	5	6
Total H ₂ Consump, mg/g maf coal ^d	31	29	34	34
a. Pretreated coal prepared in 1-liter autoclave with 0.19M Na ₂ CO ₃ (3.7 wt% maf coal), 800 psig CO, 310±5°C. b. NiMo/alumina (2.8 wt% Ni, 12.4 wt% Mo) ground to -100 mesh; dimethyldisulfide added to provide a S/added metal(s)(mol/mol) ratio of 2. c. 63 wt% Fe. d. Includes hydrogen from tetralin solvent.				

TASK 2.1.3 SOLVENT PRETREATMENT (SANDIA)

Solvent pretreatment work at Sandia involves the formation of hydrogen from an in situ water-gas shift reaction to concurrently hydrogenate a solvent in a trickle-bed reactor. Experiments conducted last quarter used dewaxed V1074 heavy distillate in the microflow reactor. The dewaxed distillate was prepared by CONSOL at -5°C using acetone as the dewaxing solvent. The elemental analysis of the hydrogenated products and others were reported in the Sept.-Dec. 1992 quarterly report.

Coated NiMo HTO Catalyst Tests

Table 14 presents the proton NMR results which were acquired this quarter along with other process data for a few of the solvents hydrogenated in December using the coated NiMo hydrous titanium oxide (HTO) catalyst. The catalyst used in these tests was a thick-film hydrous titanium oxide coated onto an alumina substrate and had 8.1% molybdenum and 2.7% nickel as the active metals.

Table 14 Proton Distribution for Hydrogenated Solvents (%) Coated NiMo HTO
Selected Results

SAMPLE	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	H (wt%)	WHSV (hr ⁻¹)
-5°C * Dewax	16.5	5.1	18.4	9.2	17.4	21.3	12.1	8.6	NA
-5°C Dewax	16.0	6.0	18.5	8.7	17.8	21.9	11.2	8.6	NA
121503	9.8	6.0	19.5	9.3	20.5	22.4	12.5	9.4	0.37
121602	11.3	5.9	18.3	8.9	20.6	22.8	12.1	9.6	0.45
121604	11.0	7.5	20.4	9.2	18.9	21.1	12.0	9.0	0.96

* NMR result from CONSOL

Line one of **Table 14** shows the proton NMR results for the -5 °C dewaxed V1074 heavy distillate which were determined by CONSOL. All other NMR results in **Table 14** were determined by Sandia. Proton assignments were the same as those prescribed by CONSOL.²

In general hydrogenation with the water-gas shift reaction resulted in decreased condensed aromatic protons and increased cyclic alpha and cyclic beta protons. Sample 121503 was a sample taken early in the run and was extensively hydrogenated at 300 °C owing to the high activity of the fresh catalyst. Samples 121602 and 121604 were hydrogenated at 325 °C. Sample 121604 was also used as a liquefaction solvent for microautoclave tests using Wyodak coal (reported in section 2.2.3).

Bulk NiMo HTO Tests

Solvent pretreatment reactions this quarter were performed using a bulk NiMo HTO (9.8% molybdenum and 3.2% nickel) catalyst to hydrogenate dewaxed V1074 heavy distillate. As in the past, hydrotreatment took place in a series of experiments performed over three days. The third day was used to test the effects of using hydrogen instead of the water-gas shift reaction for hydrogenation. On this day the gas phase of the reactor was adjusted to 1000 psig H₂, 670 psig H₂, and 330 psig H₂ (system pressure was kept at 1000 psig; nitrogen was added to adjust the hydrogen partial pressure). Proton NMR results and elemental analyses of the products from the hydrotreating reactions are shown in **Table 15**.

Again, hydrogenation with the water-gas shift reaction resulted in decreased condensed aromatic protons and increased cyclic alpha and cyclic beta protons. Samples 20302 and 20303 were hydrogenated at 300 °C using the water-gas shift reaction. These samples showed that the condensed aromatic concentration was reduced from 16% to 7.7% and 9.5% respectively. Samples 20403, 20405, and 20407 were hydrogenated at 325 °C. These samples show an increase in hydrogen content of about 0.5wt% and a decrease in condensed aromatic hydrogen from 16% to about 12%. The second day (samples labeled with prefix 0204) showed that the catalyst had deactivated somewhat compared to the previous day but had also lined-out during the second day as evidenced by samples 020405 and 020407 which

were sampled at two hours apart. Hydroaromatic hydrogen concentration (cyclic alpha + cyclic beta) increased from 36% to nearly 40% for most of the samples.

Table 15 Proton Distribution for Hydrogenated Solvents (%) Bulk NiMo HTO Results

SAMPLE	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	H (wt%)	WHSV (hr ⁻¹)
-5°C Dewax	16.0	6.0	18.5	8.7	17.8	21.9	11.2	8.6	NA
20302	7.7	5.3	17.1	8.9	23.2	24.5	13.3	9.6	0.28
20303	9.5	5.3	18.7	9.3	21.5	23.4	12.4	9.2	0.27
20403	10.3	5.4	18.8	9.2	20.8	22.9	12.6	9.1	0.72
20405	12.9	5.6	19.0	8.9	20.4	21.8	11.4	9.1	0.78
20407	12.5	5.1	19.3	9.5	19.6	22.1	11.9	8.8	0.78
20502 ^A	11.3	5.4	19.5	9.5	20.0	22.3	12.0	8.9	0.75
20506 ^B	14.0	5.2	20.3	9.2	19.1	21.2	10.9	8.3	0.72

A) 1000 psig hydrogen only

B) 330 psig hydrogen in nitrogen

TASK 2.2.3 MODIFIED REACTOR CONCEPTS (SANDIA)

The goal of these experiments is to effectively manage solvent hydrogen in order to reduce first stage pressures during donor solvent initiated dissolution with an aim toward reducing first stage processing pressures.

Several coal liquefaction tests were run in stainless steel microautoclaves this quarter using autogenic reaction conditions (300 psig nitrogen), and hydrogen pressurized conditions (800 psig hydrogen). These tests were used to evaluate the solvent quality of hydrotreated distillates produced with the in situ water-gas shift reaction. Wyodak subbituminous coal

Coal conversion is equal to (100-%IOM). Time at temperature was 30 minutes. Corrections were made for pentane insoluble material in starting solvents. Catalyst code: FeS₂ is iron pyrite, SFIO is Superfine Iron Oxide from MACH I Inc., and Shell is Shell 324M sulfided catalyst.

Nitrogen gas phase tests - Table 16 shows that at 400°C under nitrogen, coal conversion was 68% for the unhydrogenated and the hydrogenated solvents. Oil yield was negative for the unhydrogenated solvent and 19% for the hydrogenated solvent. At 425°C the coal conversion increased to 81% for the hydrogenated solvent and to 75% for the unhydrogenated solvent. When unhydrogenated dewaxed distillate was used, the net oil yield was a large negative number (-36%) indicating that the distillate was consumed to form pentane insoluble material. These results show that using nitrogen overpressure at 425°C with the unhydrogenated dewaxed feed yields lower coal conversion with an appreciable amount of retrogressive reaction leading to asphaltene formation. In summary, results from the nitrogen overpressure tests show that the dewaxed feed is a poorer hydrogen donor than the hydrogenated solvent and that the hydrogen deficiency of the unhydrogenated solvent becomes more significant at 425°C.

Hydrogen gas phase tests - The bottom portion of Table 16 shows the results from the hydrogen overpressure tests using the unhydrogenated and hydrogenated dewaxed solvent. Results from thermal and catalytic tests are shown. The catalytic tests used FeS₂, Superfine Iron Oxide (SFIO) and Shell 324M as catalysts at 7 wt% catalyst to coal loading.

Unhydrogenated Dewaxed Distillate - Product distributions for experiments using dewaxed distillate (without hydrotreating) indicate that yields of pentane soluble material are negative at the more severe temperature (425°C). During the initial stage of liquefaction the unhydrogenated solvent does not have the available donor hydrogen to prevent retrogressive reactions from occurring. In addition to negative oil yields, coal conversions are somewhat lower using the non-hydrotreated dewaxed solvent rather than the hydrotreated dewaxed distillate.

from the Argonne Premium Coal Sample Program was used. Several types of catalysts were tested in the hydrogen overpressure experiments. Products from the microautoclave experiments were characterized using solvent separation techniques. Insoluble organic matter (IOM) is the THF insoluble portion of the product minus the mineral matter, the PA+A is the THF soluble-pentane insoluble fraction, gases were determined by GC analysis and the oils are determined by difference. Results from the liquefaction tests are presented in Table 16. Table 16 includes results from experiments using the hydrotreated dewaxed distillate (121604, 0.4% added hydrogen).

Table 16 Product Yield (%dmmf) for Microautoclave Tests with Wyodak Coal

Solvent Used in Test	Cat	Solv to Coal	Press, psig	Gas	Temp °C	% IOM	% PA+ A	% Oils	% Gases	% Conv.
121604	none	2:1	300	N ₂	400	32	44	19	5	68
-5°C dewax	none	2:1	300	N ₂	400	32	69	-8	5	68
121604	none	2:1	300	N ₂	425	19	63	10	3	81
-5°C dewax	none	2:1	300	N ₂	425	25	99	-36	12	75
-5°C dewax	none	2:1	1000	H ₂	425	17	86	-15	12	83
-5°C dewax	FeS ₂	2:1	1000	H ₂	425	20	89	-18	9	80
-5°C dewax	SFIO	2:1	1000	H ₂	425	26	105	-44	13	74
-5°C dewax	Shell	2:1	1000	H ₂	425	19	89	-20	12	81
121604	none	2:1	1000	H ₂	425	5	68	22	5	95
121604	FeS ₂	2:1	1000	H ₂	425	7	67	21	5	93
121604	SFIO	2:1	1000	H ₂	425	4	73	16	8	96
121604	Shell	2:1	1000	H ₂	425	4	60	30	12	96

Hydrogenated Dewaxed Distillate - The most notable result from these tests is that coal conversion was >90% for experiments using hydrotreated distillate under a hydrogen atmosphere. Clearly the hydrogen atmosphere enhanced coal conversion. In addition the Shell 324M proved to be the most effective catalyst for oil formation from coal. These results indicate that the donor solvent is even more effective under a hydrogen atmosphere. Hydrogen consumption data will be determined in order to design future experiments which substitute synthesis gas for hydrogen in order to test the effect of this atmosphere on oil yield and coal conversion.

Proton NMR Studies of Liquefaction Product Oils

In the effort to evaluate the effects of using low pressure nitrogen instead of high pressure hydrogen for coal dissolution, pentane soluble oils were collected from the microautoclave products described in **Table 16** and submitted for proton NMR analysis. The results from these analyses are presented in **Table 17** and show the effects of prior solvent hydrogenation, liquefaction temperature and the effect of using hydrogen or nitrogen for the liquefaction experiment.

Nitrogen Overpressure Tests

Tests using nitrogen overpressure (12902,12904,12901) show that condensed aromatics increase in the product oil from the liquefaction tests and that the increase in condensed aromatic content is more pronounced at higher temperatures. A concomitant decrease in hydroaromatic hydrogen is shown in the cyclic alpha and cyclic beta proton concentrations. When the hydrotreated solvent is used with nitrogen overpressure at 400°C (12901), the final concentration of condensed aromatic hydrogen is lower than the experiment conducted with the unhydrogenated solvent (12902). This may indicate that under mild liquefaction conditions the hydrotreated solvent may not be completely depleted of donor hydrogen.

Table 17. Proton Distribution for Solvents Recovered from Microautoclave Experiments (%)

SAMPLE	Sample Description	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
-5°C	Dewaxed Solvent	16.0	6.0	18.5	8.7	17.8	21.9	11.2
12902	N2 400°C	21.7	2.1	17.3	8.2	15.8	23.0	12.0
12904	N2 425°C	23.2	3.0	17.8	8.6	14.1	22.0	11.2

SAMPLE	Sample Description	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
121604	Hyd. Dewaxed	11.0	7.5	20.4	9.2	18.9	21.1	12.0
12901	N2 400°C	17.6	6.0	16.9	8.4	16.9	22.4	11.9
20101	H2 425°C	21.5	2.9	20.1	8.9	15.7	20.9	10.0
20104	H2 425°C, Catalyst	21.3	6.2	17.0	8.5	15.0	21.2	10.8

Hydrogen Overpressure Tests

Product oils from experiments which used hydrogen overpressure (20101,20104) show that at 425°C the condensed aromatic hydrogen concentration almost doubles. This indicates that, at 425°C a considerable amount of hydrogen has been transferred from the solvent. In addition, the uncondensed aromatic hydrogen is enriched (20104 VS 20101) in the product oil from the catalyzed liquefaction experiment. The increase in uncondensed aromatic hydrogen could be due to catalytic cracking of hydroaromatic compounds in the solvent since the concentration of hydroaromatic protons is lower than the equivalent proton classification in the products from the uncatalyzed experiment.

Conclusions

In general, hydrogen overpressure yields higher coal solubility at similar reaction severity with this solvent. Hydrotreating the dewaxed solvent appears to increase the solvent quality and presumably will enhance liquefaction processing and yield structure. Savings in capital costs for lower pressure operation would have to be weighed against operability concerns when solvent hydrogen is limited by solvent makeup or reactor configuration.

Solvent Upgrading Using In Situ WGS Reaction

Solvent pretreatment experiments to produce a high quality donor solvent also provide an opportunity to evaluate solvent upgrading potential using synthesis gas as the source of hydrogen. Table 18 presents results of nitrogen and sulfur analyses for the hydrotreated samples from the trickle bed reactor. Since sulfur is present in such low amounts and since it is also easier to remove than nitrogen the following discussion will concentrate on nitrogen removal only.

Sample 020403 shows 45% removal of nitrogen at 325 °C with a WHSV of 0.4 hr⁻¹. The lined-out nitrogen removal using the water-gas shift reaction at a WHSV of 0.8 hr⁻¹ and 325 °C was 17%. When the reaction gas was changed to hydrogen only on the third day (samples 020502, 020504, and 020506) the amount of nitrogen removed increased at similar space velocities. Nitrogen removal at 1000 psig and 670 psig hydrogen was 28% and 23% respectively. The estimated hydrogen partial pressure from the combined water-gas shift solvent hydrogenation experiment with "near equilibrium" conversions of carbon monoxide is approximately 670 psig (2/3 of system pressure) since the reaction at completion would be:

Carbon monoxide conversion was greater than 95% for all experiments involving synthesis gas.

Table 18 Nitrogen and sulfur removal with synthesis gas and steam

Sample	WHSV (hr⁻¹)	Temperature (°C)	Nitrogen (ppm)	Sulfur (ppm)
5°C dewax	NA	NA	6400	490
20302	0.28	300	1120	140
20303	0.27	300	2900	140
20403	0.38	325	3500	120
20405	0.72	325	4380	110
20406	0.82	325	5240	120
20407	0.78	325	5330	120
20502*	0.75	325	4600	160
20504*	0.83	325	4900	130
20506*	0.72	325	5200	120

* Hydrogen only (No WGS reaction)

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS (UK/CAER)

Iron Impregnated Coal by Incipient Wetness

Our research activities in this area were introduced in the previous quarterly report.³

Experiments were designed to evaluate the effect of the preparation scheme outlined in **Figure 14** on the dispersion of metal onto the coal and the liquefaction of the resulting material.

Additional variables that have since been identified require expansion of the investigation.

Following is an update on the thinking regarding the preparation of IW-impregnated coals and their performance in liquefaction.

Moisture Content of Coal - Several investigations have shown that the level of drying can affect the structural features of a coal and result in an impact on the coal's performance in liquefaction. Vorres recently found that drying proceeds through two stages.⁴ For a low rank North Dakota lignite, the first stage accounts for about 85% of the moisture while the second stage accounts for the remaining 15%. Miknis, et al., observed a similar pattern using a Microwave drying technique for a Powder River Basin subbituminous coal. They reported that in this technique approximately 75% of the moisture was removed at coal temperatures of approximately 100°C. Additional moisture was removed only after the coal reached higher temperatures.⁵ The earlier work of Silver and Frazee had shown that removing more than 75% of the moisture actually had a detrimental effect on liquefaction resulting in a decrease in both conversion and 850°F distillate yield.⁶ Miknis, et al. speculated that moisture removed at temperatures above 100°C is "an integral part of the gel or pore structure of the coal.....(that).....results in possible disruption of part of the coal matrix enabling some retrograde reactions to take place that diminish the reactivity toward liquefaction."³ Because of this possibly detrimental effect on liquefaction, the revised preparation scheme in **Figure 15** has been expanded, in part, to include the additional variables resulting from removing less water from the IW coal samples. Also, the results of Silver and Frazee showed that drying Wyodak coal in air had no observable effect on liquefaction performance.⁴

Figure 14 Outline for Preparation of Fe IW-Impregnated Coal

The final drying step as originally outlined in Figure 15 involved one of three possible drying routines, either a final dry at 40°C/10 Torr, at 100°C/125 Torr, or at 40°C/flowing nitrogen/atmospheric pressure. This step is being expanded as noted in Figure 15 to examine procedures to get to levels of moisture in the product coal comparable to the original "as received" coal and moisture levels in which less than approximately 75% of the water in the "as received" coal has been removed. Lee, et al., prepared Fe-IW coals having moisture contents between 5-12 wt% by drying in flowing nitrogen.⁷ In our work we found during preparation of sample CH-13 that drying 19 grams of material in nitrogen flowing at 140 ml/min at 1 atm. at 40°C for 20 hours gave a product containing 9 wt% moisture.⁸ Therefore, drying in flowing nitrogen at a somewhat lower temperature should give the desired moisture levels. Comparable drying in air to get to these levels that are equal to or less than the moisture levels in the "as received" coal will also be evaluated. The latter is based upon the results of Silver and Frazee who found that drying in air at these low temperatures had no detrimental effect on the subsequent liquefaction reaction.⁴

Chemical Cost - Because of the considerable constraint on catalyst cost in the liquefaction process, it is evident that the costs that can be incurred for chemicals in preparation of the catalysts must be limited. In the original preparation scheme in Figure 14, the only option being evaluated for the deposition of iron on the coal was the formation of the insoluble FeOOH in the presence of ammonium hydroxide. The mole/mole ratios of $\text{NH}_4\text{OH}/\text{Fe}$ that were evaluated were 31 and 138. It is evident now that the amount of base must be restricted or preferentially eliminated in order to provide a reasonable cost for the application of these approaches. Therefore, we are evaluating lower levels of NH_4OH addition as well as examining the iron deposition when no base is used in the IW process. This will change the actual deposition step as well as the resulting chemistry of the metal on the surface, which will be evaluated by XPS.

Figure 15 Modified Preparation of Metal IW-Impregnated Coal

Characterization of Fe IW-Coals - A range of different samples were prepared to explore the variables outlined in **Figure 14**. The key to those preparations is shown in **Table 19**. The variables examined in these samples were the impregnating salt, the use of as-received coal and coal predried at 110°C/10 Torr/20 hrs, the use of $\text{NH}_4\text{OH}/\text{Fe}$ ratios of 31 to 138, the final water washing of the coal, and final dry at 40°C/10 Torr/20 hrs, 100°/10 Torr/20 hrs, or in flowing N_2 at 40°C/20 hrs. Both Fe^{+3} and Fe^{+2} salts, in which the anion was varied between nitrate and sulfate, were examined. Two samples containing Mo are also included that were impregnated first with ammonium molybdate solution followed by impregnation with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution.

One of the concerns in this preparation method is the amount of metal actually retained on the surface after the impregnation and subsequent washing step. In the previous report, the ion concentrations in the resulting filtrates were reported to be extremely small, indicating that all of the metals were being deposited on the coal. In this report, additional data are available which further confirm the essentially quantitative retention of the metals by the coal. The data in **Table 20** show that with $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ as the impregnating salt (CH-51), iron was retained and the removal of the sulfate was essentially quantitative.

The surface composition of these various coals was evaluated by XPS as shown in **Table 21**. The relative concentrations on the surface of carbon, oxygen, nitrogen, iron, calcium, aluminum, silicon and sulfur were determined. In a few samples containing vanadium, some magnesium was observed. However, magnesium was not detected in the other samples. In several of the cases, bulk compositions of the samples were available for comparison with the surface concentrations. In most cases the amount Ca, Al, Si, and Fe on the surface exceeded the bulk composition. As noted earlier, this also applies to the coal to which no iron has been added. This effect is related to the grinding process where the fracturing of the particle occurs along mineral rich planes. Usually as the iron in these materials increased, the amount of oxygen on the surface increased and carbon, the other major surface constituent, tended to decrease. The surface concentration of the iron on these samples always

Table 19 . IW-Impregnated Coal Samples

Sample ID	Fe, wt% ^a	Mo, wt% ^a	IW Salt ^b	Starting Coal ^c	NH ₄ OH/Fe ^d	Washing ^e	Final Dry ^f	Run No
CH-1	0.275		N	P	138	No	L	41-1
CH-1W	0.275		N	P	138	No	L	73-1
CH-2	0.275		N	P	138	No	H	325-1
CH-3	1.0		N	P	138	No	L	324-1
CH-4	1.0		N	P	138	Y/200 ml	L	
CH-6	0.77	0.1	N+AM	AR	138	No	L	62-1
CH-8	0.76		N	AR	31	No	L	324-2
CH-10	0.15		N	AR	138	No	L	15-3
CH-11	0.275		N	AR	138	No	L	22-1
CH-12	0.275		N	AR	138	No	L	7-1
CH-13	0.275		N	AR	138	No	N ₂	15-1
CH-15	1.0		N	AR	138	No	N ₂	
CH-20	0.55		N	AR	138	No	L	29-1
CH-21	0.55		N	AR	138	No	H	13-1
CH-22	0.55		N	AR	138	Y/200 ml	H	13-2
CH-31	0.77		N	AR	138	No	L	15-2
CH-41	1.0		N	AR	138	No	L	41-3
CH-45	1.0		N	AR	138	Y/500 ml	N ₂	43-1
CH-51	2.0		Fe(III)	AR	138	Y/500 ml	L	55-1
CH-52	0.77		Fe(II)	AR	138	Y/500 ml	L	69-1
CH-53	0.77		Fe(III)	AR	138	Y/500 ml	L	69-2
CH-61	0.71	0.05	N+AM	AR	138	No	L	73-2

^a wt% dry coal. ^b N=Fe(NO₃)₃·9H₂O; Fe(III) = Fe₂(SO₄)₃·5H₂O; Fe(II) = FeSO₄·7H₂O; N+AM = Fe(NO₃)₃·9H₂O/(NH₄)₂MoO₄. ^c AR = as received; P = predried at 110°C/20 hrs/40 Torr. ^d mol/mol. ^e Y = yes; ml water used. ^f L = 40°C/10 Torr/20 hrs; H = 115°C/10 Torr/20 hrs; N₂ = 140 ml/min, ambient pressure, 40°C, 20 hrs, 20 hrs.

Table 20. FILTRATE ANALYSIS BY DIRECT CURRENT PLASMA EMISSION SPECTROMETRY (DCP)

Coal Sample No.	NH ₄ OH Filtrate						Washwater Filtrate				
	CH-1	CH-3	CH-13	CH-15	CH-21	CH-51 ^c	CH-45	CH-22 ^a	CH-4 ^b	CH-51 ^c	CH-45
Dry coal, grams	20	15	15	15	15	-	-	8	4.08	-	-
Fe ⁺³ , wt% dry coal	0.275	1	0.275	1	0.55	2.04	1.0	0.55	1	2.04	1.0
Fe Added, grams	0.055	0.15	0.04125	0.15	0.0825	-	-	-	-	-	-
N added as NO ₃ , grams	0.0414	0.113	0.031	0.113	0.0621	0	-	0.00224	-	-	-
Ca in dry coal, grams	0.20	0.15	0.15	0.15	0.15	-	0.15	-	-	-	-
Washing	NO	NO	NO	NO	NO	NO	NO	YES	YES	YES	YES
Filtrate, g	77.6	188	73.9	242.8	144.7	229.6	257.4	195	166.5	517.5	493.7
Fe											
ppm	0.67	0.01	0.33	0.32	0.17	0.05	0.05	0.13	0.24	0.20	0.3
Recovery %	9.4	0.1	5.9	5.2	3.0	0.4	0.2	3.1	9.8	3.3	9.9
(× 10 ²)											
Nitrogen as NO ₃											
wt%	0.050	0.050	0.050	0.050	0.040	0.37 ^d	0.037	-	-	0.02 ^d	0.002
Recov %	94	83	119	108	93	108	85	-	-	14	10.6
Calcium											
ppm	1.5	0.86	1.56	0.88	1.24	2.6	0.7	0.17	0.31	0.2	0.3
Recovery, wt%	0.06	0.10	0.07	0.14	0.11	0.39	0.11	0.02	0.12	0.07	0.10

a. CH-22 originated from CH-21. b. CH-4 originated from CH-3 c. Fe added as the SO₄⁼. d. Sulfur as SO₄⁼

Table 21. Surface Concentration of Elements as Determined by XPS^{a,b}

As Received	Starting Coal ^c	Moisture wt%	Added Fe	Fe	C	O ^d	N	Ca	Al	Si	S
	-	22.4		(0.19)	(57.8)	(29.6)	(1.2)	(0.75)	(0.56)	(1.1)	(0.46)
CH-BT	AR	2.6	0	0.33	71.1 (70.3)	20.6 (17.8)	1.3 (1.2)	0.5	2.0	4.0	0.2 (0.5)
CH-10	AR	3.6	0.15	1.0	62.3	25.5	1.4	1.0	3.4	3.5	n.a. ^e
CH-11	AR	1.8	0.28	1.4	66.2	23.5	1.7	1.0	2.4	3.5	0.3
CH-13 ^f	AR	5.4	0.28	1.9	64.1	23.9	1.7	1.2	3.1	3.8	0.3
CH-1	PD	1.4	0.28	2.7	63.5 (67.4)	24.7 (19.4)	1.7 (1.5)	1.0	2.5	3.6	0.4 (0.4)
CH-1W	PD	2.7	0.28	2.0	63.1	25.3	1.7	1.0	3.2	3.7	n.a.
CH-2	PD	3.9	0.28	2.2	62.8	27.1	1.3	0.3	2.9	3.3	0.1
CH-20	AR	0	0.55	2.4	63.5	25.2	1.5	1.0	2.9	3.3	0.2
CH-8 ^g	AR	5.4	0.77	3.2	66.8 (68.1)	20.2 (19.2)	0.8 (1.8)	0.7	1.9	4.6	n.a. (0.4)
CH-31	AR	2.9	0.77	4.2	62.4	24.8	1.2	1.0	2.5	3.3	0.6
CH-41	AR	2.7	1.0	6.3	59.6	25.6	1.6	1.0	3.8	3.4	0.3
CH-3	PD	3.9	1.0	8.3	54.2 (65.4)	28.2 (21.2)	1.0 (1.6)	0.8	3.8	3.1	0.4 (0.5)
CH-45 ^f	AR	6.1	1.0	12.5	49.3	30.7	0.8	0.3	3.8	2.5	0.1
CH-51 ^h	AR	2.2	2.0	7.9	50.9	30.6	1.0	0.9	4.3	4.2	0.2
CH-52 ⁱ	AR	0	0.77	1.2	66.3	23.2	1.3	0.8	2.6	4.1	0.4
CH-53 ^h	AR	0	0.77	1.5	67.9	23.1	1.1	0.8	2.6	2.5	0.4
CH-6 ^{j,k}	AR	0.6	0.77	2.5 ^m	62.7	24.4	1.5	1.3	3.5	3.8	0.05
CH-61 ^{k,l}	AR	1.3	0.71	3.0 ⁿ	63.9	24.4	1.4	0.9	3.4	2.8	0.03

^a () Denotes bulk composition, wt% of sample. ^b Starting coal impregnated with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 0.74 ml water/g for as-received coal and 0.90 ml/g for predried coal, treated with 1.54M NH_4OH at 138 NH_4^+/Fe ratio, vacuum filtered, and dried at 40°C/10 Torr/20 hrs. ^c AR is as-received coal, PD is predried coal at 110°C/10 Torr/20 hrs. ^d Includes oxygen associated with moisture in sample. ^e n.a., not available. ^f Dried at 40°C/1 atm/flowing N_2 /20 hrs. ^g Washed with 1.54M NH_4OH at 31 NH_4^+/Fe ratio. ^h Used $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ as impregnating salt. ⁱ Used $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as impregnating salt. ^j Contains 1000 ppm Mo. ^k Impregnated first with $(\text{NH}_4)_2\text{MoO}_4$ solution followed by impregnation with the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. ^l Contains 500 ppm Mo. ^m Surface contains 0.163 wt% Mo. ⁿ Surface contains 0.195 wt% Mo.

exceeded the concentration of added iron in these samples. The surface concentration of Fe ranged up to 12.5%; this was observed in one of the samples to which 1 wt% Fe had been added.

A plot of the iron distributions on the surface of these samples versus the bulk concentrations of added iron is shown in **Figure 16**. A best fit of those samples that had been prepared starting with as-received coal and final dried at 40°C/10 Torr/20 hours are shown in the figure, with the greatest departure occurring at the 1 wt% Fe level. Although the fit is certainly not exceptional, the slope of the line indicates that the ratio of iron concentration on the surface is 4 fold greater than the bulk concentration. Quite a difference in surface and added Fe concentration was observed for coals that had been predried at 110°C prior to the addition of the metal. The surface iron concentrations for these samples were significantly higher than for the as-received samples both at the 0.28 and 1 wt% iron addition levels. Also, coals that were final dried in nitrogen at 40°C at 10 Torr also had very high surface concentrations relative to the as received prepared samples. Also note that the use of $\text{SO}_4^{=}$ results in a lower surface Fe concentration than nitrate (compare CH-52 and CH-53 with CH-8 and CH-31).

Coals prepared with Mo co-impregnated with the iron were also analyzed by the XPS (CH-6, CH-61). These samples, which contained 0.77 wt% Fe, had slightly lower surface iron concentrations than the Fe-only coals (CH-8, CH-31). Molybdenum concentrations observed at the 1000 and 500 ppm addition levels were 1600 and 2000 ppm, respectively. These addition levels appear to significantly affects the surface concentrations. However, at this time analysis of the filtrates from the ammonium hydroxide wash step have not been completed. Thus we cannot determine if the Mo remained on the coal surface during the wash step. This is of concern because of the significant solubility of the ammonium molybdate in water at these pH levels. The liquefaction results discussed above suggest that Mo must have been present because of their higher activities.

An analysis of the bonding types on the surface of these impregnated samples is shown in **Table 22**. The coal itself shows the $\text{Fe}_{2p\ 3/2}$ and the O_{1s} peaks correspond to a major

Figure 16

Surface Fe on Fe-IW-Impregnated Coals

Table 22. Binding Energies for Fe IW-Impregnated Coals and Reference Materials										
	Fe ev				O _{1s} ev	N _{1s} ev	Si _{2p} ev	Al _{2p} ev	Ca _{2p} ev	
	Fe _{2p} 3/2	Fe _{2p} 1/2	Fe _{3p}	Δ Fe _{2p} 1/2-Fe _{2p} 3/2					Ca _{2p} 3/2	Ca _{2p} 1/2
CH-BT	709.3	722.3	52.3	13.0	532.7	399.4	104.2	75.2	347.2	350.3
CH-10	711.6	725.5	56.7	13.9	532.6	399.9	104.0	75.2	347.3	350.8
CH-11	711.5	725.2	n.d.	13.7	532.4	399.1	104.9	75.4	347.5	350.7
CH-20	711.4	725.5	n.d.	14.1	532.4	399.9	104.6	75.6	347.8	350.8
CH-31	711.1	725.1	n.d.	14.0	531.7	399.1	103.8	75.0	346.2	351.0
CH-8	711.4	725.1	56.5	13.7	531.8	399.8	103.0	75.0	347.4	351.2
CH-41	711.2	725.1	n.d.	13.9	531.3	399.2	103.4	74.6	346.6	351.0
CH-4	711.2	724.7	56.6	13.5	531.3	399.4	103.6	74.5	347.3	350.8
CH-3	711.2	724.9	56.6	13.6	531.5	399.5	103.6	74.6	347.4	350.8
CH-1	711.6	725.5	n.d.	13.9	532.3	399.6	103.6	75.3	347.7	349.2
CH-2	711.3	725.3	56.0	14.0	531.6	399.5	103.6	75.5	348.2	350.9
CH-45	711.3	724.8	56.1	13.5	531.2	399.1	102.4	74.1	347.6	350.6
CH-13	711.3	725.0	56.4	13.7	532.2	399.5	103.6	75.0	347.4	349.9
α -FeOOH	711.0- 711.8		56.6 $\pm$ 0.2		530.1- 531.8					
α -Fe ₂ O ₃	710.8- 711.4		55.7 $\pm$ 0.15		529.8- 530.2					
FeO	706.9- 710.3		54.9 $\pm$ 0.3		529.8- 530.1					
Fe ₃ O ₄	708.3- 711.4		53.9 $\pm$ 0.2		530.0 $\pm$ 0.01					
SiO ₂					532.8		103.6			
Al ₂ O ₃					531.8			74.7		

contribution from the FeOOH structure. Whether this material is goethite or ferrihydrite, both of which are hydroxylated iron oxides, is at present unknown. The O_{1s} peak suggests that the Fe_2O_3 , Fe_3O_4 , and FeO structures are less important. In the case of no added Fe, or lesser amounts of added Fe up to about 0.55 wt%, the oxygen peak is shifted to higher energy, suggesting that a larger amount of the coal surface has remained free of Fe. At the higher concentrations sufficient iron is present to significantly coat the coal particle to reduce the participation of the organic and mineral oxygen in the peak position. A plot of the O_{1s} peak positions versus the added iron concentrations for the various impregnated coals is shown in **Figure 17**. The good correlation indicates higher binding energies at the lower loadings, in agreement with more exposed surface of the coal. Relative intensities of the 530.0 eV (Fe_2O_3), 531.8 eV (FeOOH), and 533.0 (other oxides) O_{1s} deconvoluted peaks have only been partially calculated for samples thus far analyzed, as shown in **Table 23**. The most striking result from these analyses is that the 531.8 eV component is out of line for the CH-2 sample which was both predried at 110°C and final dried at 110°C. The other samples were all predried at 110°C but final dried at the lower 40°C condition.

An analysis of the nitrogen bonding peak indicates that nitrogen is bound up as organic nitrogen in these samples. No evidence of nitrate was observed.

Liquefaction of Fe-IW Coals - In the following discussion, the status of the evaluation of these individual steps is updated based upon information gathered during this reporting period.

Effect of Moisture Content of Pre-Dried Coal - In the preparation scheme moisture removal can occur at two different points. In the first case, water is removed before the impregnation step while in the second water is removed in a final drying step. The first drying step is optional while the second must be performed in order to reduce the moisture to an acceptable level to feed into the liquefaction reactor. Both are being studied here. The effect of the initial moisture content on the liquefaction of the Black Thunder coal was determined in the following set of experiments. Coals having two different levels of initial

Figure 17

O(1s) Peak Position in Fe IW-Impregnated Coals

Table 23. Deconvoluted O _{1s} Peak Intensities				
	CH-1	CH-2	CH-8	CH-3
Added Fe, wt%	0.28	0.28	0.77	1.0
Predrying °C	110	110	-	110
Final Dry °C	40	110	40	40
Intensities %				
530.0 eV (Fe ₂ O ₃)	22.4	31.9	28.6	32.5
531.8 eV (FeOOH)	40.8	34.9	45.4	51.2
533.0 eV (other)	36.7	33.1	26.0	16.3
I _{531.8} /I _{530.0}	1.8	1.1	1.6	1.6

moisture were impregnated by the IW method. One was the starting Black Thunder coal having slightly more than 20 wt% moisture while the other was essentially a dry coal having 2-3 wt% moisture. Depending on the initial moisture content, the impregnation was done either with 0.9 ml water/g dry coal for the as received coal or 0.75 ml water/g dry coal. Each of the samples were then treated with NH₄OH at a 138 NH₄⁺/Fe mole/mole ratio and then allowed to drain and were then dried at 40°C/20 hours/10 Torr. Liquefaction results on these samples are shown in **Table 24**.

About 3 wt% moisture remained in the coal after the initial drying step. This is approximately 10 wt% of the moisture in the "as-received" coal. The moisture content of the samples after impregnation and treatment with the NH₄OH ranged from 1.2-3.2 wt% with the higher moisture levels corresponding to the higher iron content samples. Moisture content in the final samples corresponds to moisture removals of at least 88% of the original

conversion. Gases, however, appear to be unaffected by the predrying.

Effect of Final-Drying Conditions on Coal Liquefaction - Final drying is, of course, necessary to prepare a coal for injection into the dissolver stage. Any sizable amount of water present in the coal will reduce the hydrogen partial pressure and increase the heat load on the slurry preheater. Therefore, reduction of the moisture content is necessary. The effect of the conditions for the final dry was evaluated for both as-received coal as well as one predried at 110°C/20 hours/10 Torr prior to the impregnation step. The conditions that were evaluated for the final dry were (1) 40°C/20 hours in flowing nitrogen at one atmosphere, (2) 40°C/20 hours at 10 Torr and (3) 100-115°C/20 hours at 10 Torr. These results are shown in Table 25.

The THF conversions for each of the three levels of iron concentration (Table 25) increased with iron concentration. The values for the two 110°C/20 hrs/10 Torr predried samples (CH-2, CH-1) were clearly lower than for those samples starting with as-received coal. However, these differences of at least 2% may be related to the higher iron concentration in the as-received samples (0.275 wt% vs 0.55-1.0 wt%), instead of the final drying conditions used in the experiments. Therefore, we cannot interpret these conversion data as showing any bias regarding either pretreat or final treatment temperatures.

A different pattern is evident for the oil yields which are shown for each of the pairs of samples in Table 25. The oil yields in each of these pairs, namely, CH-21/CH-22 vs CH-2/CH-1 vs CH-41/CH-45, are directly related to the iron concentration. As with conversion, the higher Fe concentration resulted in higher oil yield. Further, within the pairs of samples comparing 100°C vs 40°C final dry, the lower temperature final dry gave higher oil yields by 3.2 to 4.1 wt%.

The sample dried in flowing nitrogen at 40°C/1 atm. (CH-45) gave higher oil yield than the corresponding sample dried at 40°C/10 Torr (CH-41). These oil yields suggest a detrimental effect of the higher temperature final dry and improvement from drying in flowing nitrogen.

The latter may be related to the fact that 23 wt% of the water in the coal was not removed in the drying process. As discussed above, this higher moisture level may not have had a significant effect on the liquefaction of the coal. In all these samples the hydrocarbon gases were nearly the same. However, the CO+CO₂ yield was higher for those samples subjected to the 100°C final drying.

Overall, the oil yield results indicate a detrimental effect of a higher temperature final dry on the IW coals. Likewise, removing only 75% of the moisture appears to give better oil yield than coals final dried to lower moisture levels. This indicates that even a milder final dry may be beneficial. The conversion data for these various final dry samples show no particular bias other than with regard to iron concentration.

Effect of NH₄⁺/Fe Ratio - The effect of NH₄⁺/Fe ratios of 31 and 138 indicated possibly higher conversion and higher oil yield at the lower ratios of NH₄⁺/Fe.⁹ These runs were made on as-received coal containing 0.77 wt% added Fe that was dried at 40°C/20 hrs/10 Torr. Another data point has since been obtained at an intermediate NH₄⁺/Fe ratio of 84 as shown in Table 26.

The data from Run 50-2 are consistent with the trends of the samples prepared at both lower and higher NH₄⁺/Fe ratios. The conversion for the new point lies between the other two data points indicating that the higher ratio must have some slight detrimental effect on the conversion. The oil yield data suggest that the lower NH₄⁺/Fe ratio favors higher conversion values, though the magnitude of the difference is quite small. The hydrocarbon gases agree for all three runs. However, the CO+CO₂ number for the new run is somewhat lower than for the other two. Whether this is significant is not known. Based upon the continued trend for better results at the lower ratios, additional comparisons at still lower iron ratios will be made to find out if still lower ratios would provide any additional improvement.

Table 24. Effect of Initial Moisture on Liquefaction of Fe IW-Impregnated BT Coal ^a				
Sample ID	CH-1	CH-11	CH-3	CH-41
Fe, wt% dry coal	0.275	0.275	1.0	1.0
Starting Coal ^b	P	AR	P	AR
Fe(NO ₃) ₃ soln, ml/g dry coal	0.90	0.75	0.90	0.75
S/Added Fe in Cat	1.4	3.2	1.3	1.2
Final IW Coal Moisture, wt%	1.4	1.8	3.9	2.7
Product, wt% maf coal ^c				
HC Gases	1.06	1.09	1.09	1.23
CO ₂ +CO	3.8	3.4	3.7	3.9
Oils	41.0	44.2	45.9	46.4
PA + A	38.7	38.5	39.2	37.9
IOM	15.4	12.9	10.1	10.6
THF Conv, wt% maf coal	84.6	87.1	89.9	89.4
H ₂ Consump. mg/g maf coal	35.4	38.8	44.4	39.9
Run Number	41-1	22-1	324-1	41-3
<p>a. Metal added as Fe(NO₃)₃·9H₂O in water to coal sample; impregnated coal treated with 1.54 M NH₄OH solution at a ratio of 138 moles NH₄OH/mole Fe; samples were drained and dried at 40 °C for 20 hours at 10 Torr.</p> <p>b. P = Predried at 110°C/20 hrs/10 Torr to moisture content of 3 wt%; AR = "as received" moisture content of 22 wt%.</p> <p>c. Liquefaction conditions: 415°C, 1 hour, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).</p>				

moisture present in the coal. At both stages, the moisture level significantly exceeds the 75 wt% discussed above as an upper limit.

Liquefaction results show that at the lower 0.275 wt% Fe level, predrying appears to result in a decrease in conversion of 2.5 wt% while at the 1% Fe level the conversion is essentially unchanged. The conversion level apparently reaches the maximum conversion plateau of ~90% observed in these runs in tetralin. Oils appear to follow the same pattern as

Table 25. Effect of Final-Dry Condition on Coal Liquefaction ^a						
	Final Drying Temperature, °C ^d					
	40	40 ^e	100	40	115	40
Pressure During Dry, Torr	10	760 ^f	10	10	10	10
Sample No. ^b	CH-41	CH-45	CH-21	CH-20	CH-2	CH-1
Fe Added, wt% dry coal	1.0	1.0	0.55	0.55	0.275	0.275
Starting Coal ^c	AR	AR	AR	AR	P	P
S as DMDS/Added Fe in Coal	1.2	1.3	1.2	1.0	1.2	1.4
Final IW Coal Moisture, wt%	2.7	6.1	3.6	-0.8	3.9	1.4
% Yields on MAF coal						
HC Gases	1.2	1.2	1.2	1.1	1.1	1.1
CO ₂ +CO	3.9	3.8	4.3	3.6	4.4	3.8
Oils	46.4	48.0	41.7	44.9	36.9	41.0
PA + A	37.9	36.1	40.3	37.0	41.9	38.7
IOM	10.6	10.9	12.6	13.4	15.8	15.4
THF Conv	89.4	89.1	87.4	86.6	84.2	84.6
H ₂ Consump, mg/g maf coal	39.9	45.4	40.6	40.2	37.3	35.4
Run Number	41-3	43-1	13-1	29-1	325-1	41-1
<p>a. Liquefaction conditions: 415°C, 1 hour, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).</p> <p>b. Metal added as Fe(NO₃)₃·9H₂O in water to coal sample; impregnated coal treated with 1.54 M NH₄OH solution at a ratio of 138 moles NH₄OH/mole Fe; samples were drained and dried as specified.</p> <p>c. P = Predried at 110°C/20 hrs/10 Torr to moisture content of 3 wt%; AR = "as received" moisture content of 22 wt%.</p> <p>d. 20 hours/10 Torr at temperature.</p> <p>e. Sample washed with 500 ml water based on 15 g "as-received" coal (dry coal basis).</p> <p>f. Nitrogen flow of 140 ml/min.</p>						

Table 26. Effect of NH ₄ OH Concentration on Liquefaction of 0.77 wt% Iron IW Impregnated As-Received BT Coal ^a			
Catalyst Sample No.	CH-0	CH-32	CH-31
NH ₄ ⁺ /Fe Ratio	31	84	138
Added Fe, wt% dry coal	0.77	0.77	0.77
S/Added Fe, m/m	1.1	1.3	1.4
Products, wt% maf coal ^b			
HC Gases	1.1	1.1	1.2
CO ₂ +CO	4.4	3.5	4.4
Oils	45.9	46.4	43.0
PA + A	38.9	37.8	39.2
IOM	9.7	11.1	12.2
THF Conv	90.3	88.9	87.8
mg H ₂ Consumed/g maf coal	38	33	37
Run Number	324-2	50-2	3-15-2
<p>a. Metal added as Fe(NO₃)₃·9H₂O in 0.75 ml water/grams as-received coal; impregnated coal treated with 1.54 M NH₄OH solution at the mole ratio of NH₄OH/Fe as indicated; samples were drained and then dried at 40 °C for 20 hours at 10 Torr.</p> <p>b. Liquefaction conditions: 415°C, 1 hour, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).</p>			

Impregnation Compound - As-received coal samples impregnated with 0.77 wt% Fe were prepared using both ferrous and ferric sulfate in addition to ferric nitrate. Also, samples of iron-molybdenum have been prepared and the liquefaction results obtained. The concentrations of the various ferric and ferrous iron salts as well as the molybdenum salt used to prepare these coals are shown in **Table 27**.

Liquefaction results for the Fe impregnated coals are shown in Table 28. The conversions for these samples were within 1 wt% of each other with the oil yields showing a somewhat greater spread. The coal prepared with the ferric sulfate salt gave the highest oil yield of almost 50 wt% with the lowest yield being with the salt prepared from the nitrate. The yields of hydrocarbon and CO+CO₂ gases were nearly the same. In each case the final coal sample had been almost completely dried, which, as we have already seen, can have a detrimental effect on the performance in liquefaction.

Table 27. Concentration of Impregnating Salt in IW Water		
	Salt	"As Received" Coal
CH-41 (0.77 wt% Fe)	Fe(NO ₃) ₃ ·9H ₂ O	7.5 wt%
CH-53 (0.77 wt% Fe)	Fe ₂ (SO ₄) ₃ ·5H ₂ O	4.6 wt%
CH-52 (0.77 wt% Fe)	FeSO ₄ ·7H ₂ O	4.9 wt%
CH-6 (0.77 wt% Fe/1000 ppm Mo) ^a	Fe(NO ₃) ₃ ·9H ₂ O (NH ₄) ₂ MoO ₄ ^b	10.1 wt% 0.88 wt%
CH-61 (0.71 wt% Fe/500 ppm Mo) ^a	Fe(NO ₃) ₃ ·9H ₂ O (NH ₄) ₂ MoO ₄ ^b	10.1 wt% 0.44 wt%
<p>a. As-received coal impregnated first with (NH₄)₂MoO₄ solution followed by impregnation with the Fe(NO₃)₃·9H₂O solution; samples were then treated with 1.54 M NH₄OH solution at 138/1 NH₄OH/Fe molar ratio; samples were drained and then dried at 40 °C for 20 hours at 10 Torr.</p> <p>b. 85% MoO₃</p>		

Coals impregnated with both iron and molybdenum were also evaluated. These samples were prepared from as-received coal using a total of 0.75 ml water/g dry coal. The ammonium molybdate was added first as either a 0.44 wt% (500 ppm Mo/dry coal) or 0.88 wt% (1000 ppm/dry coal) solution to the as received coal. Ferric nitrate was then added in the remaining IW water as a 10.1 wt% solution to the samples. 1.54 M NH₄OH solution at the mole ratio of NH₄OH/Fe of 138 was then added to the samples. After drying,

Table 28. Effect of IW Salt and Iron Oxidation State on Liquefaction			
Fe Oxidation State	Fe ⁺⁺	Fe ⁺⁺⁺	Fe ⁺⁺⁺
Sample ID	CH-52	CH-53	CH-41
Fe Added, wt% dry coal ^a	0.77	0.77	0.77 ^b
Impregnating Salt	FeSO ₄ ·7H ₂ O	Fe ₂ (SO ₄) ₃ ·5H ₂ O	Fe(NO ₃) ₃ ·9H ₂ O
S/Added Fe in Cat, mol/mol	1.3	1.6	1.2
Moisture, wt%	0	0	2.7
Products, wt% maf coal ^c			
HC Gases	1.2	1.2	1.2
CO ₂ +CO	4.0	3.7	3.9
Oils	47.7	49.8	46.4
PA + A	35.5	34.1	37.9
IOM	11.7	11.3	10.6
THF Conv	88.4	88.7	89.4
mg H ₂ /g maf coal	37.1	38.5	39.9
Run No.	69-1	69-2	41-3
<p>a. Metal salt added in 0.75 ml water/grams as-received coal (19 g total); impregnated coal treated with 1.54 M NH₄OH solution at the mole ratio of NH₄OH/Fe of 138; samples were washed with 500 ml water, drained and then dried at 40 °C for 20 hours at 10 Torr.</p> <p>b. The 500 ml washing step was omitted for this sample.</p> <p>c. Liquefaction conditions: 415°C, 1 hour, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).</p>			

the samples were evaluated for liquefaction as shown in **Table 29**.

Results from the liquefaction show that the added Mo has no effect on the THF conversion since these two Fe/Mo samples are the same as a corresponding sample with Fe-only addition. Oil yield, however, reflects the benefit of adding Mo to the coal, increasing from 43.0 wt% for the Fe-only sample to 50.5 wt% for the 1000 ppm Mo sample. The 500 ppm

Mo sample falls between these values. This occurred even though these samples had all been dried to extremely low moisture levels, i.e., less than 3 wt% dry coal. The CO+CO₂ yields were lower for the molybdenum samples.

Table 29. Liquefaction of Fe/Mo IW-Impregnated Coal ^a			
	Fe/Mo	Fe/Mo	Fe
Sample ID	CH-6	CH-61	CH-31
Added Fe, wt% dry coal	0.77	0.71	0.77
Mo, ppm dry coal	1000	500	0
S/Added Fe in Cat		1.6	
% Moisture	0.65	1.3	2.9
Products, wt% maf coal ^b			
HC Gases	1.1	1.2	1.2
CO ₂ +CO	3.4	3.4	4.4
Oils	50.6	45.2	43.0
PA + A	32.6	37.2	39.2
IOM	12.2	12.6	12.2
Conv	87.8	87.4	87.8
mg H ₂ /g maf coal	42.8	N.A. ^c	37
Mo Add, ppm maf coal	1069	535	0
Run Number	62-1	73-2	15-2
<p>a. As-received coal impregnated first with (NH₄)₂MoO₄ solution followed by impregnation with the Fe(NO₃)₃·9H₂O solution; samples were then treated with 1.54 M NH₄OH solution at 138/1 NH₄OH/Fe molar ratio; samples were drained and then dried at 40 °C for 20 hours at 10 Torr. Fe-only sample impregnated with Fe(NO₃)₃·9H₂O solution only.</p> <p>b. Liquefaction conditions: 415°C, 1 hour, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).</p> <p>c. N.A. - not available</p>			

TASK 2.3.3 CATALYST STUDIES (SANDIA)

A bulk hydrous titanium oxide catalyst exchanged with nickel and molybdenum was formulated for testing with the dewaxed distillate. The catalyst had 9.8 % molybdenum and 3.2% nickel. Results from tests with this catalyst are reported in section 2.1.3. The extent of hydrogenation and measurements of catalyst deactivation are similar to previous results using supported NiMo catalysts (see Sept.-Dec. 1992 Quarterly Report). The carbon content of the NiMo HTO catalyst was 8.1 wt% at the feed end of the trickle bed reactor. This is equivalent to the carbon content on the Shell 324M catalyst after similar treatment with the -5°C dewaxed feed (8.9 wt%).

A coated HTO catalyst was formulated using an alumina support and platinum as the active metal. Preliminary screening with this catalyst showed that it lacked hydrogenation activity when tested with the pyrene hydrogenation test.¹⁰ The rate constant for pyrene hydrogenation was 0.09 sec⁻¹ per gram of catalyst compared to 0.2 sec⁻¹ per gram of catalyst for an active catalyst. This catalyst will not be used for solvent hydrogenation, however the reason for the low activity will be investigated.

TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT

Baseline Economic Assessment

Preparation of the baseline economic assessment, based on Wilsonville Run #263J, was completed. This baseline study (see **Figures 18 through 21**) serves as the reference against which the results of this program will be compared.

The economic portion of the baseline assessment was completed. Investment costs for the process units (**Table 30**) and offsite units (**Table 31**) were determined on a mid-1992, Wyoming plant site basis. The cost of the process units can be split into three distinctive groups, namely liquefaction, makeup hydrogen production and upgrading of the liquefaction

distillate to gasoline. With this grouping, the process units cost breakdown is:

	Millions	%
Liquefaction	\$883	39.8
Makeup Hydrogen	\$857	38.6
Upgrading	\$480	21.6

Total plant cost (Table 32), the total capital required (Table 33), and the annual operating costs (Table 34) were also determined. A discounted cash flow (DCF) economic analysis indicated that the required gasoline selling price (RGSP) is a strong function of the assumed DCF real rate of return as indicated below:

Discounted Cash Flow Real Internal Rate of Return, %	Relative Required Gasoline Selling Price
2.5	0.618
5.0	0.724
7.5	0.851
10.0	1.000

At the highest rate of return (10%), capital costs account for almost two-thirds of RGSP, while at the lowest rate of return (2.5%), capital costs are only 44% of the RGSP.

Assessment of Improved Coal Conversion Case

This was the first alternative case selected for comparison with the above base case. The improved coal conversion case (ICC) was investigated in order to estimate the benefit of improved coal conversion without defining, at this time, the costs associated with obtaining

such improved coal conversion. The ICC case had an assumed overall coal conversion of 96.8% as compared with 93.6% coal conversion in the base case. A technical and economic assessment of the ICC case was made and reported on at the March 25-26 Quarterly Project review meeting. The ICC case had a lower total plant cost (approximately \$75 million) and lower operating cost (approximately \$8 million/yr) than the base case. At a DCF real rate of return of 10%, the RGSP for the ICC case was \$1.32/bbl less than the RGSP for the base case.

Upgrading of Dewaxed Oil and Slack Wax

Ed Klunder of PETC advised us that AMOCO would be unable to perform microscale selective cat cracking tests for upgrading our slack wax under their existing DOE contract. Apparently funding by CAER will be needed if such tests are to be run, but such funds are not currently in our program budget at this time.

FIGURE 18
BLACK THUNDER LIQUEFACTION STUDY
UPGRADING UNITS SIMPLIFIED BLOCK FLOW DIAGRAM
HYBRID CASE BASED ON WILSONVILLE RUN # 263J

CONCEPTUAL COMMERCIAL PLANT BASED ON WILSONVILLE RUN #263J

Figure 20 ASH CONCENTRATE GASIFICATION

Figure 21 MAKEUP HYDROGEN VIA COAL GASIFICATION

TABLE 30
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
PROCESS UNIT INVESTMENT

<u>UNIT</u>	<u>INVESTMENT</u> (Millions of Mid '92 \$:Wyoming Location)
COAL GRINDING	34
COAL SLURRY PREPARATION & DRYING	77
FIRST STAGE REACTION SYSTEM	304
SECOND STAGE REACTION SYSTEM	122
LETDOWN SYSTEM	39
VACUUM FRACTIONATION	146
ROSE UNIT	44
RECYCLE HYDROGEN RECOVERY & COMPRESS'N	117
ASH CONCENTRATE GASIFICATION SYSTEM	161
COAL GASIFICATION SYSTEM	326
OXYGEN PLANT	169
STEAM REFORMER	86
MAKEUP HYDROGEN COMPRESSION	115
UPGRADING UNITS	<u>480</u>
TOTAL PUI = 2,220	

LDP ASSOCIATES 1/31/93

TABLE 31
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 262E
OFFSITE UNITS INVESTMENT

<u>UNIT</u>	<u>INVESTMENT</u> (Millions of Mid '92 \$:Wyoming Location)
LIQUID TANKAGE	195
ELECTRICAL DISTRIBUTION	184
SEWERS AND WASTEWATER TR'TMENT	181
SITE DEVELOPMENT	136
COAL RECEIVING & STORAGE	121
WATER SYSTEMS	116
INTERCONNECTING PIPING	107
BUILDINGS	61
FIRE SYSTEMS	42
STEAM GENERATION & BFW PREP'N	40
SULFUR PLANT	29
FLARE SYSTEM	24
RAILROAD & TRUCK FACILITIES	24
SOUR WATER TREATING	20
OTHER UNITS (6)	<u>53</u>

TOTAL OFFSITES = 1,333

LDP ASSOCIATES 3/3/93

TABLE 32
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
TOTAL PLANT COST

	<u>INVESTMENT (\$ Millions)</u>
PROCESS UNITS	2,220
OFFSITE UNITS	1,333
ESTIMATING ALLOWANCE @ 15%	<u>533</u>
TOTAL PLANT COST (Mid '92\$, Wyoming) = 4,086	

TABLE 33
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
TOTAL CAPITAL REQUIREMENT.

	<u>INVESTMENT (\$ Millions)</u>
TOTAL PLANT COST	4,086
INVENTORY CAPITAL	121
PRE-PRODUCTION COSTS	168
INITIAL CATALYSTS & CHEMICALS	<u>55</u>

TCR (Mid '92\$, Wyoming) = 4,430

\$/BPSD of Gasoline = 88,600

TABLE 34
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
ANNUAL OPERATING COSTS

	<u>COST (\$ Millions/Yr.)</u>
MF COAL: 17,004T/D @ \$10/T	54.4
PURCHASED ELECTRICAL POWER, 248 MW @ 4¢/ Kw-hr.	76.2
LIQUEFACTION SYSTEM ADDITIVES :	
- Sulfiding Agents @ \$0.072/lb.	8.8
- Dispersed @ \$3.20/ lb.	33.0
- Supported @ \$3/lb.	38.7
UPGRADING UNITS CATALYSTS & CHEM.	12.0
OTHER CATALYSTS & CHEMICALS	21.4
OPERATING LABOR	16.3
MAINTENANCE @ 2% of TPC + ICC	82.8
INSURANCE & LOCAL TAXES @ 1.5% of TPC + ICC	62.1
ADMINISTRATION & OPERATIONS SUPPORT	<u>12.2</u>
	AOC = 417.9

OPERATING COST = \$ 26.12/ Bbl. of Gasoline

REFERENCES

1. Schweighardt, F. K., Kingsley, I. S., Cooper, F. E., Kamzelski, A. Z. and Parees, D. M., DOE/OR/03054-61, Sept. 1983.
2. R. A. Winschel, G. A. Robbins, F. P. Burke. Fuel 1986, Vol. 65, 526-532.
3. Quarterly Report, Oct-Dec. 1992, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-21, February 1993, p79ff.
4. K. S. Vorres, Am. Chem. Soc. Div. of Fuel Chem. Preprints, 1993, 38 (2), 587.
5. F. P. Miknis, D. A. Netze. and T. F. Turner, Am. Chem. Soc. Div. of Fuel Chem. Preprints, 1993, 38 (2), 609.
6. H. Silver, and W. S. Frazee, Integrated Two-Stage Coal Liquefaction Studies, EPRI Report AP-4193, 1985, p. 3-91.
7. T. L. K. Lee, A. Comolli, E. Johanson and R. Stalzer, Am. Chem. Soc. Div. Fuel Chem. Preprints, 1993, 38 (1), p 107.
8. Quarterly Report, Oct-Dec. 1992, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-21, February 1993, p103.
9. Quarterly Report, Oct-Dec. 1992, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-21, February 1993, p100.
10. H. P. Stephens and R. J. Kottenstette, Preprints of Papers, American Chemical Society, Fuel Division, Vol. 30, No. 2, 345 (1985).

SECTION II

ADVANCED DIRECT LIQUEFACTION CONCEPTS

for PETC GENERIC UNITS

**Quarterly Technical Progress Report
for Period January 1993 through March 1993**

by

CONSOL Inc.

to

University of Kentucky Research Foundation

under

Contract No. UKRF-4-25582-92-76

The solvent qualities of these four hydrotreated dewaxed distillate samples also were determined. Solvent quality is determined as the percent conversion of Indiana V, Old Ben No. 1 coal at modified equilibrium conditions (30 min at 750 °F in 1.5:1 solvent:coal). The results of the solvent quality determinations are also shown in Table 2. The original V-1074 distillate and the -5 °C acetone dewaxed V-1074 composite from which the Sandia samples were prepared are shown in this table for comparison. Although, sample 5C-111903 is hydrogenated to a significantly greater degree than the other samples, Table 2, there is no indication that this sample is over-hydrogenated with respect to donor solvent quality. All four hydrotreated oils had solvent quality (SQ) indices of about 90%. These significantly improved solvent qualities are consistent with those observed for the other Sandia-hydrotreated samples.

The phenolic -OH concentrations of the four Sandia-hydrotreated dewaxed oil samples were determined by FTIR, Table 2. The composite hydrotreated -5 °C dewaxed oil (SC-1) was quite wet, and the sample hydrotreated with the in-situ water-gas shift reaction (5C-121603) was slightly wet. The phenolic -OH concentrations of the hydrotreated samples ranged from 0.12 to 0.38 meq/g, significantly lower than the value of 0.56 meq/g in the dewaxed sample before hydrotreating. The extreme values of 0.12 and 0.38 meq/g resulted from hydrogenation over the Sandia-developed Pt-HTO catalyst. The remaining samples had intermediate concentrations of about 0.26 meq/g (wet sample basis).

Wilsonville personnel verified that no ash-SO₃ correction was applied to plant balances when low-rank coals were run. Ash-SO₃ corrections were explored in Run 246, after which it was recommended that the corrections be used in future low-rank coal runs. This recommendation was not followed. In Run 246, the ash-SO₃ corrections reduced coal conversions by about 3% absolute¹. Although ash-SO₃ corrections were not made in subsequent runs, the plant ash balances were not accepted until the ash flows in and out agreed to within 5% absolute (typical agreement was 2 to 3%). We must determine what adjustments to the reported plant results from period 263J are necessary for the baseline economic assessment by LDP Associates.

Progress was made in obtaining the alternative coal and oil feedstocks for this program, so that feedstock effects (Task 2.5) can be explored. Alternative

SECTION TWO

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

TASK 1.2 - LABORATORY SUPPORT (CONSOL)

Summary

Solvent qualities of four hydrotreated dewaxed distillate samples received this quarter from Sandia were higher than those of the respective feeds. Phenolic -OH determination by FTIR showed that hydrotreatment of the dewaxed distillate at Sandia significantly reduced the concentration of phenolic -OH in the four samples.

Wilsonville personnel verified that no ash-SO₃ correction was applied to plant balances when low-rank coals were run. CONSOL will determine what ash-SO₃ adjustments are appropriate in the reported plant results from period 263J, which is used in the baseline economic assessment by LDP Associates.

Progress was made in obtaining samples for use as alternative feedstocks for this project. A sample of Illinois No. 6, Burning Star 2 coal received from HRI was prepared. However, the coal has an atypical analysis, and it will be replaced. We received the Martin Lake lignite sample we requested from TUMCO. We shipped deashed resid to Amoco in anticipated exchange for their supply of lignite oils from Wilsonville Run 255. We began determining the suitability of the Wilsonville Run 260 end-of-run inventory of V-1067 as a supply of Mo-free ashy recycle material for this project.

Discussion

Four samples of hydrotreated distillate were received from Sandia this quarter. These samples were all produced by hydrotreating -5 °C acetone dewaxed V-1074 distillate. The hydrotreatment conditions used by Sandia are shown in Table 1. ¹H-NMR determination of proton distributions in these materials is given in Table 2. Hydrogenation lowered the aromatic proton concentration (particularly the condensed aromatics) while slightly increasing the cyclic beta and alkyl beta proton concentrations. Sample 5C-111903 appears to be hydrogenated to a significantly greater degree than the other samples. The aromatic proton concentration in this sample is only about half that in the other samples.

feedstocks to be obtained include lignite and lignite-derived oil, Illinois 6 bituminous coal and oil, and perhaps Pittsburgh seam coal and oil. We received 15 gal (about 32 kg) of Burning Star No. 2 (Illinois 6 seam) coal from HRI. This coal was intended to be used as the bituminous coal for this project. The sample was mixed and riffled into 9 x 4 lb bags and 32 x 1 lb bags. This sample, 1621-22-7, was submitted to the lab for routine coal analysis. This coal has an ash content of about 15 wt % MF, which is too high for normal Burning Star 2 product (typically about 11 wt % MF ash). HRI was contacted for more information about the sample history, and we alerted them that it is atypical. This sample will be replaced. We received about 15 gal of lump (4") Martin Lake lignite from TUMCO. Because Black Thunder coal exhibits limited cleanability by oil agglomeration, alternative subbituminous coals may be examined. Using DOE washability data for low-rank coals, we identified a few prospective coals from the Powder River Basin which may be cleanable by agglomeration.

We requested information on the availability of oils derived from lignite and Illinois 6 bituminous coals from Amoco. Amoco has a very limited supply of Burning Star No. 2 coal-derived oils. We shipped 8.6 lb of V-130 deashed resid from Wilsonville Run 262E to Amoco in anticipated exchange for their supply of lignite oils from Wilsonville Run 255.

Distillation data provided by Wilsonville personnel on V-1067 samples from periods preceding the one we have from Run 260 (from end-of-run inventory) indicate that only 3 wt % of the sample boils below 650 °F. We may supply this material to Sandia and CAER as one component of our new baseline Mo-free ashy recycle solvent. We will first confirm that the sample contains little light material, or distill it, as necessary.

HRI's TGA method for 975 °F* resid determination was obtained and sent to the University of Kentucky and Sandia.

Task 2.1.2.1 - Pretreatment Work at CONSOL - Dewaxing

Summary

Five hundred mL of oil produced by dewaxing V-1074 distillate at -35 °C in 55/45 (vol %) acetone/MEK was sent to Sandia for hydrotreatment studies. A clean wax yield of 3.1 wt % MAF (slack wax yield of 3.5 to 4.0% MAF) was determined for the

wax yield increased to 1.3 wt % MAF after clean-up by alumina contacting. The waxes included n-paraffins from C₂₀ to C₃₄. This range of n-paraffins is virtually the same as that obtained when the V-1074 oil is dewaxed. A second 120-min run was made with one g of Criterion 324 catalyst added (presulfided at Wilsonville in preparation for Run 260, ground in a mortar and pestle at CONSOL). The catalyst was added to promote resid conversion. The paraffin wax (C₂₀ to C₃₄) recovery was 5.3 wt % MAF in this run; however, the presulfided Criterion catalyst used in this run was found to yield 8.0 wt % paraffin waxes (C₁₅ to C₂₇, after clean-up by alumina contacting) when reacted without coal at the same conditions. This wax contaminant undoubtedly contributed to the wax yield observed in the catalyzed liquefaction of Black Thunder coal. Subtracting out this catalyst contaminant wax gives a net yield of 3.1 wt % MAF clean wax from the Black Thunder coal. The estimated slack wax yield, based on our earlier wax clean-up work is ~3.5 to 4 wt %. This is significantly higher than we found for uncatalyzed liquefaction of the same coal and agrees relatively well with reported literature values for Wyoming coals.

Wax Properties

Simulated distillations were conducted on the wax composites from the -5 °C and -35 °C acetone dewaxings of V-1074 distillate from Wilsonville Run 262, Period E. The results are shown in Table 4. The boiling ranges of the two waxes were very similar. The IBP of each was 349 °C and the mid points were 437 °C and 431 °C for the -5 °C wax and the -35 °C wax, respectively. These data will be used by LDP Associates to help evaluate the suitability of these waxes for catalytic cracking.

Calculated Solvent Qualities

Correlations have been developed to predict microautoclave test solvent qualities from ¹H-NMR proton distributions.⁴ The correlation for the modified equilibrium solvent quality test uses an aromatic parameter, based on the condensed and uncondensed aromatic proton concentrations, and a hydroaromatic parameter, based on the ratio of cyclic/total aliphatic protons. These parameters can be expressed by the following equations:

$$\text{Aromatic parameter} = \frac{(\text{condensed aromatics} + \text{uncondensed aromatics})}{(1 - \text{condensed aromatics} - \text{uncondensed aromatics})} \quad (1)$$

liquefaction of Black Thunder coal. Simulated distillation of the waxes separated from Wilsonville V-1074 oil at -5 °C and -35 °C in acetone gave an IBP of -350 °C and a mid-point of -435 °C.

Microautoclave tests were made in which Black Thunder coal was liquefied in simulated Wilsonville Run 262E recycle solvents containing dewaxed and hydrogenated-dewaxed V-1074 (the distillate recycle component). The purpose of these tests was to identify microautoclave conditions for evaluating solvent quality improvements. Conversions at 824 °F, 5 min, and 1.5:1 recycle:coal ratio are in the range of 90% MAF coal (SO₃-free ash basis). Therefore, these are suitable conditions to simulate Wilsonville coal conversion results. At these conditions, the combination of dewaxing and hydrogenation of the recycle distillate component results in a 4-5% increase in MAF coal conversion.

Discussion

Production of Acetone/MEK Dewaxed Oil

Approximately 900 g of Wilsonville V-1074 distillate from Run 262 was dewaxed at -35 °C with a 55 vol % acetone/45 vol % MEK solvent. Six 150 g batches of the V-1074 heavy distillate were dewaxed at -5 °C with the 55/45 (vol %) acetone/MEK solvent using the procedure described for acetone dewaxing.² The properties of this dewaxed oil are given in Table 3. Approximately 750 g of dewaxed oil with a solvent quality of 83.6% was produced. This compares well with the solvent quality of a trial batch of the V-1074 dewaxed at the same conditions and reported last quarter,³ 83%. Five hundred mL of this dewaxed distillate was shipped to Sandia for hydrotreatment.

Wax Yields

A literature review (see Appendix 1) indicated that the potential wax yield from Wyoming coal is approximately 4-5 wt %. A microautoclave test was run with 2.5 g Black Thunder coal and 7 g of tetralin at 750 °F and 1500 psig (cold) hydrogen for 60 min to determine experimentally the paraffin wax yield from Black Thunder coal. Coal conversion was 82.6% MAF. The measured wax yield from this test was 0.8 wt % MAF after clean-up by alumina contacting. This is significantly less than indicated by the literature survey. Therefore, a second microautoclave run was made in which the reaction time and the quantity of each reactant were doubled. The coal conversion was 91.9% MAF. At the 120 min reaction time, the

$$\text{Hydroaromatic parameter} = \frac{(\text{cyclic } \alpha + \text{cyclic } \beta)}{(\text{cyclic } \alpha + \text{alkyl } \alpha + \text{cyclic } \beta + \text{alkyl } \beta + \gamma)} \quad (2)$$

The predicted modified equilibrium test solvent quality can then be expressed in terms of these two parameters by the following equation³:

$$SQ = 40.1 - 20.9(\text{Aromatic parameter}) + 110.4(\text{hydroaromatic parameter}) \quad (3)$$

Figure 1 is a plot of calculated solvent quality versus dewaxed oil yield for all the dewaxing experiments that have been made at CONSOL under this contract for which ¹H-NMR proton distributions were determined. Measured solvent qualities, if available, are shown for comparison on this plot. For coal conversions (i.e., solvent qualities) above ~75 wt %, the calculated and measured solvent qualities agree well (within ~5%) with each other; however, the calculated conversion is consistently greater than the measured value. At lower coal conversions, the difference between the measured and calculated solvent qualities increases, with calculated conversions as much as 15 wt % greater than the measured values. This deviation below about 75 wt % conversion is consistent with the data from which the original correlation was derived.³ However, in the 75-90 wt % conversion range, the calculated and predicted coal conversions agree well. Therefore, solvent qualities calculated from the measured proton distributions may be used for comparison and for discerning trends if it is not practical to make microautoclave determinations of solvent quality.

Development of Microautoclave Test for Composite Recycle Solvent Quality

CONSOL's traditional microautoclave solvent quality test involves the liquefaction of Indiana V coal at relatively mild conditions (750°F, 30 min, no H₂) to provide a relative measure of the donor hydrogen content of the solvent. In the current work, it is important to have a more reliable measure of the potential absolute improvement in process performance that can be achieved by the various solvent pretreatment steps, principally dewaxing and hydrogenation, envisioned in the integrated process. Therefore, a series of microautoclave

tests was made using simulated Wilsonville Run 262E recycle solvent to define conditions for solvent testing.

In these tests, the recycle material was a composite made in the same proportion from the three components produced in Run 262E: distillate (V-1074), ashy resid (V-1082), and deashed resid (V-130). In some cases, the original V-1074 was replaced in the recycle mix with dewaxed or hydrogenated-dewaxed V-1074. All conversions were measured by the THF solubility of the reaction products, corrected for the ash-SO₃ contents of the coal and recycle materials. The conversions are expressed both on an MAF-coal-fed basis and on a total-IOM-fed basis (i.e., including the IOM in the ashy resid in the denominator of the conversion calculation). Expressing the conversion on an MAF coal basis gives an indication of the steady-state conversion one might expect in a recycle system. Expressing the conversion on an IOM-fed basis gives a better indication of the per-pass conversion activity.

The results of these experiments are given in Table 5. The variables included residence time, recycle distillate component, and recycle ratio. The earliest tests were made at residence time of 15-30 min, a rough approximation of the residence times in the Wilsonville reactors. However, conversions at these conditions were well over 100 wt % MAF coal, compared to approximately 90% observed at Wilsonville with subbituminous coals. Therefore, these conditions were too severe to provide a reasonable simulation of Wilsonville conversions. Because the Wilsonville reactors are highly back-mixed, the required residence time for a batch reactor, like the microautoclave, is shorter to achieve a comparable conversion. For first order kinetics, the idealized kinetic expressions for the two systems are as given below.

$$C/C_o = 1/(1 + k_c t_c) \quad \text{Continuous Stirred Tank Reactor}$$

$$C/C_o = \exp (-k_b t_b) \quad \text{Batch Reactor}$$

Assuming that the intrinsic kinetics are the same for each system (i.e., $k_c = k_b$), the expressions can be combined to give the ratio of each required residence times in the batch and continuous systems:

$$\frac{t_c}{t_B} = \frac{\left[\frac{1}{(1-Conv)}\right]^{-1}}{-\ln(1-Conv)} \quad (4)$$

where Conv is the fractional conversion, in this case of MAF coal to THF solubles. At 90% conversion, this expression evaluates to a four-fold greater required residence time in the continuous system than in the batch system. For this reason, subsequent microautoclave tests were made at a five-minute residence time.

The results of the five-minute runs are given in Table 5, and shown in Figure 2, plotted as a function of recycle-to-coal ratio. Conversions in the 90% range were obtained at recycle-to-coal ratios of 1.5 and above. Therefore, it appears that microautoclave tests at these conditions (i.e., 824 °F, 5 min, 1.5 recycle-to-coal) provide a reasonable simulation of Wilsonville coal conversion results. Furthermore, at these conditions, there was a clear improvement in conversion when the dewaxed V-1074 and the hydrogenated-dewaxed V-1074 were substituted for the original V-1074 distillate in the recycle mixture. The overall improvement is in the range of 4-5 wt % MAF coal.

For example, Run 21, Table 5, was made for 5 min at 824 °F under 1500 psig (cold) hydrogen pressure with a 1:1 solvent/Black Thunder coal blend (MAF). The solvent composition simulated that from Wilsonville Run 262E except that the Sandia-hydrogenated, -5 °C dewaxed V-1074 distillate, SC1, was substituted for the original V-1074. Coal conversion was significantly improved by the use of the hydrogenated, dewaxed distillate (80 wt % vs. 72 wt % on an SO₃-free-ash basis, Run 19). When the Sandia-hydrotreated (-5 °C dewaxed) sample was substituted for V-1074 in the solvent blend at S/C = 1.5, a small but significant improvement in coal conversion was found (92 wt % vs. 88 wt % with the original V-1074 and 89 wt % with the -5 °C dewaxed V-1074).

Microautoclave runs were made with a 1:1 S/C ratio using V-1074 (Run 23, Table 5) and the Sandia-hydrotreated product, SC1 (Run 22, Table 5), at 840 °F, the temperature used in Wilsonville run 263, Period J. This is the Wilsonville run period used as a base case by LDP Associates in their economic studies. V-1074

distillate was used in the solvent blend in Run 23 and the Sandia-hydrotreated product, SC1, was substituted for V-1074 in the Run 22. The coal conversions in both runs were higher than the conversions observed in previous 5-min tests with the same blends at 824 °F. For the V-1074 case, SO₃-free coal conversion increased from ~72% (Run 19) to ~78% and for the SC1 case, coal conversion increased from ~80% (Run 21) to ~83%.

When the hydrotreated dewaxed distillate was used at a 2.3 S/C ratio, Run 27, the coal conversion was 94 wt %, compared with 89 wt % and 90 wt % when V-1074 and dewaxed V-1074 were used, respectively.

Coal conversions and total IOM conversions for five-minute tests with the three distillate components (V-1074, dewaxed V-1074 and hydrotreated dewaxed V-1074) at three S/C ratios (2.3, 1.5 and 1.0) with Black Thunder coal are compared in Figures 2 and 3, respectively. The MAF coal conversion increases when the S/C ratio is increased from 1 to 1.5 and is relatively unchanged as the S/C ratio is further increased to 2.3. The conversion of resid IOM complicates interpretation of these data. The effect of S/C ratio on conversions is more clear from the total IOM conversion plot, Figure 3. The rise in total IOM conversion, observed in this figure when the S/C ratio is increased from 1 to 1.5, is apparently due to the increased ratio of donor solvent to IOM. The observed decrease in total IOM conversion as the S/C ratio is increased beyond 1.5 is due to the increase in the ratio of the less reactive resid IOM to more reactive coal.

A five-minute microautoclave test (Run 24, Table 5) was made at a 1.5:1 S/C coal ratio, 824 °F and 1500 psig (cold) H₂ with V-130 deashed resid substituted for the V-1082 ashy resid in the simulated Wilsonville blend to determine the coal conversion (without interference from simultaneous conversion of the resid IOM). Measured coal conversion was 62.2 wt % (SO₃-free ash basis). This is significantly lower than is suggested by the data from runs in which both coal and resid IOM are present. Replacing the V-1082 ashy resid with V-130 deashed resid at a 1.5 S/C ratio with hydrogenated dewaxed distillate (SC1) resulted in 72 wt % Black Thunder coal conversion, Run 26. This compares with 63 wt % when the original V-1074 distillate was used instead of the hydrogenated dewaxed distillate at the same conditions, Run 24. The measured conversions of both the coal and resid IOM are significantly lower than the total IOM conversions observed in

any of the runs in which both coal and resid IOM were present, Table 5. This is probably due to catalysis of the coal conversion by the Mo and Fe catalysts present in the V-1082 ashy resid. The presence of catalyst in the ashy resid component of the recycle solvent used in our tests complicates evaluation of the effects of solvent upgrading on conversion. A Mo-free ashy resid (see Task 1.2), which we are obtaining for future work, should cause less interference.

Microautoclave Runs 25 and 28 were made to determine the conversion of resid IOM that occurs during the microautoclave liquefaction of Black Thunder. In these tests, MF coal was replaced by ashy resid (V-1082). Run 25 was made as if there were a S/C ratio of 1.5, except that the coal was replaced by additional V-1082. The reaction time for this test was 5 min. The observed IOM conversion was 14.5 wt % (SO_3 -free ash basis). A second test, Run 28, was made at an equivalent S/C ratio of 2.3 for 30 min reaction time. Resid IOM conversion in this run was 37.1 wt %. Thus, recycled IOM is moderately convertible at reaction conditions.

The conversions greater than 100%, at 15 and 30 min residence times, Runs 5, 6, 8 and 11, Table 5, confirmed earlier CAER results, and demonstrate that the recycle IOM is moderately reactive toward additional conversions. This suggests the possibility that improvements in solvent quality or catalyst activity can be beneficial in increasing both coal and recycle IOM conversion. For example, at 5 min, 2.3 recycle-to-coal, the conversion on an MAF coal basis is 93.6%, but the conversion on a total IOM basis (Coal + recycle IOM) is only 74.1%. Improving the per-pass coal conversion or the total IOM conversion could improve yields directly or through process modifications.

Task 2.1.2.2 - Pretreatment Work at CONSOL - Agglomeration

Summary

The objectives of oil agglomeration are to reject coal ash, to recover and dewater pretreated coal, to integrate agglomeration with CO-pretreatment, to disperse catalyst, and to reject resid ash within the framework of the liquefaction process.

The CO-pretreated coal received from CAER was agglomerated with Wilsonville recycle distillate in two runs made at 50 °C and 175 °C. The pretreated coal produced large agglomerates with a low oil dosage, but virtually no ash rejection

took place. The products had 23 to 36 wt % moisture when surface-dried, but the moisture content decreased to 1 to 7 wt % after air drying overnight. We sent CAER the requested samples of agglomerate products and unused pretreated coal.

A new sample of Burning Star 2 coal (atypical, see Task 1.2), an existing sample of Martin Lake (Texas) lignite, and an existing sample of Spring Creek subbituminous coal were each agglomerated with No. 6 fuel oil at 50°C. Physical ash rejection was about 30 wt % with Burning Star 2 coal and about 25 wt % with Martin Lake lignite. Repeat runs will be made with replacement samples of both coals. Although we previously identified Spring Creek coal to be potentially cleanable by oil agglomeration, on the basis of its reported washability, results were poor. Large agglomerates were produced, but ash rejection was low, similar to that of Black Thunder coal.

Much of the work performed this quarter was focused on dewatering. We performed our part of a small cooperative project with Argonne National Laboratory to investigate dewatering effects of agglomeration of Beulah-Zap (North Dakota) lignite. Physical ash rejection with this coal ranged from 4 to 12 wt %, but ash rejection including dissolution was 71 to 77 wt % (tests at pH 1). Wet product agglomerates had moisture contents that ranged from 41.8 to 68.2 wt % moisture, but agglomerates air-dried overnight had 3.6 to 14.3 wt % moisture content, much lower than that of the feed coal (32.2 wt %). Three agglomeration runs were made with Black Thunder coal and No. 6 fuel oil to determine the degree of dewatering. No pore dewatering effect was evident, but coal moisture is not greatly increased by agglomeration, provided that surface moisture can readily drain away. Air-drying can reduce product moisture below that of the feed coal. A complete report is included as Appendix 2.

Column flotation tests were performed by Ames Lab on the Black Thunder coal. The coal showed poor cleanability, confirming our oil agglomeration experience. A report of their results is included as Appendix 3.

The reported particle size of the Black Thunder feed coal (95% -200 mesh) was confirmed by laboratory measurement using a laser diffraction method.

Discussion

CO-Pretreated Coal

CONSOL received 160 g of CO-pretreated from CAER in a sealed tri-layer bag. The sample was identified by CAER as 2.1.1.1. Pretreatment conditions were: 800 psi CO, 310-315 °C, 1 h, 150 g as-received Black Thunder coal, 300 mL H₂O, 3 g NaOH. The entire pretreated coal sample received about 24 hours of exposure to the air (in a sealed jar). After that time, the sample was maintained under a nitrogen atmosphere, except for temporary exposure to the air when the jar was opened to obtain samples. The entire sample of CO-pretreated coal was ground with a mortar and pestle to -28 mesh and an aliquot was analyzed. Analyses of the feed coal and the pretreated coal are given in Table 6. Relative to the feed coal, the pretreated coal has lower moisture, total sulfur, and oxygen by difference contents, and higher heating value, carbon, and hydrogen contents. It is evident that the pretreatment produces chemical changes in the coal, among which is a modest reduction in oxygen content. The pretreated coal was agglomerated with V-1074 recycle distillate in two runs made at 50 °C and 175 °C (Table 7). The temperature of 175 °C was chosen as a convenient one for process integration, because it is approximately the slurry tank temperature that was used at Wilsonville. In the higher-temperature run, the oil was added and initial agglomeration took place at about 97 °C before the reactor was sealed. In both runs, the coal was readily agglomerated with a low (~15 wt %) oil dosage. Virtually no physical ash rejection took place. Consequently, no reject samples were included in the material sent to CAER. Large (~1 mm dia.) agglomerates were made in the 50 °C run. A pressure leak during the 175 °C run caused about 75% of the water to escape. Consequently, most of the small agglomerates initially produced were caked together in the dry part of the reactor. The rinsed products had 23 to 36 wt % moisture after removal of surface moisture with paper towels, and moisture content was 1 to 7 wt % after air-drying overnight. Although the CO-pretreatment may remove pore moisture from the coal, these limited agglomeration experiments have not produced dry coal without additional drying, such as air-drying.

The unused portion (~100 g) of the CO-pretreated coal generated in CAER's laboratory was shipped back to J. Lim at CAER. Shipped with it were two 10 g samples of agglomerated pretreated coal. Sample 1621-22-1B-UK1-A1 was from Run

B24, and sample 1621-22-1B-UK1-A2 was from Run B25H. The samples sent to CAER were sealed under nitrogen in a tri-layer bag.

Alternative Feedstocks

The atypical Burning Star 2 coal from HRI (see Task 1.2) and an existing sample of Martin Lake (Texas) lignite were each agglomerated with No. 6 fuel oil at 50 °C in the large agglomeration vessel (Table 7, Runs A21 and A22). Physical ash rejection was about 30 wt % with Burning Star 2 coal, and about 25 wt % with Martin Lake lignite, similar to previous results obtained with these coals. The Martin Lake lignite sample was from previous agglomeration work in this lab. Repeat runs will be made with new replacement samples of both coals (see Task 1.2).

Based on reported washability, we previously identified Spring Creek subbituminous coal to be potentially cleanable by oil agglomeration. A four-year old sample of the coal in our inventory was ground from about -3/8" to -200 mesh and agglomerated with No. 6 fuel oil at 50°C (Table 7, Run A23). Large agglomerates were produced but ash rejection, which was similar to that of Black Thunder coal, was poor.

Dewatering - Beulah-Zap Lignite

Mr. Karl Vorres of Argonne National Laboratory supplied a sample of premium Beulah-Zap North Dakota lignite for agglomeration testing. Wet agglomerates were shipped to Argonne, where they will be analyzed by thermogravimetric analysis to determine the amount of surface and macropore moisture. A comparison of the feed and product coals is expected to show if the coal was dewatered by agglomeration. Four tests (Table 7, Runs B19 - B22) were made; agglomerates were produced in two tests (B21 and B22) with about 14 wt % No. 6 fuel oil at 50°C and pH 1 (adjusted with H₂SO₄). Physical ash rejection was 4 to 6% in these runs, but ash rejection including dissolution was 71 to 75%. Run B20, made at pH 1 and a high oil dose, apparently did not agglomerate, but produced distinct water and oil phases. Physical ash rejection was 12% in this unusual run (ash rejection was 77% including dissolution). To supplement Argonne's dewatering results (which are not yet available), we determined the moisture content of as-screened (wet) and air-dried (for about 16 hours) agglomerates. As expected, the as-screened and air-dry moisture contents of the larger-sized product agglomerates from test B21

were lower than those of the smaller-sized agglomerates from test B22 (though other factors may have contributed to the moisture differences). The feed coal moisture content was 32.2 wt %; as-screened (or total) product moisture contents were 68.2 wt % for the small agglomerates (B22), 41.8 for the large agglomerates (B21), and 45.4 wt % for the oily semisolid from the unusual run (B20). Air-dried moisture contents were 14.3 wt % for the small agglomerates (B22) and 3.6 wt % for the large agglomerates (B21). These results demonstrate that the agglomerate products can be readily air-dried to a moisture content substantially lower than that of the feed coal. The results are described in more detail in the report in Appendix 2.

Dewatering - Black Thunder Coal

Three agglomeration runs were made with Black Thunder coal and No. 6 fuel oil to examine whether any dewatering results from the process (Table 7, Runs A18-A20). Product agglomerates contained 27 to 32 wt % moisture when wet (as screened), 26 to 29 wt % moisture when dried of surface moisture with paper towels, and 15 to 25 wt % moisture when air-dried overnight. The surface-dried product retained slightly more moisture than the feed coal had (22 wt %), but air-drying generally lowered the moisture content below that of the feed coal. Thus, agglomeration at these conditions (natural slurry pH, and 50 to ~97 °C) did not cause oil to displace pore moisture. However, the results show that agglomeration did not greatly increase product moisture, provided that surface moisture can readily drain away from the product.

Black Thunder Coal Cleanability

Ames Lab tried to clean our -200 mesh Black Thunder coal by column flotation. Their best results gave 9% ash rejection at 92% MAF coal recovery. Cleanability improved somewhat when the coal was first micronized. This confirms our conclusion that this coal is not cleanable by physical means at -200 mesh. A report which they provided to us is included as Appendix 3 of this report.

Particle size measurements, made with a Malvern Model 2600 laser diffraction particle size analyzer, were made on the Black Thunder coal. The coal was found to have a D_{10} of 7 μm , a D_{50} of 32 μm , and a D_{90} of 72 μm (all volume %), which agrees well with the size consist of 95 wt % -200 mesh (74 μm) which was reported by Wilsonville personnel.

Task 2.3.2 - Catalyst Studies (CONSOL)

No work was performed on this task.

Task 2.4.2 - Solids Separation (CONSOL)

Summary

Two approaches are being taken to deashing liquefaction bottoms (resid) by agglomeration. These are: 1) to use the resid as the hydrophobic solid (instead of or along with coal); and 2) to use the ashy resid as the agglomerating oil, and use dilution and high temperature to reduce oil viscosity to the desired level. The first approach produced substantial ash dissolution and a small amount of physical ash rejection, when used at conditions of low pH and room temperature with an appropriate oil.

The second approach has not resulted in resid deashing. Three pressure agglomeration runs were made with Black Thunder coal and ashy resid diluted with distillate at natural pH, pH 1, and pH 13 using resid only (no coal), so that resid deashing would be easily detected. Results ranged from no phase separation to 8 wt % physical ash rejection.

The particle size of finely-ground (ball-milled) ashy resid was found to be quite small (volume % D_{50} of 9 μm), though the extent of ash liberation is unknown. Examination of a sample of the THF-insoluble fraction of the ashy resid by SEM/EDX showed that there is a significant fraction of liberated mineral matter (quartz, calcite, pyrrhotite, 10 to 20 μm) in the insolubles.

We located sufficient material and began exploring the possibility of selectively rejecting ash from an ash concentrate material from Wilsonville. Some process benefits may result if this can be done.

Discussion

Low-Temperature Approach

Two agglomeration runs (B16R and B17R, Table 7) were made at room temperature and low pH with ball-milled V-1082 ashy resid as the feed and white kerosene as the agglomerating liquid. One run produced a small amount of physical deashing and a significant amount of ash dissolution; the other produced ash dissolution

without physical deashing. Run B16R (Table 7) was made with the slurry pH adjusted to 2.5 (H_2SO_4) just prior to agglomeration. There was agglomeration, but essentially no physical deashing. A significant portion of the ash (20% or less) apparently dissolved in the acidic water, however. In Run B17R (Table 7), V-1082 ashy resid was ball-milled overnight at pH 1 (H_2SO_4) and used as the feed to one agglomeration run with kerosene at room temperature. Ash rejection (including water-soluble ash, not shown) was about 33%, with 99.8% organic recovery. Most of the ash rejection resulted from dissolution, but there was about 5% physical ash rejection (recovered rejected ash). The acid reacted with the resid during grinding to produce some H_2S , perhaps from pyrrhotite present in the resid. We may further explore this method of resid treatment, since it is the only one which has resulted in resid ash rejection so far.

High-Temperature Approach

Two pressure agglomeration runs were made with Black Thunder coal and distillate/resid blends at 200 to 250 °C (B15H and B18H, Table 7). The runs produced small agglomerates, but no resid deashing. Run B15H was made with 25/75 wt % distillate/ashy resid at 200 °C and a slurry pH of 3. Run B18H was made with the 50/50 wt % distillate/ashy resid blend at 250 °C. An agglomeration run (Table 7, Run B23H) was made at 300 °C and 1300 psig with Black Thunder coal and a 75/25 wt % distillate/ashy resid blend. Physical ash rejection was 4% and ash rejection including dissolution was about 15%. This is similar to previous results obtained with this coal without the ashy resid (unpressurized, with only the distillate as the agglomerating oil). Therefore no resid deashing is evident. A unique aspect to this run was that the water turned orange in color and hydrogen sulfide was evidently produced (as detected by odor).

Three agglomeration runs were made at 300 °C and 1300 psig with a 75/25 wt % distillate/ashy resid blend (Table 7, Runs B26H, B27H, and B28H). The runs used no coal so that resid deashing would be easily detected. The results were: no deashing at natural pH, no phase separation at pH 13.1, and 8 wt % physical ash rejection at pH 1.

Liberation of Ashy Resid Minerals

Particle size measurements were made on one sample of V-1082 ashy resid which had been ball-milled overnight (1:1 resid:deionized water by weight). The

ball-milled resid (feed to agglomeration run B16R) was found to have a (volume %) D_{10} of 2 μm , a D_{50} of 9 μm , and a D_{90} of 26 μm . This is quite fine, though we do not know how fine the grinding must be for effective ash liberation.

A sample of the THF-insoluble fraction of the ashy resid was examined by SEM/EDX to examine the degree of mineral-organic matter association and the mineral particle morphology. There appears to be a substantial (unquantified) fraction of liberated mineral matter (quartz, calcite, pyrrhotite, 10 to 20 μm) in the insolubles. Thus, it appears that it should be possible to reject ash from the resid by oil agglomeration, if the solubles can be stripped from the minerals at the elevated temperature and high shear conditions. There has been only minimal success with this approach.

Miscellaneous

Some potential exists for agglomeration or another method to be used to deash the ash concentrate, as a supplement or alternative to deashing the ashy resid. Possible benefits include recovery/recycle of resid, IOM, deashing solvent, and perhaps catalyst normally sent to gasification. We found enough ash concentrate (V-107) from Wilsonville Run 263J (the baseline period for the project's economic assessment) to explore this idea in the laboratory.

Task 2.6.2 - Coker Overhead Characterization (CONSOL)

Summary

CONSOL's role in the fluid coker aspect of this project is to characterize the coker overheads, to determine if the coker results are consistent with prior, related work, and to use our experience to evaluate the potential of using the coker overhead as a component of the liquefaction recycle oil.

CONSOL characterized four coker overheads produced by CAER from the V-1082 ashy resid. The overheads were all produced at a relatively low coking temperature of 500°C, but at steam/resid ratios varying from 4.4 to 13. Tentative overhead yields increased from 43% to 53% with increasing steam/resid ratio. Other than differing in solids content, the overheads differ from the feedstock in that they are somewhat more aromatic and less paraffinic and they have slightly elevated oxygen-by-difference contents. As received by CONSOL, the overheads were quite wet. They contain some form of silicon that is not removed by filtration.

Perhaps this is silicone grease contamination; it yields about 1% of a pure silica ash. The relatively minor difference between the compositions of the overheads and that of the feedstock indicate that the overheads were produced primarily through steam distillation and entrainment, and not primarily through pyrolysis. The calculated solvent quality indexes of the overheads and feedstock are similar. The steam/resid ratio had only a minor effect on overhead composition.

The characteristics of the coker overheads are consistent with coker overheads produced previously from liquefaction resids in the Lummus-Crest, Inc. continuous stirred coking unit, if the lower coker temperature employed by CAER is considered. The CAER tests were conducted at a lower temperature, but at much higher steam/feed ratios than the Lummus tests.

The characteristics of the coker overheads indicate that they should be suitable components of the liquefaction recycle oil. The "soluble" silicon and high moisture contents of the samples examined were unexpected. It should be determined if these overhead components are contaminants introduced during sample collection and handling.

Solubility fractionation analyses were conducted on the four overheads and on the feedstock. Solubility fractionation analyses show that the coker overheads have lower concentrations of preasphaltenes than the soluble portion of the feedstock; i.e., similar to the ROSE process, coking selects for hexane-soluble oils and against preasphaltenes in the product.

Discussion

We received four samples of coker overhead from Mr. J. K. Neathery of CAER for characterization. The samples were produced in scouting runs of CAER's three-inch fluid coker. The feedstock was the Wilsonville Run 262E V-1082 (ashy resid). The coker operating conditions used to produce the overheads, as reported by CAER,⁵ are shown in Table 8. After collection of the overheads, CAER filtered them in methylene chloride solution to remove particulates, stripped off the methylene chloride, and sent them to CONSOL for characterization.

Upon receipt of the overheads, we found them to contain substantial amounts of water. Perhaps the water is condensed steam that passed through the filter paper and was not stripped from the samples along with the methylene chloride. It proved quite difficult to completely dry the overheads, and NMR analysis indicated the presence of residual methylene chloride; therefore, we chose to perform the bulk of our analyses on the dry tetrahydrofuran (THF)-soluble samples. The THF solubles were prepared by dissolving the overheads in THF, filtering the solution through Whatman No. 42 paper, and removing the THF by rotary evaporation.

Analytical results are shown in Table 9. The last sample received, B9301, was characterized less extensively than the first three samples received. The analyses of the feedstock V-1082 ashy resid and of the V-130 deashed resid are shown for comparison. The four overheads, particularly SR-3, were quite wet. Although they were filtered in methylene chloride solution by CAER, they contained about 1.5% ash on a dry basis.

The elemental analyses of the THF-soluble overheads shows little difference from the V-130 and V-1082 materials. For example, the H/C ratio of the overheads is the same as that of the V-130 and slightly higher than that of the insolubles-containing V-1082. There is perhaps a several percent increase in oxygen content (determined by difference) in the overheads; however, the phenolic -OH concentration is slightly lower in the overheads than in the feedstock.

Surprisingly, the THF-soluble overheads contain about 0.5% ash. The crucible residue was filamentous and pure white. Under the scanning electron microscope, the ash appeared to be a filigree structure with 2 μm spheres dispersed over it. Energy dispersive X-ray analysis indicates that this ash is nearly pure silicon dioxide. The genesis of this "soluble" silicon is unknown, but perhaps it is the result of contamination by silicone grease. If this is the case, the contamination occurred before our receipt of the samples. Silicone contamination of the THF-solubles could not be confirmed by ^1H -NMR (no peak at ~ 0 ppm) or by FTIR (no substantial peak at $\sim 1050\text{ cm}^{-1}$).

The proton distributions show that the overheads, except for sample B9301 which was produced at the lowest steam/feed ratio, are somewhat less paraffinic (alkyl

beta), slightly less naphthenic (cyclic beta), and slightly more aromatic (condensed aromatic) than the soluble portion of the feedstock. This would suggest that some loss of alkyl side chains or paraffins and some aromatization of naphthenes. Directionally, this is as would be expected for products of coking. For example, these are the same directional changes observed in the Lummus-Crest, Inc. continuous fluid coking study.⁶ However, the changes are small. In fact, the proton distribution of sample B9301 is nearly the same as that of the feedstock. This, along with the only minor changes in elemental composition, indicates that these coker overheads are not products of extensive cracking; rather, they appear to have been produced substantially through a combination of steam distillation and entrainment.

The three overheads produced at the higher steam/resid ratios had characteristics that did not differ greatly from the organic portion of the V-1082 feedstock. They were all somewhat more aromatic than the feedstock, and they increased slightly in aromaticity with increasing steam/resid ratio. Sample (B9301), Table 8, was produced at the lowest steam/resid ratio and it has an aromaticity more similar to the feedstock than the three other overheads. The high paraffinicity (alkyl beta and gamma protons) of this overhead sample may indicate that paraffinic moieties selectively report to the overhead at the combination of low steam/resid ratio and low temperature.

Solvent quality tests were not conducted on the overheads. However, a previously developed correlation⁴ between the proton distribution and donor solvent quality of distillate liquefaction oils was used for their evaluation. Though the correlation was not developed for coker overheads, it is expected to provide a good relative indication of their donor solvent quality. The solvent quality index shown in Table 9 was calculated from Equation 4 of Reference 4. Since the solvent quality index is calculated from the proton distribution data, it only refers to the soluble portion of the sample. The high paraffinicity of the B9301 overhead contributes to its relatively low calculated solvent quality index.

Solubility fractionation analyses were conducted on the four coker overheads, the feedstock (V-1082) and the deashed resid (V-130) by the LCF method (Table 9). The four overhead samples yielded generally similar results with no clear trend as a function of steam/resid ratio. All four overhead samples have lower

concentrations of preasphaltenes (benzene insoluble, THF soluble) and asphaltenes (hexane insoluble, benzene soluble) and higher concentrations of oils (hexane soluble) than the THF-soluble fraction of the feedstock V-1082 oil. Thus coking selects for oils and against preasphaltenes in the product. The ROSE process shows similar selectivity, though perhaps to a different extent. This is illustrated in Table 9 by the analyses of the V-1082 ashy resid and the V-130 ROSE-deashed resid.

Coking temperature was the operating condition that had the greatest influence on overhead composition in the Lummus⁶ work. The overheads examined here were all produced at the same temperature (500 °C), and, except for moisture content, the three overheads have very similar compositions.

Table 10A provides comparisons of CAER coker Run SR-3 with Lummus continuous stirred coker (CSCU) Run CSCU-8. Run CSCU-8 was performed at Lummus' lowest over target temperature of 1000°F (actual temperature = 544°C). The Lummus steam/feed ratio was much lower than that of CAER (the injection steam to feed ratio employed by Lummus never exceeded 0.5, this was supplemented by additional purge steam at a steam to feed ratio of 1.3 to 2.0). The feedstock to Run CSCU-8 was bituminous coal, yet its characteristics were similar to the subbituminous-produced CAER feedstock (Table 10B). The overhead yields from the two runs were apparently quite similar at about 44% (Table 10A). Though the feedstocks had similar characteristics, the product coker overheads from the two runs differed (Table 10C). The Lummus overhead is more aromatic, contains less hydrogen, and has a lower calculated solvent quality index. These differences are expected from the coker temperature difference; the Lummus overhead shows greater signs of being produced by pyrolysis.

The coker temperature used by CAER (500 °C) is lower than that tested by Lummus (538 to 649 °C); however, it is nearly within the range of 510 to 566 °C recommended⁷ in a review of the Lummus project for maximizing liquid yield in the Lummus CSCU. One apparently substantial difference between the operation of the two units was the much greater steam/feed ratio employed by CAER.

Task 3.2 - Economic Evaluation (CONSOL)

No work was performed on this task.

References

1. Catalytic, Inc., Wilsonville Advanced Coal Liquefaction R&D Facility, Technical Progress Report, "Run 246 with Wyodak Coal", DE86-000566, August 1985, p52.
2. Project Status Report for the Period 1 July - 30 Sept., 1992, Subcontract UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040.
3. Project Status Report for the Period 1 Oct. - 31 Dec., 1992, Subcontract UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040.
4. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Correlation of Microautoclave and ¹H-NMR Measurements of Coal Liquefaction Solvent Quality" *Fuel* 1986, 65, 526-532.
5. Neathery, J. K. (UK/CAER), letters to R. A. Winschel (CONSOL), January 15 and February 15, 1993.
6. Winschel, R. A.; Burke, F. P. "Recycle Oils from Fluid Coking of Coal Liquefaction Bottoms", *Energy & Fuels* 1989, 3, 437-443.
7. Daley, D. P. (Burns & Roe), letter to R. Hickey (DOE/PETC) "Contract No. DE-AC22-89PC88400, Subtask 43.01, Delivery of Revised Fluid Coking Test Data Review and Analysis Meeting Notes", May 23, 1989.

TABLE 1
CONDITIONS FOR SANDIA HYDROTREATMENT STUDIES

Sample No.	Hydrotreatment Conditions				
	Feed (c)	Catalyst	Temp., °C	WHSV (hr ⁻¹)	Pressure (psig)
5C-111903	-5 °C dewaxed Distillate	Pl-HTO	325	0.78	1000 (a)
5C-111907	-5 °C dewaxed Distillate	Pl-HTO	325	0.74	333 (a)
5C-121603	-5 °C dewaxed Distillate	Criterion 324	325	0.46	1000 (b)
5C-SC1	-5 °C dewaxed Distillate	composite	composite	composite	1000 (b)

(a) = Hydrogen only, no carbon monoxide or steam.

(b) = Equimolar CO/steam/H₂.

(c) = Run 262E V-1074, acetone dewaxed.

TABLE 2
PROPERTIES OF HYDROTREATED DISTILLATE SAMPLES

	Sample Number					
	5 (b)	5C (c)	5C-S-111903	5C-S-111907	5C-S-121603	5C-S-SC1
¹H-NMR						
Condensed Aromatics	11.3	16.5	7.0	14.4	11.7	12.0
Uncondensed Aromatics	3.6	5.1	3.3	5.2	5.3	4.6
Cyclic Alkyl	14.7	18.4	13.0	17.6	17.2	17.3
Alpha Alkyl	7.6	9.2	7.8	9.2	9.5	9.7
Cyclic Beta	15.8	17.4	22.4	17.8	18.7	18.8
Alkyl Beta	34.6	21.3	27.4	22.0	23.1	23.3
Gamma	12.3	12.1	19.2	13.8	14.4	14.0
Phenolic -OH						
Concentration, meq/g	0.44	0.56	0.12	0.38	0.24 (d)	0.28 (d)
ν , cm^{-1}	3306	3304	3316	3309	3313	3313
Solvent Quality (a)	63.8	81.1	89.2	88.4	90.1	90.0

- (a) = Solvent quality defined as wt % MAF conversion of Indiana V coal to THF solubles at 750 °F for 30 min and 1.5 S/C ratio.
- (b) = Original V-1074 Distillate
- (c) = -5 °C dewaxed V-1074 composite
- (d) = "as received" (wet) sample basis, moisture not determined. Other samples were received dry.

TABLE 3
DEWAXING OF V-1074 AT -35 °C IN
55/45 (vol %) ACETONE/MEK

Material	Dewaxed Oil	Wax
Yield, wt %	82.4	17.3
¹ H-NMR		
Condensed Aromatics	14.5	0.8
Uncondensed Aromatics	5.4	0.7
Cyclic Alkyl	16.9	3.4
Alpha Alkyl	9.0	2.7
Cyclic Beta	17.1	11.2
Alkyl Beta	23.5	68.1
Gamma	13.5	13.0
Phenolic -OH		
Concentration, meq/g	0.46	
ν , cm ⁻¹	3308	
Solvent Quality (a)	83.6	

(a) = Solvent quality defined as wt % MAF conversion of Indiana V coal to THF solubles at 750 °F for 30 min and 1.5 S/C ratio.

TABLE 4

SIMULATED DISTILLATION OF COMPOSITE WAXES FROM ACETONE
DEWAXING OF WILSONVILLE V-1074 DISTILLATE

Cumulative wt % Distillate	Boiling Point, °C	
	-5°C Composite Wax	-35°C Composite Wax
IBP	349	349
5	395	395
10	403	401
15	407	405
20	411	408
25	415	412
30	419	416
35	424	420
40	427	423
45	433	427
50	437	431
55	442	434
60	446	438
65	451	443
70	455	446
75	460	450
80	465	455
85	472	460
90	478	465
95	486	477

TABLE 5

**MICROAUTOCLAVE CONVERSIONS - BLACK THUNDER COAL - COMPOSITE SOLVENT WITH V-1074,
DEWAXED V-1074 AND HYDROGENATED DEWAXED V-1074**

Run No.	Temp. °F	Time Min	Recycle/ MF	COAL	RECYCLE					Conversion, %MAF		Comments
					Comp 1	wt. g	Comp 2	wt. g	Comp 3	wt. g	Coal ²	
19	824	5	1.04	BT	6.16 V-1074	2.18 V-130	0.34 V-1082	2.59	71.8	64.1	5-minute runs using the original V-1074 as the distillate portion of the recycle. Recycle/coal ratio variable. 824°F. Concentrations as in original Wilsonville composite solvent.	
14	824	5	1.51	BT	4.55 V-1074	2.33 V-130	0.36 V-1082	2.76	87.5	74.6		
12	824	5	2.3	BT	3.84 V-1074	3.00 V-130	0.46 V-1082	3.56	88.8	70.3		
20	824	5	1.04	BT	6.16 35°C DW	2.18 V-130	0.34 V-1082	2.59	76.6	68.4	Same as above but with dewaxed V-1074.	
16	824	5	1.51	BT	4.55 35°C DW	2.33 V-130	0.36 V-1082	2.76	89.0	76.0		
15	824	5	2.3	BT	3.84 35°C DW	3.00 V-130	0.46 V-1082	3.56	89.7	71.1		
21	824	5	1.04	BT	6.16 SC-1	2.18 V-130	0.34 V-1082	2.59	79.7	71.2	Same as above but with hydrogenated, dewaxed V-1074.	
18	824	5	1.51	BT	4.55 SC-1	2.33 V-130	0.36 V-1082	2.76	92.1	78.6		
27	824	5	2.3	BT	3.84 SC-1	3.00 V-130	0.46 V-1082	3.56	93.6	74.1		
11	824	15	2.3	BT	3.84 V-1074	3.00 V-130	0.46 V-1082	3.56	106.4	84.2	15-minute run with V-1074.	
8	824	30	1.51	BT	4.55 V-1074	2.33 V-130	0.36 V-1082	2.76	103.5	88.3	30-minute runs with V-1074 in Wilsonville composite solvent. Recycle/coal ratio variable.	
5	824	30	2.3	BT	3.84 V-1074	3.00 V-130	0.46 V-1082	3.56	109.5	86.7		
6	824	30	2.3	BT	3.84 V-1074	3.00 V-130	0.46 V-1082	3.56	109.0	86.3		
9	824	30	1.51	BT	4.55 35°C DW	2.33 V-130	0.36 V-1082	2.76	104.4	89.1	30-minute runs with dewaxed V-1074. Recycle ratio variable.	
7	824	30	2.3	BT	3.84 35°C DW	3.00 V-130	0.46 V-1082	3.56	108.8	86.2		
22	840	5	1.04	BT	6.16 SC-1	2.18 V-130	0.34 V-1082	2.59	82.7	73.9	5-minute runs, 840 °F, using V-1074 and hydrogenated, dewaxed distillate.	
23	840	5	1.04	BT	6.16 V-1074	2.18 V-130	0.34 V-1082	2.59	78.0	69.7		
25	824	5	1.5 ³	NONE	V-1074	2.33 V-130	0.36 V-1082	6.38	.	14.5	Blank Run - no coal - to measure IOM conversion.	
28	824	5	2.3 ²	NONE	V-1074	3.00 V-130	0.46 V-1082	6.61		37.1		
24	824	5	1.51	BT	4.55 V-1074	2.33 V-130	3.12		62.6	62.6	Replace V-1082 (Ashy Resid) with V-130 (Deashed Resid)	
26	824	5	1.51	BT	4.55 SC-1	2.33 V-130	3.12		71.8	71.8		
10	752	60	3.52	BT	2.50 Tetralin	7.00			81.4	81.4	Runs made to estimate the wax yield from Black Thunder Coal.	
13	752	120	3.52	BT	5.00 Tetralin	14.00			90.5	90.5		
17	752	120	3.52	BT	5.00 Tetralin	14.00 Catalyst	1.00		95.1	95.1		

¹ Residence time includes 2-minute heatup. All runs at 1500 psig (cold) H₂

² SO₃ - free ash basis

³ No coal charged, coal replaced by additional V-1082

TABLE 6
CONSOL ANALYSES OF CARBON-MONOXIDE-PRETREATED BLACK THUNDER COAL

Sample 1621-22-1B-UK1
(CAER Sample No. 2.1.1.1)

Analysis, Dry Basis Except as Noted	Feed Coal	Pretreated Coal
Wt % As-Received Moisture	22.40	5.42
Wt % Ash	6.69	6.30
Wt % Volatile Matter	-	53.46
Wt % Fixed Carbon	-	40.24
Heating Value, Btu/lb (Dry)	11,978	13,328
Wt % Carbon	70.32	74.45
Wt % Hydrogen	4.68	5.79
Wt % Nitrogen	1.04	1.10
Wt % Total Sulfur	0.50	0.39
Wt % Oxygen (Diff.)	16.74	11.97

Table 7. First Quarter 1993 Agglomeration Results

Run(a)	Feed Coal	Oil	Oil Dosage, wt % MF Coal	pH	pH Agent	Organic Recovery, wt %	Ash Rejection (b) (Dissolved and Physical), wt %	Physical Ash Rejection, (c) wt %	Ash Balance, (d) wt %	Prod. Moisture, wt %	
										Air-Dry	1Total (e)
B24	PBT	C1	14.1	6.0 (f)	None	99.7	4.3	2.3	98.1	7.1	28.5
B25H (g)	PBT	C1	16.1	5.5 (f)	None	99.8	16.1	0.5	84.4	1.4	41.7
A21	BS	P1	25.7	3.5 (f)	None	95.9	36.8	29.7	92.9	11.8	-
A22 (h)	OML	P1	14.4	5.2	None	99.3	45.5	24.3	78.8	46.0	-
A23	SC	P1	21.5	6.1	None	100.0	12.1	4.4	92.2	26.7	34.8
B19 (i)	ABZ	C1	96.6	8.2	None	100.0	NA	NA	NA	-	-
B20	ABZ	C1	53.9	1.0	H ₂ SO ₄	99.8	76.9	12.3	35.4	-	45.4
B21	ABZ	C1	21.2	1.0	H ₂ SO ₄	100.0	70.8	4.2	33.4	3.59	41.8
B22 (j)	ABZ	C1	20.8	1.0 (f)	H ₂ SO ₄	99.4	75.2	5.5	30.3	14.32	68.2
A18 (k)	BT	C1	42.3	5.6 (f)	None	100.0	16.0	5.9	89.9	14.53	27.4
A19 (k)	BT	C1	33.9	5.6 (f)	None	100.0	26.8	5.8	79.0	18.28	30.9
A20	BT	C1	34.3	5.6 (f)	None	100.0	17.9	4.0	86.1	25.14	32.2
B23H (m)	BT	C1	34.0	5.6 (f)	None	97.8	15.3	3.8	88.5	2.53	-
B16R	WAR	P2	26.2	2.5	H ₂ SO ₄	99.4	20.3	0.7	80.4	-	-
B17R	WAR	P2	48.5	1.0	H ₂ SO ₄	99.8	33.1	4.4	71.3	-	-
B15H	BT	C2	48.0	3.0	H ₂ SO ₄	97.3	17.3	1.7	84.4	-	-
B18H	BT	C3	45.2	5.6 (f)	None	98.9	10.3	0.8	90.6	-	-
B26H (m)	-	C4	-	7.0 (f)	None	100.0	48.7	0.1	51.4	53.4	-
B27H (m)	-	C4	-	13.1	NaOH	-	-	-	-	-	-
B28H (m)	-	C4	-	1.0	H ₂ SO ₄	96.8	-15.4 (n)	8.1	123.5	6.0	-

TABLE 7. FIRST QUARTER 1993 AGGLOMERATION RESULTS

TABLE 7. FIRST QUARTER 1993 AGGLOMERATION RESULTS (Continued)

Common conditions: 50°C, except as noted.

Coals: PBT = CO-pretreated Black Thunder, BS = Burning Star 2, OML = Martin Lake (old sample), SC = Spring Creek (old sample), ABZ = Argonne premium Beulah-Zap (ND) lignite, WAR = Wilsonville ashy resid (V-1082, instead of coal) BT = Black Thunder.

Oils: P1 = No. 6 fuel oil, C1 = V-1074 recycle distillate from Wilsonville Run 262, C4 = 75/25 wt % oil C1/V-1082 ashy resid from Wilsonville Run 262, C2 = 25/75 wt % oil C1/V-1082 ashy resid, C3 = 50/50 wt % oil C1/V-1082 ashy resid, P2 = white kerosine.

- (a) Run numbers with prefix A were made in the large vessel, those with prefix B were made in the small vessel, an H suffix indicates a high pressure run, an R suffix indicates ashy resid (instead of coal) was the feed to the run.
- (b) Based on feed ash which was not recovered in the product. Reported value may be larger than actual value due to unaccounted ash-SO₃.
- (c) Based on feed ash which was recovered in the solid reject (filter cake).
- (d) Ash balance does not include dissolved ash.
- (e) Determined on as-screened product (oily semisolid Run B20 product was rinsed, but not screened).
- (f) Measured at end of run.
- (g) Agglomerated at 97°C, reactor was then sealed and heated to 175°C for continuation of the run.
- (h) Cresylic acid (1.4 wt % as-received coal) was added as an agglomeration promoter prior to oil addition.
- (i) Cresylic acid (0.5 wt % as-received coal) was added as an agglomeration promoter.
- (j) Estimated.
- (k) Agglomerated at 97°C, cooled to 50°C before run termination.
- (l) Natural (unadjusted) slurry pH was not measured in every run.
- (m) Run temperature was 300°C.
- (n) Negative value results from excessive material balance.

TABLE 8
COKER OPERATING CONDITIONS AND YIELDS

Coker Overhead Sample No.	Coker Operating Conditions		Overhead Yield, % (Tentative)
	Steam/Resid Ratio, lb/lb	Temperature, °C	
B9301	4.39	500	43
SR-3	8.52	500	44
SR-4	12.34	500	46
SR-5	13.01	500	53

Source: Reference 5

TABLE 9
ANALYSIS OF COKER OVERHEADS AND FEEDSTOCKS

	B9301	SR-3	SR-4	SR-5	V-130	V-1082 (c)
Total Moisture, wt %	-	22.10	6.02	4.13	-	-
Total Ash, wt % Dry (a)	-	1.38	1.62	1.43	0.73	20.28 (16.04)
THF Insol. Organic Matter, wt % dry	-	0.21	0.02	0.12	-	16.8 (21.1)
THF Insol. Ash, wt % Dry (a)	-	0.43	0.04	0.29	-	-
Analysis of Dry THF Solubles, wt % (b)						
C	-	87.53	86.59	87.23	89.79	72.59
H	-	6.95	6.97	6.89	7.26	5.40
N	-	1.11	1.11	1.08	0.86	0.88
O (diff)	-	3.53	5.07	3.99	1.33	-1.08 (3.15)
S	-	0.05	0.04	0.03	0.03	1.93
Ash (a)	-	0.83	0.22	0.78	0.73	20.28 (16.04)
Phenolic -OH Anal. of Dry THF Solubles						
Concentration, meq/g	-	0.77	0.78	0.81	0.90	0.96
ν , cm^{-1}	-	3296	3295	3295	3298	3296
Proton Distribution of THF Solubles, % (d)						
Cond Arom	21.4	26.6	25.9	25.4	21.0	22.6
Uncond Arom	7.8	7.4	8.4	9.8	7.0	6.3
Cyclic Alpha	15.7	18.6	18.0	16.9	18.1	20.2
Alkyl Alpha	9.8	9.4	9.7	10.2	9.5	10.0
Cyclic Beta	12.6	13.7	13.1	12.9	14.4	14.5
Alkyl Beta	22.1	15.9	16.4	16.5	21.3	19.1
Gamma	10.7	8.3	8.5	8.4	8.6	7.3
Solubility Fractionation Analysis of THF Solubles						
Oils	80.7	73.0	77.8	76.9	71.6	59.2
Asphaltenes	12.4	17.2	16.3	16.1	21.7	25.0
Preasphaltenes	6.9	9.8	5.8	7.0	6.6	15.7
Solvent Quality Index (e)	75.5	83.3	81.4	79.5	81.8	85.4

- a) Total ash and sum of soluble and insoluble ash do not agree because of analytical uncertainties.
b) Analysis of V-130 and V-1082 are analysis of whole sample, i.e., not THF solubles.
c) Values in parentheses are based on SO_2 -free ash.
d) Analyzed in CDCl_3 solution.
e) cf. text.

TABLE 10
COMPARISON OF LUMMUS AND CAER COKER TESTS

10A - Coker Conditions and Yields

Coker	Run No.	Feedstock	Coker Conditions		Overhead Yield, wt %
			T ₂ °C	Steam/Feed Ratio	
Lummus	CSCU-8	W'ville 254 vac bottoms	544	0.34	44.5 (a)
CAER	SRC-3	W'ville 262E V-1082	500	8.52	44 (b)

(a) wt % of ash-free recovered material

(b) Tentative

10B - Feedstock Characteristics

Coker Run No.	Ash, wt % as Det.	wt % MAF (a)						Proton Dist., %			Calc SQ Index (c)
		C	H	N	S	O (diff)	Insol Org Matter	Arom	Cyclic Beta	Paraf (b)	
Lummus CSCU-8	15.4	88.1	6.5	1.0	2.6	1.8	9.2	29.5	14.6	25.8	82.6
CAER SR-3	16.0	86.5	6.4	1.0	3.8	2.3	25.1	28.9	14.5	26.4	85.4

(a) All analyses of CAER SR-3 feedstock calculated from SO₃-free ash

(b) Alkyl beta plus gamma

(c) cf. text

10C - Coker Overhead Characteristics

Coker Run No.	wt % MAF					Proton Dist, %			Calc SQ Index
	C	H	N	S	O (diff)	Arom	Cyclic Beta	Paraf	
Lummus CSCU-8	91.0	6.3	1.0	0.1	1.6	42.1	10.3	21.4	68.8
CAER SR-3	88.3	7.0	1.1	0.0	3.6	34.0	13.7	24.2	83.3

Modified Equilibrium Test

Figure 1. Solvent Quality vs Dewaxed Oil Yield,
Wilsonville Run 262 V-1074 Distillate.

Figure 2. Conversion of Black Thunder Coal to THF Solubles vs. Solvent/Coal Ratio.

Figure 3. Conversion of Total IOM to THF Solubles vs. Solvent/Coal Ratio.

APPENDIX 1

CONSOL Inc.

Research & Development
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February 4, 1993

Mr. Michael Peluso
LDP Assoc.
603 Fairview Avenue
Piscataway, NJ 08854

Dear Mike:

I examined the literature to estimate the potential wax yield from a liquefaction plant equipped with a dewaxing unit. The literature does provide some guidance, although it cannot provide a precise answer. It appears that 4 to 5% MAF yield is a reasonable estimate of potential wax make for a plant that processes Black Thunder coal. A draft of the report is attached. I would like to hear any comments you may have. The final version probably will be included in a monthly/quarterly report.

By the way, in case you did not know it, HRI tested Black Thunder coal in their 3 ton/day PDU in 1992. Their process oils were extremely waxy, similar to Wilsonville Run 262 oils. Filtration rates decreased late in the run; HRI thinks the waxes may have been at least partly responsible for the decrease.

Sincerely,

R. A. Winschel
Research Group Leader
Exploratory Research Group

/ls

cc: F. P. Burke
M. S. Lancet
G. A. Robbins
F. J. Derbyshire
E. B. Klunder
R. J. Kottenstette

bc: Technical Records (1621-22)

Introduction and Summary

A brief literature survey was performed to provide an indication of the paraffin contents of coals. It would appear that the paraffin content of a coal, as determined after, for example, a batch liquefaction experiment, is an upper limit for wax yield during continuous liquefaction. From the literature examined, several conclusions can be drawn: Liquefaction produces a greater paraffin yield than solvent extraction, supercritical extraction, pyrolysis, hydrous pyrolysis or hydropyrolysis. Clearly, liquefaction is the preferred way to determine the paraffin content of coal. Paraffin yields from liquefaction appear to be 4 to 6% MAF for most low-rank coals, 1 to 3% MAF for most bituminous coals and somewhat higher for sapropelic (boghead and cannel) coals. Normal paraffins appear to account for 60% to almost all of the total paraffins. The n-paraffins recovered typically range from about C_{16} to about C_{36} . In a liquefaction plant that produces a product with a boiling point below 650°F, paraffins smaller than about C_{20} (b. pt. = 649°F) would be taken out as net product and not processed in the dewaxing unit; larger paraffins would be processed in the dewaxing unit or recycled until they crack into the product range. Thus, it appears reasonable to project from the literature that the wax yield in a liquefaction plant equipped with a dewaxing unit that processes the entire distillable portion of the recycle oil could be 4 or 5% MAF for a plant processing Powder River basin subbituminous coal and could be 2% MAF for a plant processing Illinois basin or high-volatile bituminous Appalachian basin coal. Of course, actual yields would depend on plant design and operating conditions.

Relevant Literature

Yields from Liquefaction Tests

Youtcheff et al.⁽¹⁾ examined the alkanes in three bituminous coals. The liquefaction conditions were: 5 g coal, 18 mL tetralin, 400°C, 1h (no added pressure reported). After removal of tetralin and its products, the hexane-soluble product was loaded on an alumina column and alkanes (predominantly n-paraffins from C_{14} to C_{35}) were eluted with hexane. Alkane yields on a wt % dmmf coal basis were: Clintwood seam (VA), 0.80; Ohio No. 12A, 0.80; Blind Canyon (UT), 2.9. The authors found that Soxhlet extraction in benzene/ethanol only provided 10 to 17% as much alkanes, but the distribution of paraffins was the same as those from liquefaction.

Mudamburi and Given⁽²⁾ examined the waxes from three facies of a Utah boghead coal (King Cannel seam). The coal was liquefied in tetralin (7 mL/2.5 g coal) at 400°C and 7 MPa cold H₂ for 1 h. After removal of tetralin and its products, the hexane-soluble product was loaded on an alumina column, and alkanes (predominantly n-paraffins from C₁₄ to C₃₆) were eluted with hexane. The three samples gave alkane yields of 10.2, 6.2, and 5.4% dmmf. Soxhlet extraction of the same samples in pyridine yielded fatty acids, esters and ketones equal to about 75% of the alkanes found upon liquefaction.

Hayakawa et al.⁽³⁾ liquefied four coals in tetralin at 450°C for 1 h (other conditions were not specified). The n-paraffin yield was defined as the fraction of the IBP x 538°C product that partitioned into hexane in a hexane/DMSO mixture. Yields, on a wt % MF coal basis, were 4.6% for Wyodak coal, 5.3% for Taiheiyō coal, 5.2% for Wondoan coal and 1.5% for Illinois 6 coal. Paraffins ranged from C₁₀ to C₃₅. The authors note that the recycle solvent at the Brown Coal Liquefaction Plant has a paraffin concentration that approaches 20 wt %. The authors also note that this concentration is predicted from the paraffin content of the feed coal and the known cracking behavior of paraffins.

Dong et al.⁽⁴⁾ extracted Australian Wondoan coal vitrinite with benzene/ethanol at 200°C and with pyridine at 350°C and then hydrogenated the residue (335°C, 3 h, 10 MPa H₂, Adkins' catalyst). The hexane-solubles of the various extracts were individually separated on silica gel to produce saturates, which were then separated by urea adduction. The total yield of n-paraffins was 2.2 wt % daf (ca. C₁₆ to C₃₀) and the total yield of non-n-paraffin alkanes was 1.8 wt % daf.

Kolandaisamy et al.⁽⁵⁾ showed that hydrogenation yielded more paraffins than hydrous pyrolysis. They note that hydrogenation is the preferred method for determining the paraffin content of coal. Liquefaction was conducted without a solvent but with a sulfided Ni/Mo catalyst at 330°C for 16 h at 8 MPa cold H₂. The alkanes were separated by elution from alumina with n-pentane. Normal paraffins were obtained by urea adduction. Yields of n-paraffins from various Australian coals (apparently on an as-received coal basis) were: Yallorn, 1.7%; Bacchus Marsh, 3.0%; Loy Yang, 4.0%; Millmerran, 2.1%; Wongawilli (bit.), 0.4%; Bulli (bit.), 0.4%.

Stock and Wang⁽⁶⁾ extracted coals with pyridine and then liquefied the residues in tetrahydroquinoline/tetralin at 420°C and 1 h. The analytical scheme is not clearly defined; however, reported yields (apparently on an as-received coal basis) were: Millmerran, 2.8%; Illinois 6, 1.0%; Lower Kittanning (WV), <0.1%.

Calkins⁽⁷⁾ liquefied various coals in tetrahydroquinoline (1/1 solvent/coal) at 425°C and 2000 psi cold H₂ for 2 h. The reactions were catalyzed by Na₂S and FeS. The products were filtered in methylene chloride. After removal of the methylene chloride, the "polymethylene" ((CH₂)_n) content of was determined by ¹H-NMR. The yields of polymethylene (apparently on a wt% MF coal basis) were: Pittsburgh seam, 4.4%; Texas lignite, 6.6%; Wyodak, 5.1%; Emery (UT), 7.3%; Millmerran, 9.7%; Utah B seam, 7.1%; Lower Kittanning (WV), 16.4%. These yields agreed well with the yields of ethylene plus other hydrocarbon gases obtained from pyrolysis experiments at 600°C. The reader is cautioned that Calkins polymethylene yields are not the same as paraffin contents; rather they must be upper limits.

The naphtha product from Wilsonville Run 259G, produced from Pittsburgh seam coal, contains 19.3 vol % paraffins⁽⁸⁾. If one assumes that the weight percent is the same, then this translates to a yield of 3.8 wt % of the MAF coal. (Of course, these paraffins are too low boiling to be waxes.) Since the naphtha only accounted for 26.7 wt % of the crude liquid product, the total yield of paraffins must be higher. Unfortunately, the inspection tests conducted by Conoco on the product from Wilsonville Run 260D, produced from Black Thunder coal, included a combined analysis for paraffins and naphthenes⁽⁹⁾. The combined paraffins and naphthenes in the naphtha and jet fuel cuts (42.6 wt % of total crude liquid product) accounted for 17.7 wt % of the MAF coal (assuming vol % and wt % are the same).

As noted above, the Japanese Brown Coal Liquefaction Plant recycled an oil that had paraffin concentrations approaching 20 wt %⁽³⁾. The Exxon Donor Solvent process, a similar thermal process, operated with a recycle solvent containing 20 to 25% saturates⁽¹⁰⁾ when processing Illinois 6 bituminous coal. Note that this value represents saturates, including naphthenes, and not just paraffins. Recycle distillates from subbituminous coal operations in the Lummus ITSL and H-Coal processes contained 10 to 13 wt % n-paraffins, whereas the same stream from Lummus ITSL bituminous coal operations contained about 4 wt % n-paraffins⁽¹¹⁾.

Yields from Pyrolysis

The paraffin and olefin yields of different coals during low-temperature carbonization were examined by Comberiat et al.⁽¹²⁾. The combined paraffin and olefin yields, on a wt % dry coal basis, were: Pittsburgh seam (two counties), 1.2% and 0.8%; a Utah hvBb coal, 1.8%; a Colorado subbituminous coal, 1.0%; Texas lignite, 2.1%; West Virginia cannel coals (two), 7.7% and 8.6%.

Snape et al.⁽¹³⁾ treated several coals by various means and recovered paraffins by elution of the n-pentane solubles from silica gel. Coal treatments used, in the order of increasing paraffin yields, are: supercritical extraction with toluene at 400-420°C, Gray-King assay, fluid-bed pyrolysis, and fixed-bed hydropyrolysis. Paraffin yields from hydropyrolysis (on a daf coal basis) were: unidentified U.S. lignite, 10%; Linby (U.K. bit.), 1.1%. Daw Mill coal (U.K. bit.), which was only treated by supercritical extraction, gave a paraffin yield of 0.7% daf.

Nelson⁽¹⁴⁾ flash pyrolyzed three Australian coals and then hydrotreated the product tars. Normal paraffins were determined by GC analysis and, in some cases, gravimetrically after separation on alumina and silica (the two methods agreed to $\pm 10\%$). Substantially more paraffins were obtained after hydrotreating the tars, indicating that some of the paraffins were present as attached groups on other compounds. Yields after hydrotreatment, on a wt % MAF coal basis, were: Millmerran coal, 5.8%; Yallourn coal, 2.5%; Piercefield coal (bit.), 1.3%.

Definitions and Notes

Working Definitions

- hydrocarbon - a compound that contains carbon and hydrogen, but no other elements.
- saturated hydrocarbon (saturate) - a hydrocarbon that contains no aromaticity or multiple bonds, includes naphthenes and paraffins.
- naphthene - a saturated hydrocarbon that contains at least one ring.
- paraffin (alkane) - a saturated hydrocarbon that contains no rings, general formula C_nH_{2n+2} , includes normal paraffins and branched paraffins.
- normal paraffin (n-paraffin) - a straight-chain paraffin
- wax - defined by its provenance, in this case, one product of a dewaxing unit operating on a heavy distillate coal liquid stream, predominantly

composed of n-paraffins in the range C_{20} to C_{40} with lesser amounts of branched paraffins and other saturates, depending on purity.

Coal Rank

The coals discussed here are low-rank coals (subbituminous, lignite, or brown coal) except in those cases where another rank is specified, e.g., bituminous (bit.), hvBb, etc. or the coal is a well-known higher-rank coal, e.g., Pittsburgh seam, and except in those cases in which the coal is specified as originating from regions that produce no low-rank coal, e.g., IL, OH, WV, VA, UT.

References

1. Youtcheff, J. S.; Given, P. H.; Baset, Z.; Sundaram, M. S. *Org. Geochem.* 1983, 5(3), 157-164.
2. Mudamburi, Z.; Given, P. H. *Org. Geochem.* 1985, 8(3), 221-231.
3. Hayakawa, K.; Yoa, T.; Kurachi, K.; Chikata, T. *Fuel Proc. Technol.* 1987, 17, 145-153.
4. Dong, J.-Z.; Katoh, T.; Itoh, H.; Ouchi, K. *Fuel* 1987, 66, 1337-1346.
5. Kolandaisamy, M.; Batts, B. D.; Smith, J. W. *Fuel* 1990, 69, 1323-1325.
6. Stock, L. M.; Wang, S.-H. *Energy & Fuels* 1990, 4, 335-336.
7. Calkins, W. H. *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 1983, 28 (5), 85-105.
8. Kramer, R. L. In DOE Report No. DOE/PC 89883-24, June 1991.
9. Kramer, R. L. In DOE Report No. DOE/PC 89883-34, November 1991.
10. Plumlee, K. W.; Zaczepinski, S.; Hu, A. Y., In "Proceedings of the Seventh Annual EPRI Contractors' Conference on Coal Liquefaction", EPRI Report No. AP-2718, p. 12-1, 1982.
11. Winschel, R. A.; Robbins, G. A.; Burke, F. P. *Fuel* 1987, 66, 654-660.
12. Comberiati, J. R.; Karr, C., Jr.; Childers, E. E.; Mapstone, J. O., Jr.; Estep, P. A. *J. Inst. Fuel* 1970, 43, 147-150.
13. Snape, C. E.; Ladner, W. R.; Bartle, K. D. *Fuel* 1985, 64, 1394-1400.
14. Nelson, P. F. *Fuel* 1987, 66, 1264-1268.

APPENDIX 2

AGGLOMERATION TESTS WITH ARGONNE PREMIUM LIGNITE

INTRODUCTION

Mr. Karl Vorres of Argonne National Laboratory supplied 125 g of premium Beulah-Zap lignite from North Dakota for agglomeration testing. The coal, which was -100 mesh, was provided in 25 ampules of 5 g each. Agglomerates were produced and then sealed into an airtight, N₂-purged sample bag while wet. The samples will be analyzed at Argonne by thermogravimetric analysis to determine the amount of surface and macropore moisture. A comparison of the feed and product coals is expected to show whether or not agglomeration^d dewatered the coal.

EXPERIMENTAL

Agglomeration of the coal was performed in a modified 300 mL Parr benchtop stirred autoclave using No. 6 fuel oil as the agglomerant. The autoclave is equipped with a six-bladed disk impeller and a four-plate baffle and is stirred at 2300 rpm. This autoclave allows us to use a coal charge of about 20 to 45 g, whereas our standard agglomeration vessel^{1,2} requires about 125 g of coal for a test. The smaller vessel was useful because it allowed more runs to be made with the limited amount of coal supplied. Experimental procedures are described in more detail elsewhere.^{1,2}

The equations used for organic recovery and ash rejection and balance calculations are given below.

Ash Rejection (Dissolved and Physical) = Ash Rejection (Unrecovered Product Basis) =

$$[(M_1 - M_2)/M_1] \times 100\%, \text{ where}$$

M₁ = Mass of Ash Charged (from all sources such as coal, oil, etc.), and M₂ = Mass of Ash in Agglomerate Product.

Physical Ash Rejection = Ash Rejection (Recovered Reject Ash Basis) =

$$(M_3/M_1) \times 100\%, \text{ where}$$

M_1 = Defined as above, and

M_3 = Mass of Ash Recovered in Solid Reject.

Ash Balance (Excluding Water-Soluble Ash) = $[(M_2 + M_3)/M_1] \times 100\%$, where

M_1 , M_2 , and M_3 are defined as above. Note that these three quantities are related by

Ash Balance = Physical Ash Rejection - Ash Rejection (Dissolved and Physical) + 100%.

Organic Recovery = $\{1 - [(M_4 - M_3)/(M_5 + M_6)]\} \times 100\%$, where

M_4 = Mass of Dry Reject,

M_5 = Mass of MAF Coal, and

M_6 = Mass of (Ash-free) Oil.

RESULTS AND DISCUSSION

Analyses of the feed coal are given in Table 1.³ Conditions used for the agglomeration tests are given in Table 2. Four tests were made (Runs B19 through B22), and the last two produced agglomerates. One initial difficulty we encountered was that we significantly overestimated the amount of oil required to produce large agglomerates. The dosage was based on our recent work with Black Thunder subbituminous coal, which was the only coal we had agglomerated in the small vessel. Run B19 was made at a natural slurry pH of 8.2, and with cresylic acid promoter, but the coal did not agglomerate. Additional doses of oil were added during the run and the final oil dosage is impractically high. The second run (B20) was made at a pH of 1. In that run, we obtained a gummy oil/coal phase and a distinct water/mineral phase. We separated and filtered the water phase and obtained 12% physical ash rejection. The semisolid oily phase was weighed and sampled for moisture and ash determination. In this particular run, it appears that normal agglomeration would have occurred, had a smaller oil dosage been used.

After the two unsuccessful runs, we decided to operate at conditions approximating those reported by others for agglomeration of Beulah-Zap lignite⁴ (pH of

about 1 and a much lower oil dosage). Agglomeration was successful at these conditions in the third and fourth runs. In the fourth run (B22), we allowed about three hours for the slurry to agglomerate at natural pH (about 8). When it did not, we subsequently added a small additional quantity of oil, and later added H_2SO_4 to adjust the pH to 1 (estimated). A few minutes after acid addition, agglomeration occurred. We terminated the fourth run before the agglomerates had adequate time to grow to the larger size obtained in the third run. The diameter of the agglomerates in the third run was estimated to be 1 mm, whereas the agglomerates from the fourth run were only about 0.25 mm in diameter.

The agglomerates from Runs B21 and B22 were rinsed thoroughly with deionized water over a 48 mesh Tyler screen. They were shaken to remove as much surface moisture as possible and placed on aluminum foil for weighing. After they were weighed, an aliquot of the surface-wet agglomerates was weighed into a Zip-Loc bag. The bag was purged with nitrogen and sealed. The sealed Zip-Loc bag was placed into a trilayer bag and heat-sealed for shipment to K. Vorres at Argonne. The remaining agglomerates were weighed, allowed to air-dry overnight (about 16 hours), and reweighed to determine the moisture loss from air drying. The air-dry moisture content was then determined on a sample of the air-dried product agglomerates. The as-screened (or total) moisture content of the product agglomerates was obtained by combining the moisture loss from air drying with the air-dry moisture content. The as-screened and air-dry moisture contents of the larger-sized product agglomerates are lower than those of the smaller-sized agglomerates, though other factors may have contributed to the moisture differences (presence of cresylic acid, the way the run was conducted, etc.). This trend is expected, however, from experience and considering that retention of water by capillary effects should be lower as agglomerate size increases. The air-dry moisture content of 3.6% in the Run B21 product is much lower than that of the as-received lignite (32.2%).³ The oily semisolid from Run B20 had a high moisture content of 45.5%, in contrast. This material was not returned to Argonne.

Although the main objective of these four experiments was to determine dewatering effects, it is also of interest to look at deashing. Agglomeration provided about 5% physical deashing in Runs B21 and B22. It is not clear why physical ash rejection was apparently higher (12%) in Run B20, in which there was phase

separation, but not agglomeration. In Runs B20, B21 and B22, a considerable amount of ash was dissolved in the low-pH water, giving about 70% total ash rejection in each of these runs.

Although cresylic acid was found in previous work to successfully promote agglomeration of Texas lignite,² its effect on agglomeration of Beulah-Zap lignite is unclear. It appears that pH adjustment was required to successfully agglomerate the Beulah-Zap lignite, though the minimum adjustment required is unknown.

REFERENCES

1. Quarterly Technical Progress Report, Period October 1 Through December 31, 1992, Subcontract UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040 (report in preparation).
2. Robbins, G. A.; Winschel, R. A.; Amos, C. L.; Burke, F. P. "Agglomeration of low-rank coal as a pretreatment for direct coal liquefaction", *Fuel* 1992, 71, 1039-1046.
3. Vorres, K. S. "Users Handbook for the Argonne Premium Sample Program", Report No. ANL/PCSP-89/1, Argonne National Laboratory, Oct. 1, 1989.
4. Timpe, R. C.; DeWall, R. A.; Potas, T. A. "Cleaning and Dewatering of Low-Rank Coal by Oil Agglomeration", *Coal Prep.* 1992, 11, 1-10.

TABLE 1
ANALYSES OF PREMIUM BEULAH-ZAP LIGNITE USED FOR AGGLOMERATION FEED³

Analysis	Result
Moisture, wt % as-received	32.24
Heating Value, Btu/lb as-received	7454
Ash, wt % dry	9.72
Volatile Matter, wt % dry	44.94
Carbon, wt % dry	65.85
Hydrogen, wt % dry	4.36
Nitrogen, wt % dry	1.04
Total sulfur, wt % dry	0.80
Chlorine, wt % dry	0.04
Oxygen (diff), wt % dry	18.19
Sulfur Forms, wt % dry	
Pyritic	0.14
Sulfate	0.03
Organic	0.63

TABLE 2

CONDITIONS AND RESULTS FOR AGGLOMERATION OF ARGONNE PREMIUM LIGNITE

Run	Slurry Conc., wt % as-received	Oil Dosage, wt % MF Coal	pH	pH Agent	Organic Recovery, wt %	Ash Rejection* (Dissolved and Physical), wt %	Physical Ash Rejection ^b , wt %	Ash Balance ^c , wt %	Prod Ash ^d , wt % MF	Prod. wt % Moisture	
										Alr-Dry	Total
B19	18.7 ^e	96.6	8.2	None	100.0	NA	NA	NA	NA	-	-
B20	15.8	53.9	1.0	H ₂ SO ₄	99.8	76.9	12.3	35.4	2.02	-	45.4
B21	15.8	21.2	1.0	H ₂ SO ₄	100.0	70.8	4.2	33.4	2.33	3.59	41.8 ^f
B22	15.9 ^g	20.8	1.0 ^g	H ₂ SO ₄	99.4	75.2	5.5	30.3	2.23	14.32	68.2 ^f

Common Conditions: No. 6 fuel oil, 50°C

- a) Based on feed ash which was not recovered in the product (see text).
b) Based on feed ash which was recovered in the solid reject (filter cake) (see text).
c) Ash balance does not include dissolved ash (see text).
d) Oil is included in product weight. Ash contents would be higher on an oil-free basis.
e) Cresylic acid (0.5 wt % as-received coal) was added as an agglomeration promoter.
f) Determined on as-screened product.
g) Estimated.

APPENDIX 3 //

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January 29, 1993

Dr. Richard A. Winschel
CONSOL, Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129-9566

Dear Dr. Winschel:

Please find enclosed a research report "Column Flotation of Black Thunder Coal" by Bogdan J. Slomka and James L. Pollard. This report describes our exploratory column flotation tests with Black Thunder coal. Despite a very limited number of tests which we could perform, given the size of coal sample available, we were able to approach the optimum range of flotation conditions and to identify several potential problems associated with cleaning of this coal by column flotation. I have little doubt that further improvements in the flotation efficiency are not only possible but feasible through further optimization of the column operating conditions. Feed slurry preparation procedures and water quality requirements also might have to be addressed.

Should you need any more information regarding the work performed, please call me at (515) 294-1028. I also would be grateful for any comments you might have.

Sincerely,

Bogdan J. Slomka
Associate Scientist

Enclosure

xcs: G. A. Robbins
J. L. Pollard
W. H. Buttermore

COLUMN FLOTATION OF BLACK THUNDER COAL

Research Report

November 5, 1992 - December 12, 1992

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Date Transmitted: January 1993

Prepared for: CONSOL Inc.
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COLUMN FLOTATION OF BLACK THUNDER COAL

Objective

The purpose of this work was to test the applicability of advanced column flotation to cleaning of Black Thunder subbituminous coal.

Introduction

This exploratory work was performed at the Iowa State University (ISU) Coal and Mineral Processing Facility during the period November 5th through December 12, 1992. Column flotation tests were performed with as-received -200-mesh coal and with ultra-fine ball-milled feed. The quantity of coal sample allowed for only a limited number of tests. Column flotation operating parameters were selected based on earlier successful flotations of ultrafine Pittsburgh Seam and Illinois No. 6 coals.

In general, the as-received minus 200-mesh sample of Black Thunder coal behaved rather poorly during column flotation. It required relatively large dosages of collector to form a stable froth. Even then, however, we were unable to prevent the loss of combustibles reporting in substantial quantities to the refuse stream. High recoveries of combustibles, but at low or moderate rejections of ash, were obtained only when deionized water was used for flotation. Ball-milling of Black Thunder coal to ultrafine sizes led to further improvements in flotation performance. The best cleaning results obtained for the ball-milled feed were: 79.2% wt. recovery of combustibles at 42.0 % wt. ash rejection, 4.7% wt. clean product ash content, and 12.4% wt. ash content of the refuse.

Sample Characterization and Preparation

A 4.7-kg sample of Black Thunder coal was received at Ames Laboratory on November 5, 1992. The coal was riffled into several aliquots to allow for ash and particle size distribution analyses and three flotation runs, two of them with as-received minus 200-mesh coal and one with ball-milled coal. Wet screening analysis was performed to determine particle size distribution for size range between 212 and 5 microns. ASTM standard method D-2415-66 was followed for ash content analyses. The as-received sample contained 21.3% wt. moisture (on as-received basis) and 6.5% wt. ash (on dry basis). Table 1 shows ash and particle size distribution data based on wet screening of as-received Black Thunder coal. To more accurately determine the particle size distribution below 75 microns laser diffraction measurements were performed using a Northrup Leeds Particle Size Analyzer. The results are shown in Table 2. Two data points from the wet screening analysis (25-micron and 5-micron cumulative finer) were used as a reference in the interpretation of diffraction results. Figures 1 and 2 show cumulative size distributions for as-received Black Thunder coal sample determined by wet screening and by laser diffraction, respectively.

Table 1. Particle Size Analysis by Wet Screening for Black Thunder Coal.

<u>Particle Size</u> (microns)	<u>Weight %</u> (dry basis)	<u>Cumulative Finer</u> (Wt. %, dry)	<u>Ash Content</u> (Wt. %, dry)	
			Indiv.	Cumul.
-212 +150	1.3	100.0	6.3	6.4
-150 + 75	5.6	98.7	4.5	6.4
- 75 + 45	24.5	93.1	4.7	6.5
- 45 + 25	13.1	68.6	5.5	7.1
- 25 + 5	16.8	55.5	5.8	7.5
- 5	38.7	38.7	8.3	8.3

Table 2. Particle Size Analysis by Laser Diffraction for Black Thunder Coal.

<u>Particle Size</u> (microns)	<u>Weight %</u> (dry basis)	<u>Cumulative Finer</u> (Wt. %)
-212 +150	1.3	100.0
-150 + 88	4.6	98.7
- 88 + 75	1.0	94.1
- 75 + 62	9.7	93.1
- 62 + 44	5.8	84.4
- 44 + 31	19.1	78.6
- 31 + 25	4.0	59.5
- 25 + 22	1.7	55.5
- 22 + 16	3.9	53.8
- 16 + 11	5.0	49.9
- 11 + 7.8	1.7	44.9
- 7.8 + 5.5	3.8	43.2
- 5.5 + 5.0	0.7	39.4
- 5.0 + 3.9	1.0	38.7
- 3.9 + 2.8	2.0	37.7
- 2.8 + 1.9	1.1	35.7
- 1.9	34.6	34.6

Figure 1. Cumulative weight percent versus particle size for Black Thunder as-received coal.

Figure 2. Particle size analysis by laser diffraction for Black Thunder as-received coal.

Methods

Flotation tests were carried out in a 2-inch diameter, 20-foot tall, laboratory-scale countercurrent column equipped with digital control of critical operating parameters. The slurry feed point was located 6 feet below the top of the column. Different column control strategies were used including fixing pressure differentials within the froth cleaning zone and manipulation of flow ratios. Figure 3 shows the overall configuration of the column components. Column flotations were performed with both as-received (minus 200-mesh) and ultrafine (minus 5-micron) Black Thunder coal. For these tests, coal was suspended in water at 4.0% wt. solids loading and continuously fed into the column at a rate of 200 ml/minute. Methyl-isobutyl-carbinol (MIBC) was used as a frother at a dosage of 2.0 or 4.0 lb per ton of coal processed. No. 2 fuel oil was used as a collector at a dosage of 2.0 or 4.0 lb/ton of coal. Both flotation reagents were introduced in form of an aqueous emulsion into the feed line downstream of the coal slurry feed pump. Only after stable operation of the flotation column was established, e.g., after 30 minutes of uninterrupted operation, samples of froth and corresponding samples of tailings were simultaneously collected, usually for a period of 5 minutes. Samples of froth and tailings were quantitatively transferred into Buchner funnels, filtered on a No. 5 Whatman filter paper, and dried at 105° C for 6 hours. After drying and weighing, approximately 10-g aliquots were riffled out for moisture and ash content analyses.

For all flotation tests, ash rejection results were calculated using the following formula:

$$\text{Ash Rejection (Wt.\%)} = \frac{\text{Tailings Ash (g)}}{\text{Tailings Ash (g)} + \text{Float Ash (g)}} \times 100\%$$

To assess the sharpness of separation achieved in flotation tests, a separation index (SI) was used, defined as follows:

$$\text{SI} = \frac{\text{MAF Recovery} \times \text{Rejection} - \text{MAF Recovery} \times (100 - \text{MAF Recovery})}{100}$$

where the term rejection is ash rejection. The Separation Index (SI) permits comparison of tests which achieve different recoveries and rejections by combining these factors in a single measure. SI can assume values from -25 to 100. For an ideal separation in which all the combustible material reports to the clean product and all the ash is rejected to the tailings stream, the separation index is equal to 100. The separation index is equal to zero when the fraction of combustible material reporting to the tailings stream is equal to the ash rejection

value. This case is exemplified by a feed sample "perfectly" riffled into two identical aliquots. Negative SI values are obtained, for example, ash reports preferentially to the clean product stream.

Figure 3. Overall Configuration of Instrumented Flotation Column.

Results

Flotation Test No. BT11-14.

A 1.6-kg sample of as-received minus 200-mesh Black Thunder coal was slurried with water to form a 4.0% wt. solids loading feed slurry. Raw, untreated water which is normally in supply at the ISU Coal and Mineral Processing Facility was used in this test for both feed slurry preparation and countercurrent wash. The operating parameters applied were:

feed rate: 200 ml/min.;
 frother (MIBC) dosage: 2.0 lb/ton;
 countercurrent water wash rate (CCW): 200 ml/minute;
 aeration rate: 1.4 l/minute.

No collector was used in this test. Column performance was controlled by fixing hydrostatic pressure differential within the froth cleaning zone. Initially, the pressure differential was set to 15 inches of water column across a two-foot distance measured from the feed point upward. During the test, no gradient of color of the column's contents (a quick indication of column performance) from the feed point to the base of column could be observed. A dark and uniform color indicated substantial losses of combustibles to the refuse stream. Three other different settings of the pressure differential were tested, i.e. 5.0, 9.0, and 12 in. H₂O/foot, resulting in no improvement in the flotation performance. Two sample pairs of froth and corresponding tailings were collected during this test, one at pressure differential of 7.5 in. H₂O/foot (sample No. 1) and one at 12 in. H₂O/foot (sample No. 2) - Table 3.

Table 3. Column Flotation of Minus 200-Mesh Black Thunder Coal.

Sample No.	Ash ^b (Wt.%)	Coal Recovery ^a (Wt.%)	Ash Rejection ^b (%)	Separation Index
Froth 1	6.6	61.1	36.3	-1.6
Tailings 1	6.2			
Froth 2	7.5	54.1	44.3	-0.9
Tailings 2	7.3			
Feed prior to flotation	6.4	-	-	-
Feed at end of test	7.6	-	-	-

^a moisture- and ash-free basis; ^b moisture-free basis

Low recoveries of moisture- and ash-free (MAF) coal were obtained. The SI values indicated a complete lack of selectivity in the separation of ash from combustibles. An observation was made that the ash content of feed coal increased with time of contact of coal with the raw water used in this test. The quality of water was identified as a possible reason for the poor flotation behavior. The dissolved nonvolatile solids content of the raw water, determined for water sampled on 11/14/92, was 0.7 g/l.

Flotation Test No. BT11-28.

A 1.0-kg sample of as-received minus 200-mesh Black Thunder coal was slurried with deionized water to form a 4.0% wt. solids loading feed slurry. The following operating parameters were applied: feed rate: 200 ml/min.; countercurrent water (deionized) wash rate: 200 ml/min.; MIBC dosage: 2.0 lb/ton; air rate: 1.4 l/minute. This column flotation test was performed in three stages, each at different column settings:

	Collector Dosage (lb/ton)	Pressure Differential (in. H ₂ O/foot)	Comment
STAGE 1:	0	12	weak froth
STAGE 2:	4	7.5	stable froth
STAGE 3:	4	9.0	stable froth

During the first stage of this test no collector was used. The froth was easily broken by the countercurrent water spray resulting in a fluctuating froth height of less than about 8 inches. Consequently, through most of this stage of flotation, the column was operated at or near flooding condition. The very high MAF coal recovery of 99.5% wt., Table 4, was obtained at a very low ash rejection of 1.1 percent. The SI value of 0.6 indicated an inefficient separation of combustibles from ash.

For the second and third stage of this flotation test No. 2 fuel oil was used as a collector at a dosage of 4.0 lb/ton of coal. A distinct gradient in the column contents' color from the feed point to the base of column was observed indicating little or no losses of combustibles to the tailings stream. High coal recoveries from 96.8 and 92.4% wt. were obtained at somewhat better but still low ash rejections of 6.5 and 8.8 percent for stage 1 and 2, respectively.

From comparison of the results for tests BT11-14 and BT11-28 it appears that the improved quality of water used in test BT11-28 is responsible for the increased ash rejections and, especially, for the high recoveries of combustibles.

Table 4. Column Flotation of Minus 200-Mesh Black Thunder Coal.

Sample No.	Ash ^b (Wt.%)	Coal Recovery ^a (Wt.%)	Ash Rejection ^b (%)	Separation Index
STAGE 1:				
Froth	5.6	99.5	1.1	0.6
Tailings	11.4			
STAGE 2:				
Froth	5.6	96.8	6.5	3.2
Tailings	11.0			
STAGE 3:				
Froth	5.8	92.4	8.8	1.1
Tailings	7.3			

^a moisture- and ash-free basis

^b moisture-free basis

Flotation Run No. BT12-6.

A 2-kg sample of minus 200-mesh Black Thunder coal was ball-milled at 350 r.p.m. for 5 minutes in a 1-gallon capacity Union Process stirred ball mill. The mill was charged with 40% wt. solids loading slurry of as-received minus 200-mesh Black Thunder coal in deionized water. A mixture of 75% wt. 3/16-inch and 25% wt. 1/8-inch diameter stainless steel grinding media was used. Wet screening analysis showed that 91.4% wt. of the ball-milled product was less than 5-micron in diameter while all of the product passed a 25-micron screen.

Prior to column flotation, the ball-milled slurry was diluted with deionized water to 4.0% wt. solids loading. The column operation was controlled by fixing the partition of the column's output volume into volume of froth and volume of tailings. In an attempt to find optimum flotation conditions, this column flotation test was carried out at 5 stages, each at different column settings - Table 5.

Table 5. Column Settings for Flotation Test No. BT12-6.

	Partition Ratio (% vol.)	Reagent Dosage <u>MIBC</u> <u>FO</u>		CCW (ml/min)	Comment
STAGE 1:	49	2.0	0	100	weak froth
STAGE 2:	49	2.0	2.0	100	stable froth
STAGE 3:	68	4.0	2.0	140	stable froth
STAGE 4:	44	4.0	2.0	140	stable froth
STAGE 5:	29	4.0	2.0	140	stable froth

The partition ratio in Table 5 is expressed as froth volume percent. Deionized water was used for the countercurrent water wash and in the preparation of the frother and collector emulsion. Feed rate was 200 ml/min.; aeration rate was 1.70 l/minute; MIBC was used as the frother; and No. 2 fuel oil (FO) was used as a collector. Table 6 shows the results of the flotation run No. BT12-6 for each of the column settings.

Table 6. Column Flotation of Ultrafine Black Thunder Coal. Run No. BT12-6.

Sample No.	Ash ^b (Wt.%)	Coal Recovery ^a (Wt.%)	Ash Rejection (%) //	Separation Index (%)
Froth 1 Tailings 1	6.4 5.8	66.1	30.4	-2.3
Froth 2 Tailings 2	7.2 15.6	82.7	32.5	12.6
Froth 3 Tailings 3	5.4 15.7	97.8	7.0	4.7
Froth 4 Tailings 4	5.1 14.6	87.9	30.0	15.7
Froth 5 Tailings 5	4.7 12.4	79.2	42.0	16.8

^a moisture- and ash-free basis

^b moisture-free basis

The addition of the collector in stage 2 significantly improved the flotation performance over stage 1, Table 6, in terms of coal recovery, ash rejection, and froth stability. Stages 3 through 5 were conducted to study the effect of the volumetric partition ratio on the flotation performance. The data in Tables 5 and 6 show that a decrease in the froth volume percent from 69 to 29 leads to improved separation of combustibles from ash, despite a decrease in recovery. The SI value increased from 4.7 to 16.8. In the best case, stage 5, 42.0 percent of ash was rejected at 79.2% wt. MAF coal recovery and 4.7% wt. ash content of the clean product.

The authors believe that additional improvements in the column flotation of ultrafine Black Thunder coal can be achieved by further optimization of process variables including aeration and countercurrent water wash rates, volumetric partition ratio, solids loading of the feed, and dosage of flotation agents.

Conclusions

1. The quality of water used for feed preparation and countercurrent wash is important. Poor yield and grade of clean product resulted when raw untreated water was used for the flotation of as-received Black Thunder coal.
2. High recoveries of combustibles, but at low ash rejections, can be obtained by column flotation of as-received Black Thunder coal when deionized water is used for the preparation of the feed, flotation reagent emulsions, and for the countercurrent wash.
3. A relatively large amount of collector is needed to obtain a stable froth with this coal.
4. The overall recovery and grade of the clean product are significantly higher for the ball-milled feed compared to the as-received minus 200-mesh coal.
5. For the ball-milled Black Thunder coal feed, better separations of combustibles from ash are obtained at low volumetric froth-to-tailings partitions.

Recommendations for Future Research

1. Further optimize operating conditions for the column flotation of Black Thunder coal.
2. Determine water quality requirements.
3. Determine grinding requirements for Black Thunder Coal.

END

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