1

o

f

2

MAR 17 1994
A-2
2

DOE/PC/91040-32

**ADVANCED DIRECT LIQUEFACTION CONCEPTS
for PETC GENERIC UNITS****Quarterly Technical Progress Report
for Period July 1993 through September 1993**

by

**University of Kentucky
Center for Applied Energy Research****Sandia National Laboratories****CONSOL Inc.****LDP Associates****November 1993****Prepared for****The U. S. Department of Energy****Under Contract No.****DE-AC22-91PC91040****DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER**DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED** 870

INDEX

INDEX	ii
SUMMARY	1
SECTION ONE - UK/CAER	1-1
WORK PERFORMED	1-2
TASK 1.1 LABORATORY SUPPORT (UK/CAER)	1-2
TASK 2.1.1 CO PRETREATMENT (UK/CAER)	1-7
Coal Reactions with Recycle Oil and Shell 324 at 415 °C	1-7
Coal Reactions in the Presence of V-1074 Distillate at 440 °C	1-8
Reaction of Coal with Recycle Oil at 440 °C	1-9
CO-Pretreatment	1-11
Microscopy of Water-Insoluble Products	1-14
TASK 2.3.1 IRON BASED DISPERSED CATALYSTS (UK/CAER)	1-18
Characterization and Testing of Promoted Sulfated Hematites	1-18
Characterization	1-18
Catalytic Activity	1-19
Catalytic Activity in V-131B from Run 258	1-23
Fe and Mo Impregnated Coal	1-31
Impregnated Coal Preparation	1-32
XPS Analysis	1-33
Surface Composition	1-33
Chemical Bonding of the Elements on the Surface	1-37
Thickness of the Surface Layer	1-41
TASK 4.0 TECHNICAL ASSESSMENT-Process Options	1-46
Assumptions	1-46
"Nil Reactor"	1-46
Plant Location	1-48
Resid Recycle Around 2nd-Stage Reactor	1-48
Impact of Changing Reactor Size	1-50
Low C ₁ -C ₃ Gas Make	1-51
Modification to Solids/Liquid Separation Technique	1-52

Increasing Residence Time	1-56
Replacing 1st-Stage Dispersed Catalyst	1-57
CO-Pretreatment	1-58
Oxygen Removal as CO ₂ Rather than as Water	1-62
Increased Slurry Time	1-63
Optimization of Coal Grinding	1-63
Other Options	1-64
Summary	1-64
REFERENCES	1-65

SECTION TWO - CONSOL

TASK 1.2 LABORATORY SUPPORT	1
Summary	1
Discussion	1
TASK 2.1.2.1 PRETREATMENT WORK AT CONSOL - DEWAXING	3
Summary	3
Discussion	4
Resid Conversion	4
Effect of Temperature on Conversions	5
Effect of Hydrogen Pressure on Microautoclave Conversions	8
Mo-Free Ashy Resid	8
Distillate/Resid Ratio	10
Dewaxing Texas-Lignite-Derived Distillate	11
Effect of Distillate Dewaxing and Hydrotreatment	12
Distillation Fractions of V-1074	13
Preheater Simulation	13
TGA Determination of Resid Conversion	14
TASK 2.1.2.2 PRETREATMENT WORK - AGGLOMERATION	16
Summary	16
Discussion	17
Martin Lake Lignite and Agglomeration Results	17

Agglomeration Tests with Burning Star 2 and Kemmerer Coals	19
McKinley Coal Analysis and Agglomeration Results	20
Empirical Regressions for Predicting Agglomeration	20
CO-Pretreated Coal Slurry	22
REFERENCES	24
SECTION THREE - SANDIA NATIONAL LABORATORIES	
TASK 1.3 LABORATORY SUPPORT	1
TASK 2.1.3 SOLVENT PRETREATMENT	3
TASK 2.3.3 CATALYST STUDIES	8
SECTION FOUR - LDP ASSOCIATES	
TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT	
Baseline Economic Assessment	1
Fluid Coking	1
New Moly-free Process Solvent	1
Dewaxed Oil Hydrotreating	2
Consol Microautoclave Tests with DWO's	2
Separate Dewaxing of V-1074 Fractions	2
Steady State Solvent Dewaxing Unit Balance	3
Economic Assessment of Dewaxing	3
DOE Contractors Conference & Workshop	4

SUMMARY

TASK 1.1 LABORATORY SUPPORT (UK/CAER)

A test has been established to assess the activity of various catalysts in Wilsonville process solvent from Run 258K, which contained iron but no molybdenum, since the molybdenum added during Run 262E had some observable effect on liquefaction. The effects of freshly added catalyst could be more readily observed without the background interference of the molybdenum. The test, applied to several different catalysts, was run at 440 °C and 22 minutes, reaction conditions which gave the same total resid conversion found at Wilsonville in Run 262E (namely 24% conversion).

Liquefaction experiments were performed in duplicate, and the products were then analyzed by either Soxhlet extraction or distillation. The reaction products were divided by solubility using THF and pentane. Total THF conversion of the coal is determined from the Soxhlet extraction data. The analysis by distillation follows the method of ASTM D-1160, wherein the products are distilled in a single stage, short cooling zone distillation apparatus at a reduced pressure of 1 mm to 50 mm to yield a distillate fraction with an atmospheric equivalent final boiling point temperature of 1050 °F. Percent resid conversion was then calculated.

Both the starting recycle oil and the reaction products are also analyzed by solvent extraction. The amount of 1050 °F⁻ distillate in the products are estimated, assuming that any pentane soluble products are also 1050 °F⁻ distillable. In addition, a portion of the Run 262 V-1074 distillate fraction, is also pentane insoluble and is thereby included as resid. Implicit in this calculation is the assumption that as this overlapping material is converted to a distillable, lighter fraction, new products are formed from the pentane insoluble (and 1050 °F⁺) fraction to replace it. Material balances and product distributions for a number of catalysts are given.

TASK 1.2 LABORATORY SUPPORT (CONSOL)

The samples from Wilsonville Run 255 (Texas lignite) that were received from Amoco were prepared for use in this project. Samples of Martin Lake lignite and Burning Star 2 Illinois No. 6 coal were sent to Sandia. One package of Martin Lake lignite in use at CONSOL was found

to have a relatively low ash content. CONSOL recommended that any samples of this coal found to have ash contents below 13 wt % (MF, SO₃-containing basis) be discarded.

A sample of coker tar, two samples of hydrotreated coker tars and eight hydrogenated distillate samples were received from Sandia. The hydrogenated distillate samples were prepared by hydrotreating samples of V-1074 distillation fractions and dewaxed V-1074 distillation fractions that we sent them.

Evaluation of CAER's microautoclave workup procedure to determine resid conversion is complete. Results will be sent to participants in the near future.

TASK 1.3 LABORATORY SUPPORT (SANDIA)

A high resolution gas chromatography (HRGC) technique was used to evaluate resid concentrations in mixtures of resid and heavy distillate. This method uses the adsorbent liner in the injector of a capillary gas chromatograph to trap resid components and to allow distillate to pass onto the column. The HRGC method correlated well with the TGA method (discussed in the April-June 1993 Quarterly Report) and could possibly lend more sensitivity to the resid determinations. Four tests were run using liquefaction products from microautoclave experiments, showing that resid concentrations track with liquefaction yields.

TASK 2.1 CO-PRETREATMENT

Pretreated coals were liquefied under a variety of conditions between 415-440 °C using the Wilsonville Recycle Oil from Run 262 and V131-B from Run 258. Baseline coal reactions were carried out at 415 °C for one hour with Run 262 recycle oil in the presence of 0.1 wt% Mo in the form of Shell 324. Coal conversion was just over 100% for both NaOH/CO-pretreated material and Black Thunder (BT) coal giving a 8-10 wt% increase in the oil yield. This agrees with earlier experiments with Shell 324 at 400 °C in tetralin for one hour. Gas yield for the pretreated coal reaction is lower than for the untreated case.

Experiments were also carried out at 440 °C for 22 minutes in the presence of V-1074 distillate from Wilsonville Run 262 in place of tetralin. No additional catalysts or sulfiding agents were

present during the reaction. The CO-pretreated material is significantly more reactive than the untreated coal in V-1074 and the results are highly reproducible. The average coal conversion for the pretreated coal is 76 %, compared to 65% for the untreated coal experiments. Reaction of coal with recycle oil containing de-ashed and ashy resid plus the V-1074 distillate were carried out at 440 °C for 7.5 to 30 minutes at 1000 psig hydrogen pressure. Coal conversion increased from 88 % to 103 % from 7.5 minutes to 30 minutes reaction time. At 22 min, coal conversion is marginally higher by 4%, with the improvement being mainly in the conversion of PA+A to oils. PA+A yield dropped from averaged values of 65 % at 15 min. to 52 % at 22 min. and the oil yield increased from 22% to 41%. Further increase in reaction time to 30 min. gave an oil yield of 50%.

The products obtained from reactions of CO-pretreated and untreated BT coal have been subjected to micro-distillation to obtain an equivalent 1050 °F distillate cut (atmospheric pressure). The resid conversion (+1050 °F) obtained from the liquefaction of the CO-pretreated material at 440 °C (22 min.) in the presence of V131-B without added catalyst was 22.3 wt% compared to 19.5 wt% for the untreated BT coal. This is an improvement of almost 15% over the untreated case. In addition, it is also comparable to the Wilsonville base case run where the resid conversion is 23.5 wt% in the presence of 100 ppm added Mo and Wilsonville iron oxide at 1% Fe.

The effect of various additives (sodium formate, formic acid, NH_4OH , NH_4NO_3 and NaCl) on coal pretreatment have been further examined. Earlier experiments were reported that showed that NaOH , NaHCO_3 and Na_2CO_3 are effective in promoting the pretreatment reaction. The current experiments examine the effectiveness of some non-traditional shift catalysts such as NaCl , NaOOCH , NH_4OH and NH_4NO_3 . The water-insoluble products obtained with NaCl are comparable to those obtained from pretreatment with NaOH , Na_2CO_3 and NaHCO_3 as far as THF solubility and the PA+A/(oil+gas+water) product ratio is concerned. The coal structure has undergone substantial modification as determined by optical microscopic examination of the pretreated coal product. NH_4OH and NH_4NO_3 experiments gave products which were less soluble in THF than the products from the Na^+ additive experiments; the microscopic examination indicated the coal morphology had not changed substantially.

TASK 2.1.2.1 PRETREATMENT / DEWAXING - (CONSOL)

Resid conversions as high as 30 wt % were obtained by microdistillation of the THF soluble material from microautoclave tests with Black Thunder coal. Resid conversions were found to increase with increasing temperature from 840 to 900 °F (from below 10 wt % to over 30 wt %). Resid conversions were nearly the same when the recycle solvent blend contained untreated V-1074 and hydrogenated-dewaxed V-1074.

Coal and IOM conversions were reduced by about 15 wt % by lowering the cold hydrogen pressure from 1500 psig to 800 psig in microautoclave tests with Black Thunder coal. This result is consistent with the low coal conversions observed by Sandia for tests at lower hydrogen pressures.

Ash and IOM were determined on the ashy resid produced from the Mo-free V-131B recycle solvent from Wilsonville Run 258K. Microautoclave tests were made at our standard conditions (5 min, 824 °F, 1500 psig H₂, S/C = 1.5) with this Mo-free ashy resid substituted for V-1082. Coal conversion was about 10 to 15 wt % lower with the Mo-free resid than when the Mo-containing V-1082 was used in the solvent blend.

Varying the distillate/resid ratio between 0.5 and 1.0 in simulated Wilsonville Run 262E solvent had little effect on the microautoclave coal conversion of Black Thunder coal (5-minutes, 824 °F, 1500 psig H₂, S/C = 1.5). Slightly higher coal conversions were found at the lowest distillate/resid ratio while total IOM conversions were higher at the highest distillate/resid ratio. The lower total IOM conversions at low distillate/resid ratios (higher total resid concentrations) are consistent with our earlier observation that the resid IOM is significantly less reactive than the Black Thunder coal. However, the largest observed difference in conversions, 2.5 wt %, approaches the repeatability of the test.¹

Texas-lignite-derived V-1074 distillate from Wilsonville Run 255 was found to contain about one-third to one-half as much wax as the V-1074 from Wilsonville Run 262E (Black Thunder coal).

The degree of solvent improvement, measured by microautoclave tests, produced by distillate dewaxing alone and by distillate hydrotreatment alone is significantly greater than the incremental improvement attained by hydrotreating dewaxed distillate. There appears to be an optimum level of wax removal (~20 to 25 wt %) at which dewaxed distillate is produced that results in the highest degree of coal conversion in our tests. Dewaxing and/or hydrotreatment appears to be more beneficial for the higher boiling distillate fraction from Wilsonville Run 262E than for the lower boiling distillate fraction. However, the coal conversion obtained with the untreated higher boiling fraction is about 3 wt % less than that observed with the lower boiling fraction and, therefore, the coal conversion measured with either treated (dewaxed, hydrogenated or hydrogenated-dewaxed) distillate fraction is about the same.

Wilsonville preheater simulation tests resulted in ~69 wt % coal conversion and ~4 wt % resid conversion.

A TGA method, based on a similar method used by HRI, is being developed to determine 975 °F⁺ resid on milligram-sized coal-derived liquid samples. Measurement of resid conversions by distillation and TGA is in progress and will be reported later.

TASK 2.1.2.2 PRETREATMENT / AGGLOMERATION - (CONSOL)

Several Martin Lake lignite agglomeration runs and the float/sink tests reported last quarter initially had high ash balances; the source was identified as heterogeneity of the sample bags of coal in use by CONSOL. Fresh Martin Lake lignite agglomerated with No. 6 fuel oil gave 12 to 28% physical ash rejection, reducing the ash content from 11.0 wt % MF to 8.6 wt % MF (sample 1), or from about 13.5 wt % MF to as low as 9.9 wt % MF (samples 2 and 3).

No significant improvement was obtained over previous physical ash rejection results when two-stage agglomeration of Burning Star 2 coal with No. 6 fuel oil was used. No significant improvement was obtained over previous physical ash rejection results with Kemmerer coal.

Fresh McKinley Mine (NM) coal agglomerated with No. 6 fuel oil gave 52 to 57 % physical ash rejection, reducing the ash content from 11.7 wt % MF to 4.6 to 5.1 wt % MF. Analyses

are reported for McKinley Mine coal. The ash has a very high silica content (60%), which appears to account for its excellent agglomeration performance. In previous work with Martin Lake lignite, evidently much of the rejected mineral matter was silica sand. One unusual feature of the McKinley coal is that the mineral matter rejected from agglomeration is black in color.

The coincidence of high ash SiO_2 contents and high ash rejections in agglomeration in current and previous tests prompted us to explore correlation between the two parameters in several coals. We obtained regressions which allow prediction of agglomeration performance (physical ash rejection) from ash silica content ($R^2 =$ up to 0.77) or from the "free" silica content of the ash (a representation of quartz content, calculated as wt % ash SiO_2 minus 1.25 times the wt % ash Al_2O_3) ($R^2 =$ up to 0.91). The data set consists of nine coal samples, lignite through hvAb. This empirical relation may be useful for screening coals as potential agglomeration feeds.

The CO-pretreated Black Thunder coal slurry supplied by CAER was used in three agglomeration tests. High organic recoveries are obtained when the CO-pretreated Black Thunder coal slurry is agglomerated. There is little physical ash rejection from agglomeration, but a substantial amount of slurry ash dissolution may have occurred prior to or during agglomeration.

TASK 2.1.3 SOLVENT PRETREATMENT (SANDIA)

Previous solvent pretreatment steps involved dewaxing and hydrogenation with whole V1074. Experiments this quarter were conducted with V1074 heavy distillate which had been split evenly into light and heavy fractions by distillation. Two sub-samples of the distillate products were dewaxed by CONSOL. The resultant materials were hydrotreated using a batch microautoclave and a sulfided NiMo catalyst at Sandia. Proton NMR spectroscopic analysis was performed on the hydrogenated products to determine the distribution of hydrogen in the solvents. In general, the lighter samples were more paraffinic and the heavier samples were more aromatic before hydrogenation. The dewaxed samples showed the same trend before hydrogenation, except that the level of aromaticity was up in both the light and heavy dewaxed cuts. Hydrotreating improved the hydroaromatic nature of the samples in all cases. Overall the cyclic alpha and beta proton concentration increased from 30.5% for the original V1074 to 42.5% for the heavier,

dewaxed, hydrogenated material. These materials were shipped to CONSOL for microautoclave testing.

Two series of solvent hydrogenation tests were performed in the trickle-bed reactor with dewaxed V1074 heavy distillate to evaluate the effects of catalyst, liquid hourly space velocity, and temperature using hydrogen as the gas phase. Previous tests were run using synthesis gas to generate a portion of the hydrogen in situ. At 360°C the heavy distillate increased in hydrogen content by about 0.7% at a LHSV of 0.7 hr⁻¹ and about 0.4% at a LHSV of 1.1 hr⁻¹.

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS

Characterization and testing of promoted sulfated hematites - Examination of the effect of individual promoter metals, as well as a number of combinations of multiple promoter compounds, on the activity of the sulfated hematites had shown that the addition of 0.9 wt % molybdenum and 0.7 wt % nickel to sulfated hematite resulted in a significant increase in both activity and selectivity to oils. The effect of varying the concentration of the promoter metals on the activity was further investigated during the current period.

XPS studies have shown that nickel added to the catalyst is uniformly distributed throughout the particle with the bulk and surface concentrations being identical. Both molybdenum and tungsten were observed on the surface. The effect of promoter metal concentrations on the activity was determined. A number of combinations where concentrations of promoter metals were varied from 0 to 5 wt% on iron, were prepared and tested for their activity for liquefaction. Generally, as the total promoter concentration increases, the total conversion also increases. However, there appears to be a synergistic effect between the cobalt and molybdenum, 4% molybdenum and 1.2% cobalt yields a significantly higher conversion than either 5% molybdenum or 2.5% cobalt. Oil yield showed the same trend yielding a maximum conversion of 48% for the 4% molybdenum, 1.2% cobalt catalyst. These studies also showed that the catalyst activity is more sensitive to cobalt concentration than to molybdenum concentration. By reducing the molybdenum concentration from 4% to 1% the total conversion is reduced by only 1% while the oil yield drops by 3.5%. These represent conversions higher than those obtained with 5% molybdenum alone.

The molybdenum and tungsten system with a tungsten concentration of 0.8% and molybdenum concentration at 1% gave 91.9% conversion. Maximum oil yield of 49% was obtained for 4% molybdenum and 3.1% tungsten. While the high concentrations of molybdenum and tungsten showed significant gains in total conversion and oil yield, the high cost of the tungsten may inhibit the economic efficiency of these catalysts.

The combination of nickel and molybdenum showed some surprising trends. Increasing the nickel concentration appeared to adversely impact the total conversion. The maximum oil yield of 46% is obtained at a promoter concentration of 0.9% molybdenum and 0.7% nickel, which shows the synergistic effect between nickel and molybdenum. Increasing the molybdenum loading to 4.3% resulted in a slight decrease in oil yield to 44.5% and an increase in nickel concentration to ~2% results in a decrease in catalytic activity. Nickel and molybdenum show the greatest amount of synergism of the catalysts tested here. The activity is sensitive to both molybdenum and nickel concentrations while the selectivity to oils is more sensitive to variations in nickel concentrations. Unlike the other promoter metals tested, nickel shows a distinct maximum in both total conversion and oil yield at a concentration of 0.7%. Given the relatively low cost of nickel compared to the other metals tested, the use of the 0.9% molybdenum, 0.7% nickel catalyst may have a favorable impact on the overall process economics.

In the resid conversion test, the total conversions obtained using the V-131B solvent followed the same trend as seen in tetralin. The use of 10% molybdenum gave the highest conversion (103.2%) followed by the 0.9% molybdenum, 0.7% nickel (102.2%). The lowest total conversion was obtained for the unpromoted sulfated hematite (99.3%). Resid conversions are now being determined.

Fe and Mo Impregnated Coal - The surface composition and chemical states of elements in samples of Wyodak Black Thunder subbituminous coal impregnated with Fe and Mo were investigated. The concentrations of Fe, Mo, S, Al, Si, Ca, C, O, and N were investigated by x-ray photoelectron spectroscopy (XPS) in samples impregnated with 0.7-2.0 wt% Fe and 500-1000 ppm Mo. The metals were deposited on the samples by an incipient wetness (I.W.) technique using solutions of ferric nitrate, ferric sulfate, ferrous sulfate and ammonium

molybdate. The effect of the metal precursor, the relative amounts of Fe and Mo loading, the precipitation with NH_4OH and the method and extent of drying on the surface composition and chemical states of the elements are presented. Elemental depth profiles were determined by Ar sputtering and XPS. The influence of sputtering on the chemical form of the elements was determined, and the interference of the S_{2s} and Mo_{3d} peaks was resolved.

It was found that Fe concentrations on the surface of Mo-free coals, impregnated with either Fe^{++} or Fe^{+++} sulfates, were lower than those obtained with Fe^{+++} nitrates. Likewise, Fe concentrations on the surface of Mo-Fe-impregnated coals, whether prepared from sulfate or nitrate salts, were intermediate between the Mo-free sulfate and nitrate preparations. In addition, Fe on the surface of all of the sulfate-impregnated coals was not present as FeOOH , which was the dominant form for the nitrate-impregnated, base-treated coals. Mo was present on the surface of the coal as MoO_3 . Sulfate is removed from sulfate-treated coals during the base-treatment step and the sulfur, on the surface of the non-base-treated coals that were treated with sulfates, was present as SO_4^- . Oxygen concentrations on the surface of all the 0.77 wt% Fe-impregnated coals fall within a narrow range. Si, Al and Ca concentrations on the surface of the base-treated coals tend to be lower than for the non-base-treated samples.

TASK 2.3.3 CATALYST STUDIES (SANDIA)

A bulk platinum hydrous titanium oxide (HTO) catalyst was formulated and used for testing with the dewaxed distillate. The catalyst was loaded with 5.5% platinum. Post reaction analysis of this catalyst and a NiMo (Shell 324) catalyst revealed higher amounts of carbon and nitrogen deposition on the alumina supported NiMo catalyst. This indicates that the HTO substrate may have less acidity and thus be desirable where hydrocracking is not required (i.e., for donor solvent hydrogenation).

TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP ASSOCIATES)

The sensitivity of total plant costs (TIC) on the required selling price of gasoline was determined for the revised base case (SO_3 -free ash). A 25% reduction in TIC reduces the selling price of gasoline by 18.2% at a 10% discount rate or 16.1% at a 5% discount rate.

A steady state balance was completed on a commercial scale solvent dewaxing unit assuming a 4% net wax make. A wax cracking rate of 22% was estimated from Wilsonville run data. a simplified process simulation was used to study the effect of treating 25%, 50%, 75% and 100% of the available stream. An economic assessment of dewaxing showed that if all recovered wax could be sold as fully refined paraffin wax then byproduct revenue will be sufficient to offset dewaxing unit costs at the 25% feed level. Market volume is a key factor which will impact on the feasibility of this approach. The use of catalytic dewaxing may be more attractive if byproduct revenues from solvent dewaxing are lower.

SECTION ONE

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

WORK PERFORMED

TASK 1.1 LABORATORY SUPPORT (UK/CAER)

To assess the activity of various catalysts studied under this section, liquefaction experiments were conducted in Wilsonville process solvent from Run 258K, which contained iron added during the plant run as an iron oxide catalyst, but no molybdenum. It had been determined from Mössbauer studies of the Run 262E process solvent that iron added as iron oxide accumulated in the recycle solvent predominantly in the form of pyrrhotite, and this material is presumed to be present in the 258K recycle oil also, possessing some background catalytic activity. As reported in the previous quarter, the molybdenum added during Run 262E had some observable effect on liquefaction, and studies were performed in the new plant recycle oil so that the effects of freshly added catalyst could be more readily observed in the microautoclave experiments without the background interference of the molybdenum.

Experiments were conducted with five different sets of catalysts, as described below:

1. Thermal- no iron, molybdenum nor DMDS was added to the microautoclave.
2. WIO/moly- Iron was added at a rate of 1% iron oxide on dry coal (0.7 wt% Fe) from the iron oxide source used at Wilsonville, as supplied by Kerr-McGee. Molybdenum was added at 100 ppmw on dry coal, from Molyvan L. Sulfur in DMDS was targeted at 1.2 mol S/mol Fe and 2.4 mol S/mol Mo. Now I say targeted, because if you look at the table with this data in it, you quickly realize a steadier hand will be needed in future runs to eliminate this variable!
3. SFIO- This material was added at the same iron level (0.7 wt% Fe on mf coal) as in (2.) above. Sulfur was also targeted at 1.2 mol S/mol Fe. No molybdenum was added with this iron.
4. CH-504 - 0.77% Fe on dry coal was prepared following the Incipient Wetness (IW) technique, using hydrated ferric sulfate as an iron source. As discussed elsewhere in this section, in efforts directed at improving the cost effectiveness of this preparation, the iron was not precipitated with ammonium hydroxide, also eliminating the need for further water washing. The coal sample was subsequently dried at 40 °C in flowing air.
5. CH-604 - This coal sample was prepared as described in (4) above, but with 1000 ppmw molybdenum added as ammonium molybdate.

Based on liquefaction experiments performed with Black Thunder coal in Run 262E Recycle Oil reported previously, 440 °C and 22 minutes run time were selected as microautoclave reaction conditions which gave the same total resid conversion (defined as maf coal plus recycle oil IOM and resid) as found at Wilsonville in Run 262E (namely 24% conversion). These reaction conditions were then used with Black Thunder coal and the Run 258K Recycle Oil in the catalyst systems described above. The microautoclaves were sealed, purged and pressurized to 1000 psig with hydrogen.

Analysis of the reaction products was by two methods: Soxhlet extraction and distillation. Liquefaction experiments were performed in duplicate, and the products were then analyzed by either one or the other method. The results of each are reported here in Table 1 and 2. The method using THF and pentane to divide the reaction products by solubility has been described previously.¹ Total THF conversion of the coal is determined from the Soxhlet extraction data. The analysis by distillation follows the method of ASTM D-1160, "Standard Test Method for Distillation of Petroleum Products at Reduced Pressures", wherein the products which may otherwise decompose if distilled at atmospheric pressure are distilled in a single stage, short cooling zone distillation apparatus at a reduced pressure (from 1mm to 50mm). Using the formula provided in this standard, a distillation temperature of 627 °F (331 °C) at 1mm total pressure was selected to yield a distillate fraction with an atmospheric equivalent final boiling point temperature of 1050 °F, for use in this study.

Percent resid conversion was then calculated per the following equation:

$$\%C_r = \frac{Resid_{charged} - Resid_{recovered}}{Resid_{charged}} * 100$$

The resid charged is calculated from the weight of maf coal added to the reactor, plus the 1050 °F+ fraction of the Run 258K Recycle Oil. As reported earlier, this recycle oil was determined by distillation at CAER to be 46.6% 1050 °F-, and 53.4% 1050 °F+ and ash. To calculate %C_r on an SO₃-free basis, SO₃-free ash contents were determined by CONSOL as:

- ♠ 5.54% of the mf Black Thunder coal, and
- ♠ 8.14% of the R-258K V-131B recycle oil.

The resid recovered is determined by weighing the residue remaining in the flask from the distillation described above, and subtracting from that the weight of coal ash and recycle oil ash, along with the sulfided catalyst weight.

In the case of analysis without distillation, both the starting recycle oil and the reaction products are analyzed by solvent extraction. The amount of 1050 °F⁻ distillate in the products must therefore be estimated, since it is not measured directly. As a first estimate, one could assume that any pentane soluble products are also 1050 °F⁻ distillable. However, comparison of the solvent separation and distillation analyses for the starting R-258K recycle oil shows that in that sample there is a small fraction (9.4% of the ash-free V-131B) of the pentane-defined "Oil" fraction that is not 1050 °F⁻, and therefore should be included as resid. Since the starting reactants are the same for each liquefaction experiment, the amount of non-distillable resid needed to calculate the Resid_{charged} is known for each experiment. To calculate resid conversion from solvent extraction of the products, we assumed that this weight representing 9.4% (af) of the V-131B remains the same in the reaction product Oil, although the individual molecules involved may have changed. This weight is subtracted from that fraction to be included with the resid material. Implicit in this calculation is the assumption that as this overlapping material is converted to a distillable, lighter fraction, new products are formed from the pentane insoluble (and 1050 °F⁺) fraction to replace it.

The apparatus used for the distillation included:

- 2-neck, 100 ml round bottom flask,
- heating mantle,
- 75 mm thermowell,
- Type J thermocouple with readout,
- 14/20 standard taper thermowell adapter,
- 350 °C yellow back thermometer (10/18, 37 mm immersion length),
- 14/20 standard taper vacuum adapter,

- 14/20 standard taper 50 ml round bottom flask, and
- a 0-5mm McLeod vacuum gage.

Vacuum was supplied by a Welch vacuum pump, pulling through 2 traps and a vacuum manifold. Vacuum was controlled by bleeding air into the manifold with a Whitey valve.

Table 1. Liquefaction of Black Thunder Coal in Run 258K V-131B Recycle Oil*Analysis by Soxhlet Extraction					
	Thermal	WIO/Mo	SFIO	IW Fe	IW Fe/Mo
Metals added, wt% mf Coal	0.0	.70% Fe + 100 ppm Mo	.69% Fe	.77% Fe	.77% Fe + 1000 ppm Mo
Sulfur added, mol S/mol Fe	n/a	0.8	1.2	1.9	1.7
Products, wt% maf coal					
HC Gases	2.3	2.6	2.7	2.4	2.7
CO+CO ₂	5.7	6.5	6.7	6.3	5.8
Oils	33.0	39.8	42.6	45.1	59.7
PA+A	55.3	53.1	53.6	48.4	38.0
IOM	3.7	-2.0	-5.6	-2.2	-6.2
Total	100.0	100.0	100.0	100.0	100.0
THF Conv	96.3	102.0	105.6	102.2	106.2
Run number	3118-1 3148-1	3279-1	3287-2	3286-2	3293-2
Resid conv. %	19.8	23.2	24.7	26.9	33.2
a. 440 °C, 22 minutes, 3 g Black Thunder coal, 5.4 g V-131B, 6.89 MPa H ₂ cold. SO ₃ -free ash basis.					

Table 2. Liquefaction of Black Thunder Coal in Run 258K V-131B Recycle Oil ^a Analysis by ASTM D-1160					
	Thermal	WIO/Mo	SFIO	IW Fe	IW Fe/Mo
Metals added, wt% mf Coal	0.0	.70% Fe + 100 ppm Mo	.69% Fe	.77% Fe	.77% Fe + 1000 ppm Mo
Sulfur added, mol S/mol Fe	n/a	1.0	1.3	1.7	1.8
Products, wt% maf Coal					
HC Gases	2.2	2.6	3.1	2.3	2.9
CO+CO ₂	6.0	6.1	6.3	6.5	5.9
1050 °F ⁻	40.5	36.1	49.9	28.7	53.4
1050 °F ⁺	51.3	55.2	40.7	62.5	37.8
Total	100.0	100.0	100.0	100.0	100.0
Run number	3286-1 3298-1	3281-1	3292-1	3287-1	3293-1
Resid conv %	23.3	21.3	28.2	19.1	31.0
a. 440 °C, 22 minutes, 3 g Black Thunder coal, 5.4 g V-131B, 6.89 MPa H ₂ cold. SO ₃ -free ash basis.					

TASK 2.1.1 CO-PRETREATMENT

In the last quarterly report, we presented the liquefaction activity of the CO-pretreated material in the presence and absence of a fine iron (Nanocat) and a Ni/Mo (Shell 324) catalyst in tetralin at 400 °C for an hour. Reactivity of the NaOH and Na₂CO₃ CO-pretreated coals was found to be significantly enhanced compared to base coal. In addition, a selectivity toward higher oil production and considerably lower gas yields was observed. Hydrogen consumption is apparently lower.

In this quarter, we continued to examine the liquefaction performance of the pretreated coals under a variety of conditions, specifically, coal liquefaction at higher temperatures (415-440 °C) using the Wilsonville Recycle Oil (WRO) from Run 262 and V131B from Run 258.

As part of our continuing effort to understand the pretreatment process, we investigate the effect of various additives (sodium formate, formic acid, NH₄OH, NH₄NO₃ and NaCl) on coal pretreatment.

Coal Reactions with Recycle Oil and Shell 324 at 415 °C

Coal reactions were carried out at 415 °C for an hour with Run 262 recycle oil in the presence of 0.1 wt% Mo in the form of Shell 324. No Fe was added in these experiments. The results are presented in Table 3. The results were calculated on the basis of Soxhlet extraction yields of the WRO component of the reactants with THF and subsequent work-up of the THF solubles with pentane. The THF insoluble organic matter (IOM) from extraction of the WRO is known to react during liquefaction. Thus, the coal conversion results presented are greater than 100%.

The results showed that coal conversion is just over 100% for both NaOH/CO-pretreated material and Black Thunder (BT) coal. The improvement for the pretreated coal is found in the oil yield (ca. 9 wt% maf coal). This is in agreement with our earlier experiments

with Shell 324 at 400 °C with tetralin for an hour. The amount of water produced in both reactions is unknown and is the subject of further investigation. Gas yield for the pretreated coal reaction is marginally lower than for the untreated case.

Coal Reactions in the Presence of V-1074 Distillate at 440 °C

In an earlier set of experiments, the liquefaction activity of the co-pretreated and untreated BT coals were tested in the presence of a liquefaction solvent alone. These experiments were carried out in the presence of V-1074 distillate from Wilsonville Run 262 in place of tetralin. The de-ashed and ashy resids were not included in the experiments. No additional catalysts or sulfiding agent was present in the reaction.

Table 3. Liquefaction of CO-pretreated coal with Shell 324^a

% wt. maf coal	BT coal	Pretreated coal ^b	Pretreated coal ^b
Gases	5.3	3.4	3.6
Oils	65.1	73.3	74.7
PA+A	31.2	26.1	22.9
IOM	-1.6	-2.8	-1.2
Conversion	101.6	102.8	101.2
<p>a. Run Conditions: 3.0 g Black Thunder coal (~22% moisture) or 2.6 g pretreated coal (~5% moisture); 5.4 g Wilsonville recycle oil from Run 262; 1% wt Mo as Shell 324; 1000 psig H₂; 415 °C; 1 h.</p> <p>b. Duplicate runs.</p>			

For this investigation, 3.0 g of Black Thunder coal (as received) together with 2.2 g of V-1074 distillate were charged into a 50 ml. horizontal reactor. For pretreated coal about 2.6 g of the material was used, taking into account the low moisture content (~5%). The reactor was sealed, leak tested and pressurized with 1000 psig of hydrogen. The reaction was carried out at 440 °C for 22 min. The procedure for product work-up has been previously

reported. The experiments were carried out at least twice and all results are expressed as weight percent maf coal unless otherwise stated.

It is clear from Table 4 that the CO-pretreated material is significantly more reactive than the untreated coal in V-1074 and the results are highly reproducible. The average coal conversion for the pretreated coal is 76 % compared to 65% for the untreated coal experiments, indicating significant differences on a relative basis. The improvement in conversion for CO-pretreatment is reflected exclusively in the PA+A yield. The hydrogen consumption data from the gas phase is similar for both CO-pretreated and untreated coal experiments. Hence, the results are consistent with a poor hydrogenating solvent in V-1074.

Reaction of Coal with Recycle Oil at 440 °C

In a second set of experiments, the de-ashed, ashy resid and V-1074 distillate were added to the coal and the reactions were carried out at 440 °C for 7.5 to 30 minutes at 1000 psig hydrogen pressure. For Black Thunder coal, a baseline was established to gain confidence in the results and these are presented in Table 5. Coal conversion increased from 88 % to 103 % from 7.5 minutes to 30 minutes reaction time. The IOM yield dropped from 12% at 7.5 min. to 3% at 30 minutes while at 22 min. the IOM yield was ~3 %. This increase in conversion is equally distributed between oil and gas (CO, CO₂ and hydrocarbon gases). In this period, some of the PA+A converts to oil. Gas yield remained constant. The improvement in liquefaction derived mainly from the conversion of PA+A to oils. PA+A yield at 15 min. dropped from averaged values of 65 % to 52 % at 22 min. Correspondingly, the oils increased from ca. 19% to 41%. Further increase in reaction time to 30 min. gave almost exclusive improvement in the oil yield to ca. 50%.

Table 4. Reactions of Black Thunder Coal and CO-Pretreated Coal with V-1074 at 440 °C for 22 Minutes^a (wt% maf coal)

	BT Coal ^b	BT Coal ^b	BT Coal ^b	Pretreated ^c	Pretreated ^c
Gases	6.3	7.3	7.3	4.4	5.0
Oils+water	23.3	24.3	26.5	25.1	24.5
PA+A	33.3	33.6	32.5	46.7	46.8
IOM	37.1	34.6	33.6	23.8	23.7
Conversion	62.9	65.4	66.3	76.2	76.3

a. Coal reaction conditions: 3.0 g BT coal (~22% moisture) or 2.6 g CO-pretreated coal (~5% moisture); 2.2 g V-1074; 1000 psig H₂; 440 °C; 22 min.

b. Runs made in triplicate.

c. Runs made in duplicate.

Interestingly, reactions with the NaOH-pretreated coal at 440 °C for 22 min gave similar coal conversion (within experimental error); 100% vs 101% for the untreated coal. The PA+A yield is significantly lower (32% vs. 52%) for the pretreated coal which has a correspondingly higher oil yield (62% vs. 41% for the untreated coal reaction). As yet this reaction has not been repeated. However, another reaction with this pretreated material in the absence of added molybdenum as Molyvan L gave a coal conversion of 101%, a PA+A yield of 46.3% and an oil yield of 50%. Again this is consistent with the positive effect of added molybdenum in the reaction on oil production.

Recently, the products obtained from the reactions of CO-pretreated and untreated BT coal have been subjected to micro-distillation to obtain a 1050 °F distillate cut (atmospheric pressure equivalent). In this procedure the reaction products in the reactor after liquefaction were transferred (with THF) to a micro-distillation apparatus. Excess THF was removed and the distillation was carried out to 627 °F at 1 mm Hg to give an equivalence of a 1050 °F distillate cut at atmospheric pressure.

The resid conversion (+1050 °F) obtained from the liquefaction of

Table 5. The Reaction of Black Thunder Coal with Recycle Oil in the Presence of Added Fe and Mo at 440 °C (wt% maf coal)

Products, wt% maf coal	Reaction Time (min)			
	7.5	15	22	30
Gases	6.0	11.8 (11.3)	8.1 (9.0)	8.9
Oils	12.2	18.5 (20.7)	38.8 (43.2)	49.5
PA+A	69.3	67.4 (63.1)	54.0 (50.0)	44.5
IOM	12.2	2.3 (4.8)	-1.4 (-2.4)	-2.97
Conversion	87.6	97.7 (95.2)	104.4 (102.4)	102.7
Coal reaction conditions: 3.0 g BT coal (~22% moisture), recycle oil; 1% Fe(WIO); 100 ppm Mo(MolyVan L); 1000 psig H ₂ ; 440 °C.				

the CO-pretreated material at 440 °C (22 min.) in the presence of V131-B without added catalyst was 22.3 wt% compared to 19.5 wt% for the untreated BT coal. This is an improvement of almost 15% over the untreated case. In addition, it is also comparable to the Wilsonville base case run where the resid conversion is 23.5 wt% in the presence of 100 ppm added Mo and Wilsonville iron oxide at 1% Fe.

CO-Pretreatment

The effect of various additives on CO-pretreatment of coal was further investigated. This follows from the earlier experiments

which showed that NaOH, NaHCO₃ and Na₂CO₃ are effective in promoting the pretreatment reaction. The initial pH of these solution range from ~8-14. The current experiments examine the effectiveness of some non-traditional shift catalysts such as NaCl, NaOOCH, NH₄OH and NH₄NO₃. In addition, with a base it is presumed that the salt of the formate anion is formed during the shift reaction and is the active intermediate in hydrogenating the coal. This work attempts to examine if there is a difference in the effect of NH₄⁺ in place of Na⁺.

The reactions were carried out in a 25 ml. microautoclave at 300 °C for an hour using 2.0 g (dry basis) BT coal, 5.5 ml. of 0.33 N solution and 800 psig CO. The results are presented in Table 6.

One of the criteria we have developed to assess the performance of the pretreatment process is solubility of the water-insoluble product in THF after pretreatment. The ratio of the PA+A to total oil+gas+water fractions provides an insight into the pretreatment process. For example, a high PA+A to oil+gas+water product ratio indicates that the coal has undergone favorable pretreatment in a particular set of pretreatment conditions. A low PA+A to oil+gas+water ratio is identified with a low level of hydrogenation and low quality product.

The results in Table 6 show that the water-insoluble product yields obtained in the pretreatment of BT coal with NaCl are comparable to those obtained from pretreatment with NaOH, Na₂CO₃ and NaHCO₃ as far as THF solubility and the PA+A/oil+gas+water product ratio is concerned. This is surprising since NaCl is not conventionally known as a shift catalyst. Additionally, the coal structure has undergone substantial modification as determined by optical microscopic examination of the pretreated coal product which will be discussed in greater detail below.

The NH₄OH and NH₄NO₃ experiments gave products which are significantly less soluble in THF than the products from the Na⁺

salt experiments. Their THF solubility averaged 23% (wt% maf coal) compared to 33-37% (wt% maf coal) for the latter experiments. These results are supported by microscopic evidence as the coal morphology is not changed to the extent as in the earlier work. Obviously, pH is not the primary cause of this low activity in the pretreatment reaction since NH_4OH is a relatively strong base. Whether the stability of NH_4OOCH , if it forms, has to do with the low pretreatment activity, remains to be addressed. Further work is continuing.

Table 6. The Effect of Various Additives on CO-Pretreatment of Black Thunder Coal^A (% wt., maf coal basis)

BASE	NaOH	Na_2CO_3	NaHCO_3	NaCl	NaOOCH	NH_4OH	NH_4NO_3
THF soluble	37	38	35	33	48	24	22
PA+A	25	29	21	23	16	15	9
oil+gas +water	12	9	14	10	32	9	13

^A Reactions were carried out using 2.0 g BT coal, 800 psig CO, 5.5 ml of 0.33 N additive solution at 300 °C for an hour. Sodium formate reaction was carried out with 3N additive solution

The addition of NaOOCH to the reaction mixture was based on the premise that the formate salt was the active intermediate in promoting hydrogenation of the coal. In view of this, a reaction with BT coal in the presence of NaOOCH and in the absence of CO or N_2 was carried out at 300 °C for an hour. The concentration of the HCOONa was approximately ten times that of the NaOH. The reason for adding excess salt is based on an estimation of the amount of hydrogen added to the coal during an earlier CO-pretreatment reaction. Elliott, et al.,² have shown that NaOOCH is fairly stable below 300 °C and the decomposition rate of the formate ion to form CO_2 and H_2 is apparently temperature sensitive at temperatures greater than 300 °C. The NaOOCH promoted reaction in

the absence of CO gave a very high yield of THF soluble products. In addition, a substantial amount of water soluble organic component (humic acid) was produced in the reaction. The exact amount is yet to be determined but is estimated to be in the 5% range. This is consistent with the earlier pretreatment experiments with low CO pressures or in the absence of CO, i.e., with H₂ or N₂. The pretreatment appears to have been favorable and extensive. Although it is difficult to quantify the amount of oils in the oil+gas+water fraction from the sodium formate reaction, there is some indication that they are a major component.

Microscopy of Water-Insoluble Products

Using NaCl as the water-gas shift promoter caused the huminite (Black Thunder) to soften and melt, and agglomerate into large masses. However, the extent of this reaction varies within the product; some of the huminite macerals have melted extensively, forming areas with a finely porous microtexture, whereas other huminite macerals have softened/melted, but are still present as distinct particles (although the edges are no longer angular, and remnant botanical features are rarely observed) within the agglomerates (Plate 1). These features are similar to those observed in the water-insoluble product of the NaHCO₃ promoted CO pretreatment. The liptinite and inertinite macerals are relatively unaffected by pretreatment. Thermal treatment with H₂O and NaCl only produced negligible change in the coal, except for a significant increase in the huminite mean reflectance (0.67%) as shown in Table 7; similar results were reported for thermal treatment with H₂O and NaOH.

Reaction with sodium formate (CHOONa) generated a product that is very similar in appearance, and mean reflectivity, to that produced using NaCl. However, when formic acid (CHOOH) is used, the huminite macerals softened only slightly and did not agglomerate; the coal particle outlines retain a small degree of

angularity, with some rounding present (Plate 1). The mean reflectance is only slightly higher than that of the NaOOCH reaction product. Utilizing NH_4OH as a catalyst produced a material morphologically similar to that from the CHOOH reaction. Most of the huminite has softened during the reaction, but lacks any significant agglomeration. In fact, botanical structures and bedding features are commonly observed in the huminite. This pretreatment caused an increase in the huminite mean reflectance to 0.56%.

Plate I

Reflected white light photomicrograph of water-insoluble product from CO pretreatment in the presence of NaCl. Width of field is 210 μm .

Reflected white light photomicrograph of product from reaction using formic acid (CHOOH) as a catalyst. Width of field = 210 μm . Dark areas are epoxy resin.

Table 7. Huminite Reflectance of Pretreated Coal ^a			
Wyodak Coal Source	CO Pressure, psig	Promoter	Reflectance, %
Clovis Point	-	-	0.39
Black Thunder	-	-	0.40
Black Thunder	800	NaCl	0.51
Black Thunder	N ₂	NaCl	0.67
Black Thunder	N ₂	NaOH	0.65
Black Thunder	800	NaHCO ₃	0.47
Black Thunder	800	CHOONa	0.49
Black Thunder	800	CHOOH	0.53
Black Thunder	800	NH ₄ OH	0.56
Clovis Point	800	none	0.50
a. All reactions carried out at 300 °C for 1 hr.			

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS

Characterization and Testing of Promoted Sulfated Hematites

Introduction - The results of studies of the production and characterization of promoted sulfated hematites were discussed in the previous quarterly report. These studies indicated the small size achieved by this technique and also the effect of the promoter metals on the properties of the particles. These studies were continued during the current quarter to elucidate the location of the promoter metals on the sulfated hematite particles.

The effect of individual promoter metals, as well as a limited number of concentrations of multiple promoter compounds, on the activity of the sulfated hematites was discussed in the last quarterly report. These results indicated that the addition of 0.9 wt % molybdenum and 0.7 wt % nickel to sulfated hematite resulted in a significant increase in both activity and selectivity to oils. The effect of varying the concentration of the promoter metals on the activity was investigated during the current period.

Characterization

It has been reported in the literature that the addition of the molybdenum and tungsten serves to displace the sulfur on the surface of the sulfated hematite. Results reported previously, which showed that the sulfur concentration decreased as the molybdenum concentration increased, appear to support this conclusion. In order to confirm these conclusions, XPS studies were done on the catalysts. The surface concentration was then compared to results obtained from bulk analysis. As expected, the surface concentration of tungsten, molybdenum, and sulfur were nearly twice that of the bulk.

The results of the XPS studies also indicated that the nickel added

to the catalyst was uniformly distributed throughout the particle. As shown in Table 8, the bulk and surface concentrations were identical, within experimental error. The reason for the difference in location of the metals can probably be related to the valence state of the promoter metals. Both molybdenum and tungsten are in their hexavalent state on the surface, as are the sulfur atoms. This implies that they may also be chemisorbed as MoO_3 on the surface, similar to sulfur. On the other hand, nickel and cobalt are added in a 2+ oxidation state. This may explain the difference in promoter metal distribution on the particles.

Table 8. Elemental Composition of Promoted Sulfated Hematite.		
Element	Bulk wt %	Surface wt %
Molybdenum	4.0	7.5
Nickel	2.3	2.5
Sulfur	2.7	4.7

Catalytic Activity

Results reported in the previous quarter indicated the promising increases in catalytic activity for the promoted sulfated hematites. Primarily, the addition of 0.7% nickel/0.9% molybdenum to the sulfated hematite appeared to give the highest activity and selectivity to oils. This indicated that, at the concentrations used in these experiments, nickel/molybdenum gave a higher activity than cobalt/molybdenum or tungsten/molybdenum. However, the effect of promoter metal concentration on the catalytic activity had not been determined. It is important to note that the promoter metal concentrations are reported as wt % promoter metal on iron.

In order to determine the effect of promoter metal concentrations on liquefaction activity, varying concentrations of promoter metals, from 0 to 5 wt % on iron, were prepared on the sulfated

hematite. The catalysts were tested for their activity for the liquefaction of the Black Thunder coal in tetralin. These experiments, carried out in 50 ml microautoclaves, involved the reaction of 3.0 g coal, 5.0 g tetralin, 0.07 g dimethyldisulfide and catalyst at 415 °C for 60 minutes. The catalysts were added at 1 wt% Fe on maf coal. Conversions were determined by solubility class as described in previous reports.

The effect of the variation of the cobalt/molybdenum concentrations on total conversion is shown in Figure 1. In general, as the total promoter concentration increases, the total conversion also increases. However, there appears to be a synergistic effect between the cobalt and molybdenum. This is demonstrated by the fact that 4% molybdenum, 1.2% cobalt catalyst yields a significantly higher conversion (95.3%) than either 5% molybdenum (92%) or 2.5% cobalt (88.8%) alone. Changing the molybdenum and cobalt concentrations to 0.9% and 1.3%, respectively, continued to demonstrate this synergism with a total conversion of 94.2%. The reduction of cobalt content to 0.5% with molybdenum at 1% showed significant gains in total conversion compared to 1% molybdenum or 2.5% cobalt, although it was less than that achieved with 5% molybdenum.

The oil yield showed the same trend, Figure 2, yielding a maximum conversion of 48% for the 4% molybdenum, 1.2% cobalt catalyst. This represents a 14% increase in oil yield over the unpromoted sulfated hematite. Again, changing the promoter metal concentrations to 0.9% molybdenum and 1.3% cobalt continued to show significant increases of 6.1% and 8.1% over the 1% molybdenum or the 2.5% cobalt respectively. Further reducing the cobalt content to 0.5% while maintaining the molybdenum content at 1% significantly diminishes the synergistic effect, although slight gains(1.6%) in oil yield over the 1% molybdenum alone are still observed.

The results of these studies indicate that the catalyst activity is more sensitive to cobalt concentration than to molybdenum concentration. By reducing the molybdenum concentration from 4% to 1% the total conversion is reduced by only 1% while the oil yield drops by 3.5%. These represent conversions higher than those obtained with 5% molybdenum alone. However, since the cost of cobalt is >4 times that of molybdenum, the increase in conversion does not offset the increased cost of the catalyst. Further reduction of the cobalt concentration to 0.5% reduced the activity below the level obtained with 5% molybdenum.

The effect of promoter metal concentration on total conversion for the molybdenum, tungsten system are shown in Figure 3. The higher conversion is obtained at the highest promoter metal concentration, 4% molybdenum and 3.1% tungsten. This represents an increase of 2.4% and 5.5% over 5% molybdenum and 4% tungsten, respectively, indicating a synergistic effect at these concentrations. Reduction of the molybdenum concentration to 1% while increasing the tungsten concentration to 4.1% appears to maintain the synergistic effect, yielding results (91.8%) significantly higher than either 1% molybdenum (88.5%) or 4% tungsten (88.9%) alone. Reducing the tungsten concentration to 0.8% while maintaining the molybdenum concentration at 1% showed no significant effect on the total conversion (91.9%).

The effect of tungsten and molybdenum concentrations on oil yield followed a similar trend as shown in Figure 4. The maximum yield was obtained for 4% molybdenum, 3.1% tungsten with an oil yield of 49%. This represents a significant increase over either the 4% tungsten or 5% molybdenum alone, 12.2% and 5.3% respectively. Changing the molybdenum and tungsten concentrations to 1% and 4.1%, respectively, reduced the oil yield to 41.1%. This is lower than that obtained with 5% molybdenum yet still shows a slight increase over the 1% molybdenum or 4% tungsten yields. The further

reduction of the tungsten concentration to 0.8% had only a slight effect on the oil yield.

These results indicate that the catalytic activity is significantly more sensitive to variations in molybdenum concentration than to changes in tungsten concentration. This may indicate that lowering the tungsten concentrations further may still enhance the total conversion in the presence of molybdenum. While the high concentrations of molybdenum and tungsten showed significant gains in total conversion and oil yield, the high cost of the tungsten may inhibit the economic efficiency of these catalysts.

The combination of nickel and molybdenum showed some surprising trends with variation in promoter concentration. Increasing the nickel concentration appeared to adversely impact the total conversion. As shown in Figure 5, maximum total conversion was achieved through the use of 4.3 % molybdenum and 0.7 % nickel. The total conversion (94.7%) represented an increase over 5% molybdenum and 1.4% nickel of 2.7% and 4.3%, respectively. Reducing the molybdenum concentration to 0.9% at the same nickel loading reduced the total conversion (92.2%) to near that of 5% molybdenum. At this concentration a synergistic effect between the nickel and molybdenum becomes apparent.

Unlike the other promoter metals, increasing the nickel concentration appears to adversely effect the total conversion. At a concentration of ~4% molybdenum, increasing the nickel concentration from 0.7% to 2.3% decreases the total conversion by 7.6%, to near the same level of the unpromoted sulfated hematite. Similarly, at a molybdenum concentration of 0.9%, increasing the nickel concentration from 0.7% to 2.0% resulted in a decrease in total conversion to 91%, though the effect at these conditions is less dramatic. This appears to indicate that an optimum nickel concentration may exist near the 0.7% loading.

The effect of nickel and molybdenum on oil yield is shown in Figure 6. The maximum oil yield (46%) is obtained at a promoter concentration of 0.9% molybdenum, 0.7% nickel. This clearly shows the synergistic effect between nickel and molybdenum. Increasing the molybdenum loading to 4.3% resulted in a slight decrease in oil yield to 44.5%. As previously noted, an increase in nickel concentration to ~2% results in a decrease in catalytic activity.

These results indicate that nickel and molybdenum show the greatest amount of synergism of the catalysts tested here. The catalytic activity appears to be very sensitive to both molybdenum and nickel concentrations while the selectivity to oils is more sensitive to variations in nickel concentrations. Unlike the other promoter metals tested, nickel shows a distinct maximum in both total conversion and oil yield at a concentration of 0.7%. Increasing the concentration to ~2% significantly reduces the catalyst activity. The effect of small variations of nickel concentration near 0.7% are not known at this time. Given the relatively low cost of nickel compared to the other metals tested, the use of the 0.9% molybdenum, 0.7% nickel catalyst may have a favorable impact on the overall process economics.

Catalytic Activity in V-131B from Run 258

In order to determine the activity of the catalysts in a commercial process, liquefaction runs were carried out in a recycle solvent obtained from the Wilsonville facility. These experiments were carried out in horizontal microautoclave reactors with 3.0 g coal and 5.4 g V-131B solvent. The catalysts were added at 0.7 wt% iron on maf coal and sulfur was added as dimethyldisulfide. The reactors were purged and pressurized to 1000 psig (cold) with hydrogen. Reactions were carried out at 440 °C for 22 minutes to approximate the resid conversions obtained at Wilsonville in run 262.

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

$$\text{Distillate Yield} = 1 - \left[\frac{\text{Resid}_{\text{Distillation}}}{\text{Resid}_{V131B} + \text{Coal}_{\text{maf}}} \right]$$

$$\text{Resid Conversion} = \frac{\text{Coal}_{\text{maf}} + \text{Resid}_{V131B} - \text{Resid}_{\text{Distillation}}}{\text{Coal}_{\text{maf}} + \text{Resid}_{V131B}}$$

Three catalysts were chosen for evaluation in this system. The unpromoted sulfated hematite represented the least costly of the catalyst produced in this study. The 10% molybdenum represented the highest catalytic activity in the screening runs but also a very high cost associated with the high molybdenum concentration. Finally, the 0.9% molybdenum, 0.7% nickel on sulfated hematite represented the highest overall selectivity and high activity while maintaining a relatively low cost.

As shown in Figure 7, the total conversions obtained using the V-131B solvent followed the same trend as seen in tetralin. The use of 10% molybdenum gave the highest conversion (103.2%) followed by the 0.9% molybdenum, 0.7% nickel (102.2%). The lowest total conversion was obtained for the unpromoted sulfated hematite (99.3%).

Preliminary results indicate that the resid conversion and distillate yield for these catalyst follow a different trend.

Although the 10% molybdenum catalyst showed the highest total THF conversion, the 0.9% molybdenum, 0.7% nickel catalyst demonstrated a 3.5% increase in resid conversion and a corresponding increase in distillate yield of 7% over the 10% molybdenum catalyst, as shown in Figure 8. Further research is needed to confirm this finding.

Figure 1. Effect of Co/Mo Concentration on Total Conversion

Figure 2. Effect of Co/Mo Concentration on Oil Yield

Figure 3. Effect of W/Mo Concentration on Total Conversion

Figure 4. Effect of W/Mo Concentration on Oil Yield

Figure 5. Effect of Ni/Mo Concentration on Total Conversion

Figure 6. Effect of Ni/Mo Concentration on Oil Yield

Figure 7. Effect of Solvent on Total Conversion

Figure 8. Effect of Promoter Metals on Distillate Yield and Resid Conversion

Fe and Mo Impregnated Coal

The surface composition and chemical states of elements in samples of Wyodak subbituminous coal impregnated with Fe and Mo were investigated. The concentrations of Fe, Mo, S, Al, Si, Ca, C, O, and N were investigated by x-ray photoelectron spectroscopy (XPS) in samples impregnated with 0.7-2.0 wt% Fe and 500-1000 ppm Mo. The metals were deposited on the samples by an incipient wetness (I.W.) technique using solutions of ferric nitrate, ferric sulfate, ferrous sulfate and ammonium molybdate. The effect of the metal precursor, the relative amounts of Fe and Mo loading, the precipitation with NH_4OH and the method and extent of drying on the surface composition and chemical states of the elements are presented. Elemental depth profiles were determined by Ar sputtering and XPS. The influence of sputtering on the chemical form of the elements will be discussed, as well as resolution of the interference of the S_{2s} and Mo_{3d} peaks. The direct liquefaction performance of metal-impregnated coals will be presented.

Fe and Mo Impregnated Coal

Cugini, et al.,^{3,4} previously reported that finely divided and highly dispersed FeOOH-impregnated coals prepared by an incipient wetness technique have high activity in direct liquefaction. These coals were prepared by wetting the surface of the coal with a solution of ferric nitrate followed by precipitation of FeOOH using an excess of NH_4OH . The influence of variations in the incipient wetness preparation procedure on the surface chemistry and performance of the coals were previously reported.^{5,6} However, only limited data on the application of iron sulfates and co-impregnation of Mo salts was presented.

Considerable research has been done to exploit the high performance of mixed Fe and Mo catalyst in the coal liquefaction.^{7,8} Still others found higher conversion and oil yields by simultaneously impregnating coal with 1% Fe and 0.02% Mo using solutions of 10%

ferrous sulfate and 0.5% ammonium molybdate.⁹ The iron sulfates are among the least expensive form of iron compounds that are available because of their abundance as a by-product from the iron and steel industry. Andres, et. al.,¹⁰ prepared Mo-free impregnated coals using aqueous solutions of FeSO_4 and reported poor reproducibility of the impregnation technique and relatively low catalytic activity in liquefaction. Mo-Fe catalysts were also prepared by Pradhan, et al.,¹¹ who reported increased activity for direct liquefaction of subbituminous coal with sulfated α -hematites containing small amounts of added Mo.

Since Mo is expensive, its application will depend on maximizing activity at low concentrations while simplifying the preparation in order to minimize cost. In order to optimize the metal function it is necessary to understand the surface chemistry of the catalytic components. Previous data were reported on impregnation with ferric nitrate and the present report discusses the investigation of coals impregnated with both ferric and ferrous sulfate. The effect of base precipitation and drying in air or N_2 at atmospheric pressure or under vacuum was determined for these coals. To narrow the study, coals were impregnated to metal loading of 0.77 wt % Fe and 0.05-0.1 wt % Mo.

The surface composition and chemical state of various elements were studied using XPS. A depth profile of the different elements was determined using Ar^+ sputtering in conjunction with XPS measurements. The approach for measuring low concentration Mo by XPS is discussed.

Impregnated Coal Preparation - Metal impregnation with ferric nitrate was described previously.¹² The Mo-Fe impregnation procedure started with as-received coal, which contained 21 wt% moisture. The Mo salt solution was added first by adding dropwise, while stirring, 0.25 ml ammonium molybdate solution per gram dry coal followed by adding the aqueous Fe salt solution (0.5 ml per

gram dry coal). To those samples treated with base, 1.54 M NH_4OH solution was added at an $\text{NH}_4\text{OH}/\text{Fe}$ mole ratio of 139, and they were stirred vigorously and filtered. In some cases samples were further washed with water to remove any soluble salts. All were dried to a final moisture content of 10%.

XPS Analysis - XPS analyses were performed on a LHS-10 Leybold-Heraeus spectroscope as described previously.¹³ The quantification of elemental concentrations was performed using background subtraction and element sensitivity factors. Depth profiling was carried out using Ar sputtering at 3.5 Kv, 10 mA and pressure of 5×10^{-5} Torr. Molybdenum measurements were complicated by overlap of the S_{2s} peak with the Mo_{3d} peak. Reference samples containing iron and $\text{SO}_4^{=}$ were used to correct the position of S_{2s} peak and the peak area ratio of $\text{S}_{2s}/\text{S}_{2p}$ were obtained. Based on the $\text{S}_{2s}/\text{S}_{2p}$ ratio, subtraction of the S_{2s} peak area from the Mo_{3d} peak area provided an accurate measurement of the Mo concentration.

Surface Composition

The surface composition of coals impregnated with the Fe^{++} or Fe^{+++} sulfates are shown in Table 9. Included in the table is data on both raw coal and coal impregnated with 0.77 wt% Fe as $\text{Fe}(\text{NO}_3)_3$ and precipitated by addition of NH_4OH (CH-31). The surface iron concentrations of the 0.77 wt% Fe-impregnated coals prepared from either Fe^{++} or Fe^{+++} sulfate were less than for the $\text{Fe}(\text{NO}_3)_3$ impregnated coal. For these same coals, the sulfur concentrations on the surface were significantly lower in the base-treated coals. Ion analysis of the NH_4OH filtrate from the base treatment of CH-51 indicated that all of the $\text{SO}_4^{=}$ counter ion had been dissolved in the filtrate thereby freeing the surface of any sulfur and oxygen contained in the residual $\text{SO}_4^{=}$.¹⁴ The water wash used to remove remaining sulfate in several of the NH_4OH preparations, including CH-51, as indicated in Table 9, evidently was not necessary. The surface concentrations of Si, Al, and Ca decreased on the surface when base was used, except in CH-502. There was no consistent

effect of drying in air, nitrogen or under vacuum.

Surface concentrations on Fe-Mo impregnated coals are shown in Table 10. For those coals subjected to base precipitation (CH-6, CH-61), the Mo concentration is lower (relative to CH-601 and CH-604), presumably because molybdate partially dissolved in the NH_4OH solution. For the coals where Mo was added at 500 (CH-61) and 1000 ppm (CH-6), the remaining Mo on the surface was 1100 and 1400 ppm, respectively. For the non-base-washed coals, to which 1000 ppm Mo was added, the final Mo levels were 3000 and 5100 ppm. The corresponding Fe concentrations were 2.3-2.5 wt%, which were higher than for the Mo-free coals. The oxygen levels were slightly higher while the sulfur levels were significantly higher for the non-base-treated samples indicating significant deposition of SO_4^{2-} on the surface relative to the nitrate impregnated coals. In the Mo-free coals, the surface concentrations of Si and Al decreased with the NH_4OH treatment. No difference in Ca concentration was observed. There did not appear to be any significant differences in the surface compositions of the Fe^{+++} and Fe^{++} -impregnated coals, even though in the preparations the instability of the ferrous salt solution was obvious. The original blue-green color of the FeSO_4 solution rapidly changed to yellow during the application step and some deposited particles were found in the bottom of the beaker.

Table 9. Surface Composition of Fe-Impregnated Coals, wt%									
Number		CH-31	CH-51	CH-53	CH-503	CH-504	CH-52	CH-502	CH-501
Impregnating Salt	none	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Fe oxidation state	-	+3	+3	+3	+3	+3	+2	+2	+2
Added Fe, wt% dry coal	none	0.77	2.0	0.77	0.77	0.77	0.77	0.77	0.77
Precipitated	-	Y	Y	Y	N	N	Y	N	N
Washing	-	N	Y	Y	N	N	Y	N	N
Drying @ 40 °C	-	Vac	Vac	Vac	N ₂	Air	Vac	N ₂	Air
Fe	0.33	4.2	7.9	1.5	1.6	1.9	1.2	1.9	0.8
Carbon	71.1	62.4	50.9	67.9	63.3	57.1	66.3	57.1	60.9
Oxygen	20.6	24.8	30.6	23.1	23.2	26.6	23.2	26.6	25.6
Nitrogen	1.3	1.2	1.0	1.1	1.0	1.0	1.3	1.0	1.0
Silicon	4.0	3.3	4.2	2.5	4.3	5.0	4.1	5.0	5.7
Aluminum	2.0	2.5	4.3	2.6	3.4	4.6	2.6	4.6	4.1
Calcium	0.5	1.0	0.9	0.8	1.2	1.5	0.8	1.5	0.8
Sulfur	0.2	0.6	0.2	0.4	1.9	2.4	0.4	2.4	1.2
Starting coal as "as-received" coal Precipitated with NH ₄ OH solution									

Table 10. Surface Composition of Fe-Mo-Impregnated Coals, wt%				
Number	CH-6	CH-61	CH-604	CH-601
Impregnating Salt	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Fe oxidation state	+3	+3	+3	+2
Added Fe, wt% dry coal	0.77	0.71	0.77	0.77
Added Mo, ppm on dry coal	1000	500	1000	1000
Precipitated	Y	Y	N	N
Drying @ 40°C	Vac	Vac	Air	Air
Fe	2.5	3.0	2.3	2.5
Mo	0.14	0.11	0.51	0.30
Carbon	62.8	63.9	56.3	58.7
Oxygen	24.4	24.4	25.5	25.3
Nitrogen	1.5	1.4	1.5	1.2
Silicon	3.8	2.8	5.9	5.3
Aluminum	3.5	3.4	5.5	4.9
Calcium	1.3	0.9	1.0	0.8
Sulfur	0.03	0.03	1.4	1.1
Starting coal as "as-received" coal Precipitated with NH_4OH solution				

Chemical Bonding of the Elements on the Surface

Table 11 shows the measured binding energies of the various elements in Fe-S system samples compared with those in the sample treated by ferric nitrate and base precipitation. For the samples treated by base (CH-31, CH-51, 52 and 53), the binding energies are $\text{Fe}_{2p\ 3/2}$, 711.1-711.7 eV; O_{1s} , 531.7-532.4 eV; Fe_{3p} , 56.6. For sample CH-504, the peak of $\text{Fe}_{2p\ 3/2}$ was broadened with maxima at 710.9, 711.4 and 711.9 eV, and O_{1s} at 532.7 eV and Fe_{3p} at 56.4 eV. The reference peaks shown in Table 12 indicate that the O_{1s} peak is inconsistent with FeOOH . This suggests that the sample surface contains mixed Fe oxides such as FeO and Fe_2O_3 or other complex form of sulfated Fe oxides, but that FeOOH is not a prominent form present on the surface.

A difference in the $\text{Ca}_{2p\ 3/2}$ binding energies was observed between impregnated coals treated with base. The base-treated coals had $\text{Ca}_{2p\ 3/2}$ values between 346.2-347.5 eV¹⁵ while those not treated with base had values 349.8-350.1 eV. The lower range corresponds to the binding energy of Ca in CaO while the upper range corresponds to Ca in CaSO_4 (see Table 12). The presence of the CaO , and absence of any Ca exchange from the base-treated coal, as reported earlier,^{16,17} suggests any CaSO_4 , formed during the iron sulfate treatment step is converted to Ca(OH)_2 during base treatment, leaving the Ca in place in the coal.

The strongest sulfur peak at 170.9-171.5 eV in the samples made by impregnating Fe^{+2} or Fe^{+3} sulfate without subsequent base treatment is consistent with the SO_4^{2-} species (see Table 12). The other lower energy peak at 162.1-164.8 eV was significantly less intense and corresponds to the sulfur peak observed in the background coal sample.

The silicon Si_{2p} peak was observed at 103.0-103.8 eV for the base-treated coals and at 104.0-104.5 eV for the non-base treated coals.

This shift to a lower energy peak upon use of base also corresponded to a decrease in concentration on the surface, as discussed above. For aluminum, the position of the Al_{2p} peak appears not to be affected by base-treatment, although, the surface abundance of Al, like that of Si, decreases with base treatment. The position of the nitrogen peak appears to be unaffected by any of the variables in this study as seen by comparing data in Table 10 with our previous report on ferric nitrate impregnated coals.¹⁸

The dual Mo_{3d} peaks were uniform for the Mo containing coals indicating that base-treatment had little effect on the bonding of the metal. The concentration of the metal was so small that no perturbation of the oxygen binding energy was observable. Quantification and characterization of Mo in the 500-1000 ppm range is difficult because it is close to the detection limit of XPS, even though the surface concentration is typically higher than the bulk concentration. The S_{2s} peak overlaps with the Mo_{3d} peak measurement and is especially troublesome in samples having low concentrations of Mo and high concentrations of sulfur. Pradhan, et al.,¹⁹ employed a peak subtraction method to resolve this problem. Although the Mo_{3d} peak in the Fe-Mo-impregnated coals is broadened, peak deconvolution was performed based upon external standards and knowing the S_{2s} and Mo_{3d} peak positions and the relative intensities of the S_{2p} peak (169-171 eV), which is quite intense, and of the S_{2s} peak. Standards were provided by Mo, Ni and W impregnated sulfated iron oxide samples. The S_{2s} and S_{2p} peak positions for $SO_4^{=}$ were at 169.5 eV and 232.6 eV, respectively. The relative intensity ratio of S_{2s}/S_{2p} was 0.45-0.52. The $Mo_{3d} 5/2$ peak at 232.0 and $Mo_{3d} 3/2$ at 235.1 agree with those observed for the Fe-Mo-impregnated coals. Subtraction of the half-height S_{2p} peak area from the measured Mo_{3d} peak area provided a reliable method for determining Mo concentration.

Table 11. Binding Energies for Fe and Fe-Mo Impregnated Coals

	Salt ¹	Base	Fe eV			O _{1s} eV	N _{1s} eV	Si _{2p} eV	Al _{2p} eV	Ca _{2p} eV		S _{2p} eV	Mo _{3d} eV	
			Fe _{2p 3/2}	Fe _{2p 1/2}	Fe _{3p}					Ca _{2p 3/2}	Ca _{2p 1/2}		Mo _{3d 5/2}	Mo _{3d 3/2}
CH-31	FN	Y	711.1	725.1	56.6	531.7	399.1	103.8	75.0	346.2	351.0	162.1 168.4		
CH-51	Fe ⁺³	Y	711.3	725.1	56.6	531.7	399.5					163.3 167.0		
CH-52	Fe ⁺²	Y	711.7	725.4	56.3	532.5	399.1			347.4	350.6	164.0 169.7		
CH-53	Fe ⁺³	Y	711.5	725.6	56.2	532.4	400.0	103.6		347.2	351.0	163.6 169.6 168.4		
CH-501 ²	Fe ⁺²	N	710.5 711.8	727.5 725.9	54.1	532.9	400.2 396.6	104.5	76.1 74.2	349.9	353.1	163.2 171.2		
CH-502	Fe ⁺²	N	710.0 711.4		55.6	532.6	399.8	104.1	75.6	349.8	353.3	163.3 171.1		
CH-504	Fe ⁺³	N	710.9 711.4 711.9	726.6	56.4	532.7	400.7	104.1	75.4	350.1	353.9	163.6 171.5 185.6		
CH-6	FN-AM	Y	711.3	724.8	56.1	532.2	399.6	103.0	74.8			164.8 169.2	232.4	235.9
CH-61	FN-AM	Y	711.3	725.1	56.0	532.0	399.8		74.8	347.5	351.0	163 169	232.5	235.6
CH-601	Fe ⁺² -AM	N	709.8	727.4	53.5	532.6	400.1 392.3	104.0	73.3	349.9	354.0	164.3 171.2	232.5	235.4
CH-604	Fe ⁺³ -AM	N	710.5	727.6	55.4	532.6	399.5 394.1	104.1	73.7			163.0 170.9	232.3	235.4

1. FN=Fe(NO₃)₃•9H₂O ; F⁺³=Fe₂(SO₄)₃•5H₂O ; Fe⁺²=FeSO₄•7H₂O ; AM=Ammonium Molybdate 2. CH-501 Fe_{3s}=93.8 and 96.0 eV.

Table 12. Reference Binding Energies

	Fe eV			O _{1s} eV	N _{1s} eV	Si _{2p} eV	Al _{2p} eV	Ca _{2p 3/2} eV	S eV		Mo _{3d} eV	
	Fe _{2p 3/2}	Fe _{2p 1/2}	Fe _{3p}						S _{2p}	S _{2s}	Mo _{3d 5/2}	Mo _{3d 3/2}
αFeOOH	711.0-711.8		56.6±0.2	530.1-531.8								
α-Fe ₂ O ₃	710.8-711.4		55.7±0.15	529.8-530.2								
FeO	706.9-710.3		54.9±0.3	529.8-530.1								
Fe ₃ O ₄	708.3-711.4		53.9±0.2	530.0±0.01								
FeS									163			
FeSO ₄									171			
Fe ₂ (SO ₄) ₃												
Ca or CaS								345				
CaO								346-347				
CaSO ₄								348-349	170			
SiO ₂				532.8		103.6						
Al ₂ O ₃				531.8			74.7					
Mo/Fe ₂ O ₃ /SO ₄ ⁼	710.4	724.1	55.4						169.8		232.0	235.1
W/Fe ₂ O ₃ /SO ₄ ⁼	711.0	724.5	56.1						169.3	232.5 ^a		
Ni/Fe ₂ O ₃ /SO ₄ ⁼	711.0	724.6	56.1						169.4	232.6 ^b		

a. $S_{2p}/S_{2s}=0.45$. b. $S_{2p}/S_{2s}=0.52$

Thickness of Surface Layer

An argon sputtering technique was used to explore the chemistry of the sub-surface of the metal impregnated coals. Argon sputtering at 3.5 KV, 10 mA and a pressure of 5×10^{-5} Torr. was performed for periods of up to 2 hours. The sputtering rate was calibrated with standard Au and Cu films at these same sputtering conditions. Based on the composition of the impregnated coal samples, a sputtering rate of 15 angstroms per minute was presumed. The thickness of the layer that would be sputtered from the coal then would be 0.1μ for 75 minutes and 0.2μ for 120 minutes. Generally, at these levels of intensity, sputtering for 1 minute will remove approximately 30 angstroms of surface. Several of the samples of Fe and Fe-Mo-impregnated coals were examined by this technique.

The element concentrations for ferric sulfate-impregnated coal (CH-504) was determined after 45 and 75 minute sputtering exposures (Table 13). The metals and carbon concentrations all increased with increased sputtering time. Oxygen, however, dropped quite dramatically from 26.6% to 8.2%, while sulfur decreased from 2.4% to 1.5%. With the drop in oxygen peak intensity, the relative position of the 533 eV peak did not shift, although other peaks began to appear at 524 and 540 eV as shown in Table 14. Thus, the type of oxygen bonding did not appear to change. Likewise, for the iron, the peak at 710-711 eV also did not noticeably change, suggesting no significant change in the Fe bonding.

Sputtering of a Mo-Fe-impregnated coal sample CH-604 over a period of 2 hours showed an increase in iron concentration on the surface similar to the Mo-free sample as shown in Table 15. As previously noted, however, the iron concentration on the Fe-Mo sample was higher than the Fe-only sample. Unlike the Fe-only sample, the Mo-Fe sample showed a slight loss in Si, a somewhat greater loss in Al, and no significant change in Ca, versus sizable gains for all three in the Fe-only sample. The changes in oxygen and sulfur, however, were similar to the Fe-only sample dropping quite sharply. The oxygen went from 25.5% in the unsputtered sample to 12.2% after 120 minutes. The Mo concentration that was loaded at 1000 ppm

started at 0.50 wt% on the surface in the unsputtered sample decreasing to 0.12 wt% after 120 minutes, suggesting that the deposition of the Mo was primarily on the outer most surface of the coal. The peak positions shown in Table 16 indicate that no significant change in the bonding occurred even after 120 minutes, unlike the Fe-only sample,.

It appears, therefore, that at $0.2\ \mu$ below the outer surface of the coal, the concentration of Fe is still quite high, while the Mo concentration drops off indicating that the Mo is located primarily in a thin layer of $0.02\ \mu\text{m}$ thickness. Most of SO_4^{-2} ion is contained in the $0.2\ \mu\text{m}$ thick layer. The oxygen concentration drops below the bulk level of the coal which is a result of the Ar+ sputtering effect. During sputtering, the lighter elements are more easily removed. However, for some reason, the nitrogen does not seem to be overly affected by sputtering. With the removal of oxygen atoms, a change in the oxidation state on the surface of the coal likely occurs, which for iron appears as broadening toward lower energy. This results in a deconvoluted peak at 703-704 eV, which could be a lower oxidation state of Fe such as an FeO structure or free Fe.

Table 13 . Surface Composition of Sputtered Fe-impregnated Wyodak Coal, wt%

	Coal (dry)	0.77 wt% Fe ⁺⁺⁺ CH-504		
		Not Sputtered	Sputtered 45 min	Sputtered 75 min
Impregnating Salt	None	Fe ₂ (SO ₄) ₃ •5H ₂ O	Fe ₂ (SO ₄) ₃ •5H ₂ O	Fe ₂ (SO ₄) ₃ •5H ₂ O
Fe	0.33	1.89	2.14	2.26
Carbon	71.1	57.1	62.2	64.6
Oxygen	20.6	26.6	11.4	8.2
Nitrogen	1.3	1.0	1.3	1.6
Silicon	4.0	5.0	6.8	6.8
Aluminum	2.0	4.6	5.0	5.1
Calcium	0.5	1.5	9.1	10.1
Sulfur	0.2	2.39	2.09	1.52

Table 14. Binding Energies for Fe-Impregnated Coals

	CH-504 Unspattered	CH-504 Sput-45 min†	CH-504 Sput-75 min†
Fe _{2p} 3/2	710.9 711.4 711.9	710.6 703.4	710.2 704.2
Fe _{2p} 1/2	726.6	724.7 716.8	725.5 717.7
Fe _{3p}	56.4	56.6	56.9
O _{1s} eV	532.7	533.1 523.9 539.5	532.8 524.3 540.0
N _{1s} eV	400.7	399.3	400.9
Si _{2p} eV	104.1	104.1	103.8
Al _{2p} eV	75.4	72.1	72.7
Ca _{2p} 3/2	350.1	345.9	346.9
Ca _{2p} 1/2	353.9		
S _{2p} eV	163.6 171.5 185.6	164 171	171.3 164

*CH-501 Fe_{3s}=93.8 and 96.0 eV †Sp60m = Sample Ar sputtered 60 min.

Table 15. Surface Composition of sputtered Fe-Mo-impregnated Wyodak Coal, wt%					
	0.77 wt% Fe ⁺⁺⁺ CH-604				
	Unspattered	Sputtered 15 min	Sputtered 30 min	Sputtered 60 min	Sputtered 120 min
Impregnating Salt	Fe ₂ (SO ₄) ₃ •5 H ₂ O	Fe ₂ (SO ₄) ₃ •5H ₂ O	Fe ₂ (SO ₄) ₃ •5H ₂ O	Fe ₂ (SO ₄) ₃ •5H ₂ O	Fe ₂ (SO ₄) ₃ •5H ₂ O
Fe	2.34	2.8	3.0	3.4	3.6
Mo	0.51	0.20	0.12	0.12	0.12
Carbon	56.3	64.3	66.9	68.7	71.1
Oxygen	25.5	17.6	15.0	14.4	12.2
Nitrogen	1.5	1.4	1.6	1.4	1.4
Silicon	5.9	6.2	5.9	5.5	5.5
Aluminum	5.5	5.3	5.1	4.6	4.1
Calcium	1.0	1.1	1.2	0.9	1.1
Sulfur	1.4	1.3	1.2	1.1	0.9

Table 16. Binding Energies for Fe-Mo Impregnated Coals													
	Fe eV			C _{1s} eV	O _{1s} eV	N _{1s} eV	Si _{2p} eV	Al _{2p} eV	Ca _{2p} eV		S _{2p} eV	Mo _{3d} eV	
	Fe _{2p 3/2}	Fe _{2p 1/2}	Fe _{3p}						Ca _{2p 3/2}	Ca _{2p 1/2}		Mo _{3d 5/2}	Mo _{3d 3/2}
CH-604	710.5	727.6	55.4	299.0- 14.4	532.6	399.5 394.1	104.1	73.7			163.0 170.9	232.3	235.4
CH-604 Sp15m†	710.2	728.4	55.4	298.2- 13.6	533	399.8	103.7	74.6	349.9	353.4	163.0 171.3	233.0	235.9
CH-604 Sp30m†	710.8 715.6	727.3 729.1	56.6	297.9- 13.3	533.3	400.1	104.0	74.9	350.7	354.4	163.0 171.8	234.9	237.4
CH-604 Sp60m†	710.8 715.0	724.0 729.7	56.4	297.9- 13.3	532.8	398.3 394.7	104.0	74.9	350.7	353.1	163.2 172.1	235.9	237.7
CH-604 Sp120m†	710.6	729.8	56.3	297.5- 12.9	533.1	399.4	104.3	75.4	350.7	353.3	163.5 171.1	234.3	236.1
†Sp60m = Sample Ar sputtered 60 min.													

TASK 4.0 - TECHNICAL ASSESSMENT

Process Options

Assumptions - Reference is made throughout this section to the base case as defined previously by LDP Associates.²⁰ Using the stream flows provided in that base case and summarized in Figure 9,²¹ rough economic assessments of a series of options for reducing the cost of liquefaction product were made. Specific assumptions used in this analysis were:

- Capital costs contribute \$20 to the final crude oil equivalent (COE) product.
- Operating costs contribute \$20 to the final COE product.
- Individual unit costs and overall plant costs provided by LDP Associates were used.

"Nil Reactor"

At the outset of this analysis it was desirable to determine how much effect eliminating the coal reaction section would have on product costs, thereby providing an estimate of the magnitude that changes in this section can have on the overall product cost. Thus it was assumed that reactor size had no effect on overall product distribution and could be reduced to a minimal size. It was likewise assumed that hydrogen consumption and the product slate would remain the same. The capital costs associated with the coal reaction section are:

•	1st-stage reactor	\$290 million
•	2nd-stage reactor	\$123 million
•	Rose Unit	\$ 46 million
	Total	\$459 million

The total costs represents 13% of total investment, which is equivalent to \$2.60/bbl COE. In addition, thermal efficiency would be expected to increase to 90% for the liquefaction section and 80% overall due to the lower efficiency of the hydrogen production section. The improved thermal efficiency would save ~3,000 tpd coal or 50 cents/bbl COE. A corresponding ~10% decrease in electric power would save an additional 25 cents/bbl COE. Overall savings, including

Figure 9. Base Case Stream Flows

* Includes DAS (see ref 21)

both capital and operating costs, would be about \$3.50/bbl COE. These results suggest that savings on hydrogen production and other utilities would likely be more important for reducing overall costs.

Plant Location

Since total plant costs for the base case Wyoming location is estimated to be 20% higher than a Gulf Coast location, it was desirable to understand the impact of location relative to the types of options that are practical for consideration. Note, however, that Exxon reported using a higher 40% adjustment factor. Thus, for capital related items this represents a 20% increase of \$4/bbl COE (20% of \$20/bbl capital COE). This decrease in capital would allow an equivalent 20% increase in operating cost on a COE basis. Taking all of this increase in coal cost would be equivalent to \$25/ton, i.e., $[\$10 \times (82 + 52.9) / 52.9]$, versus \$10/ton in the base case.

Moving the plant to the Gulf Coast would provide \$15/ton to cover the cost of transportation. At a different location availability of another better quality coal would have to be compared on a cost per unit energy content. Likewise, using the Exxon adjustment factor of 40% would double the amount of differential in coal cost.

Resid Recycle Around 2nd-Stage Reactor

Slurrying the coal with the richest hydrogen-donor solvent fraction that is available could both promote the coal depolymerization reaction and prevent retrogressive reactions by providing the best available solvent at the site of the initially reacting coal. This could affect subsequent processing by providing a material that is more easily hydrotreated. More intimate contact between donor-rich solvent and coal could be achieved by feeding the recycled IOM separately from the coal or sending the IOM directly to the 2nd-stage reactor. In the latter case, it could serve to reduce the exotherm in that reactor.

In Figure 10 the recycle resid stream is fed to the 2nd-stage reactor while coal is fed to the 1st-stage reactor at a solvent:coal ratio of about 1:1. In this case, where the downstream product treatment would

Figure 10. Recycle Around 2nd-Stage Reactor

be virtually unchanged, the relative sizes of the 1st and 2nd-stage reactors would change. In a full scale plant this change would presumably have little impact on overall plant investment costs.

Impact of Changing Reactor Size

Several cases that have been contemplated involve changing reactor size to give additional residence time. In order to provide directional guidance regarding the feasibility of this option, an estimate of differential costs associated with a change in reactor size was determined. The assumptions are:

- Incremental reactor costs are assumed to be \$0.8 million per ton weight of reactor, which is based upon an estimated current price for a 950 ton reactor of \$7.5 million.
- The maximum reactor size is assumed to be 1200 tons.
- Installed equipment costs are assumed to be 3 times equipment cost.

The base case contains in the 1st stage, six 700 ton reactors having an approximate cost of \$34 million. Increasing each reactor by 50% would continue to be feasible from a construction standpoint as well as be within the upper limit of capacity. Increased reactor cost would then be \$17 million. The second stage contains six 420 ton reactors having a comparable cost of \$20 million. Doubling these reactors would increase reactor cost by an additional \$20 million. The overall increase for both stages would be \$37 million.

Using the fully installed/capital item ratio of 3 would result in a total increase of \$111 million. An ammount this high is highly unlikely, since in each case the only modification is to reactor size and does not involve other major changes, such as new trains. Therefore, a more probable capital cost range would be $\$74 \pm 37$ million. On a capital cost of \$4 billion, this represents $2 \pm 1\%$ of the total. Operating costs adjustment would likely be minimal since the impact on maintenance, labor, and electrical cost would not be significant since no new pumps or trains are involved.

Increasing reactor volumes in the 1st and 2nd-stages by 50% and 100% would increase the COE price by 40 ± 20 cents/bbl with negligible effect on the operating costs. On this basis, increasing just residence time by 50 and 100% in the 1st and 2nd-stage sections, respectively, would cost only 40 cents/bbl COE. Correspondingly, reducing reactor size to a negligible size can only save 40 cents/bbl COE, assuming no other changes.

Low C_1-C_3 Gas Make

The impact of minimizing C_1-C_3 gas make was evaluated. The limiting case where all C_1-C_3 gases are eliminated was developed as shown in Table 17. In this case for each 100 pounds of coal, 8 pounds of C_1-C_3 gases are produced which incorporates 2 pounds of hydrogen. By eliminating this gas make, the hydrogen consumption is reduced by 1.8

Table 17. C_1-C_3 Gas Make - Limiting Case ¹					
		Total Weight	Carbon	Hydrogen	Oxygen
Base Case:					
In	Coal	100	80	5	15
	Hydrogen	9		9	
	Total In	109	80	14	15
Out	C_1-C_3 gas	8	6	2	
	C_4^+ Product	84	74	10	
	H_2O, H_2S, NH_3	17		2	15
	Total Out	109	80	14	15
No C_1-C_3 gas					
In	Coal	92.6	74	4.6	14
	Hydrogen	7.2		7.2	
	Total In	99.8	74	11.8	14
Out	C_4^+ Product	84	74	10	
	H_2O, H_2S, NH_3	15.8		1.8	14
	Total Out	99.8	74	11.8	14
1. For simplicity, CO_2/CO production is ignored.					

pounds (9-7.2) and the total coal feed is reduced by 8 pounds per 100 pounds coal feed at the same 84 pounds C_4^+ product make. Therefore, eliminating the C_1-C_3 gas reduces the hydrogen demand by 20% and a reduction in the ITSL reaction capacity of 8% (100-92). Subsequent refining capacity would remain unchanged since the total C_4^+ product would remain unchanged. With the loss in C_1-C_3 gas the amount of coal that would have to be gasified to produce hydrogen would have to be increased based upon a 70% efficiency around the shift converter.

Based upon these assumptions, plant capital would be reduced by ~10% and operating costs would diminish by a similar amount. This is because electricity consumption would decrease significantly and coal conversion would decrease slightly, since overall thermal efficiency would improve by ~1%. This case appears to have the potential of reducing costs by up to ~10% overall or \$4/bbl crude oil equivalent (COE). Diminishing the C_1-C_3 gas make by 1/10th would still make a very significant decrease in the product price (40¢/bbl COE).

One approach to achieve this target is to lower the initial temperature of the reaction to diminish gas make. This will require modifying the recycle from the current base case as well as subsequent hydroprocessing of the initially formed resid product. The constraint of operating in a downstream mode so as not to generate hydrocarbon gases must be met for this approach to be feasible.

Modification to Solids/Liquid Separation Technique

Other solids separation techniques have been examined over the years in various process configurations. Two different scenarios were addressed in this brief evaluation, namely, vacuum distillation and filtration.

A limiting case is illustrated relative to the base case as shown in Figure 11. In this modified base case, the product from the atmospheric flash would be fed to a mild vacuum flash stage to generate product. The overall effect would be a reduction of liquid product yield of 7 units. From this stage a total of 261 units would be produced as a bottoms product. Rather than feed all of the bottoms

Figure 11. Solids Rejection by Vacuum Distillation

to the deep vacuum flash unit, only a portion, i.e., 74 units, are fed to this unit. From this step would be produced 46 units of vacuum distillate, which would be used for recycle to give an overall volume of process solvent equal to the base case, and 28 units of vacuum bottoms.

In this case the key features are:

- Solids are discharged as a slurry containing 50% solids. The ash concentrate would differ from the ROSE unit in that the resid to ash concentrate would increase from 1:1 to 2:1.
- The loss of 7 units of heavy distillate product would require an increase in the volume of the liquefaction section of nearly 10% in order to maintain a 50,000 bbl/D product yield.
- This would require an increase of coal to grinding, etc., of 10% which would add \$50-70 million (at a 0.7-1.0 factor on 10% of \$703 million).
- Eliminating the ROSE unit saves \$46 million.
- Total coal fed to the plant would be hardly affected since the extra discharged liquid from the vacuum stage would be gasified thus reducing the gasifier coal feed.
- With the lower amount of distilled solvent, the energy consumption using the mild vacuum distillation scenario would be less than for the ROSE but more than for filtration.

Solids separation from the vacuum distillation bottoms would have an increase in capital cost of \$50-70 million plus the cost of increasing the reaction section by 10% which would exceed the cost of the ROSE unit that would be eliminated.

The corresponding case of substituting filtration for the ROSE unit for ash removal is shown in Figure 12. Product from the 2nd stage reactor is fed to an atmospheric flash unit and then to an atmospheric tower. A net increase of 5 units in distillate is projected in liquid product from the atmospheric tower with 249 units of bottoms being generated. This stream is then split sending 215 units to recycle makeup to be combined with clean filtrate. The remaining 34 units

Figure 12. Solids Rejection by Filtration

from the atmospheric tower is then sent to filtration to produce 18 units of clean filtrate and 16 units of ash concentrate comprising resid (2 units), IOM (7.5 units), and ash (6.6 units).

The key features of this case are:

- Rejection of resid with the filter cake will decrease the resid:ash ratio from 1:1 to 0.3:1.
- Cost of filtration is very similar to the cost of the ROSE unit thereby causing no change in the cost of solid separation.
- Net distillate product would increase by 5 units which would result in a reduction of the front end of the plant by ~7%.

The savings from substituting filters would be \$35-50 million which is equivalent to 1.7-2.5% of capital investment. This assumes offsites are similarly affected thereby resulting in an overall reduction of investment of 2%, i.e., 40 cents/bbl COE.

Increasing Residence Time

Base case total catalyst cost is 20% of operating cost, which is broken down as follows:

- Iron and sulfur $\approx$ 40 cents/bbl COE
- Dispersed $\approx$ \$1.60/bbl COE
- Supported $\approx$ \$1.90/bbl COE

Saving could be realized if lower cost or more active catalysts were used. If longer life could be attained with the supported catalyst to give the same yields by merely increasing residence time, substantial savings could be made. For example, if residence time over the supported catalyst could be increased by 50% by increasing the size of the reactor, the following costs impact would be realized:

- Reduction in catalyst cost of 65 cents/bbl COE
- Increase in reactor cost of 10 ± 5 cents/bbl
- Total savings would be 55 cents/bbl.

If all catalyst costs were halved by doubling residence time, the following cost impact would be realized:

- Reduction in catalyst cost of \$1.95/bbl COE
- Reactor cost would increase by 55 cents/bbl COE
- Overall savings of \$1.40/bbl would be realized

Options of reusing spent catalyst by grinding and feeding as dispersed catalyst could result in added savings. Also regeneration of supported catalyst 2 or 3 times for \$0.80 to \$1.00 per lb for each regeneration could reduce the supported catalyst cost from \$3/lb. At \$2/lb this would provide a savings of \$1/bbl COE.

Replacing 1st-Stage Dispersed Catalyst

Experimental work has shown that hydrogenated distillate solvent gave conversion and oil yield equal to that observed with addition of SFIO at 415 °C. The feasibility of hydrotreating as a trade-off against 1st-stage catalyst cost is addressed in this case. Since the rate of hydrogenation is proportional to pressure, adding 2% hydrogen in one pass is feasible at 1 LHSV at ~360 °C and 200 bar.

In this case half of the distillate solvent is hydrotreated which is equivalent to 6000 tpd (250 tph=250 m³/hr= 7500 ft³/hr). A full sized ebullated bed reactor which is 12 ft x 100 ft (1000 tons) would be used. The hydrogen production costs would remain unchanged since total hydrogen consumption would remain the same. The cost of the reactor would be ~\$10 million plus additional capital equipment such as pumps, etc. for a total of \$15 million. Using the installation factor of 3 the total installed cost would be \$45 million. (Note the 2nd-stage reactor which is three-fold larger is \$120 million.) Therefore, the capital cost of the plant would be increased by ~1% or 20 cents/bbl COE.

The potential saving in the catalyst to the first stage would be \$32 + \$9 million per year. However, approximately 200 tons of hydrogenation catalyst having a 6 month life would be required. The total cost per year would be 400 tons at \$3/lb for a cost of \$2.4

million. Saving on catalyst would be \$30 to \$39 million/yr on a total operating cost of \$412 million, or \$1.45 to \$1.90/bbl COE. Net savings would be \$1.25 to \$1.65/bbl COE.

Correspondingly, treating all of the distillate at 1500 psig would increase capital cost at a maximum of 40 cents/bbl giving a net savings $\geq$ \$1.00/bbl COE.

CO Pretreatment

Two options for employing this approach are given in the following two cases.

Case 1: In this case which is illustrated in Figure 13, a formate salt is formed in the first vessel in the presence of CO at $\sim 110^\circ\text{C}$ and CO partial pressures from 250 to 500 psig. The reaction occurs rapidly and will be exothermic. The formate solution is then contacted with the coal as a 1:1 slurry and passed to a reactor where it is heated to 300°C . The slurry is passed to solids separation where coal is removed and the liquid phase is passed to the front end where formate is reformed. Coal is then sent to liquefaction. The use of ammonia precludes the need for purchase of any sodium material and eliminates the threat of any sodium or other salt getting into the coal. The ammonia would be recovered in the gas cleanup system.

Costs would be as follows:

- The vessel in which the formate is produced would be quite inexpensive.
- The coal slurry tank would be the same cost as in the main plant.
- The cost of the 1500 psig treatment tank would be intermediate between a liquid solvent extraction (LSE) vessel and an ebullated bed reactor that operates at 3000 psig.
- Solids separation should be fast, but it involves handling sizable amounts of pretreated coal.

1-59

Figure 13. Case 1 - Low-Temperature CO Conversion

Within these limits, the costs would be similar to the cost of the first stage of a LSE plant, but would have simpler heating systems. Since the capital cost of the 1st-stage of a LSE plant costs about 12% of total plant cost, the CO-pretreatment plant would be about 10% of the total, or \$400 million capital cost or an increase of \$2/bbl COE.

Case 2: In this case illustrated in Figure 14, coal and water would be slurried, ammonia would be mixed with the slurry, and the resulting mixture passed to a reactor operating at 300 °C with 1500 psi syngas partial pressure with a total pressure of ~3000 psig. Following reaction, the slurry would be mixed with recycle solvent and steam would be released and sent to heat recovery. This scheme requires less hardware overall but would still be about 5% of total plant cost or \$1/bbl COE.

Hydrogen Addition with Syngas: Since some hydrogen is added in the CO-pretreatment step, presumably this would reduce the overall hydrogen consumption by a like amount. Therefore, some savings may result in adding hydrogen via the syngas route at the low temperature. In this cost analysis, CO is assumed to be 70% of the cost of hydrogen on an energy basis and 10% of the hydrogen is added in this step. Since hydrogen represents 25% of cost of product (capital and fuel) the savings would be 0.8% of total product ($0.1 \times 0.25 \times 0.3 = \sim 0.8\%$). Since total product is \$40/bbl, the savings by using syngas versus hydrogen would be 30 cents/bbl COE. The assumptions used in substituting syngas pretreatment are very optimistic and ignore the added complexity of syngas handling systems.

Summary: Coupling the estimate made for cost in Case 2 with the estimate regarding the addition of hydrogen using syngas suggests that the CO-pretreatment will cost at least an additional 70 cents/bbl COE. Any additional advantage in higher activity has not been considered, nor has any improved product quality that might result from this approach. If higher activity could translate to reduced catalyst cost through elimination of the 1st-stage catalyst, significant additional savings could result.

Figure 14. Case 2: High-Pressure CO Pretreatment

Oxygen Removal as CO₂ Rather than as Water

The economic sensitivity of removing oxygen as CO₂ instead of water is examined in this case. The competing reactions are:

By mass, 1/3rd the amount of hydrogen is needed relative to the amount of carbon, which is approximately the same heat content (H₂ 50,000 Btu/lb, carbon 14,000 Btu/lb). Carbon is much cheaper per Btu than hydrogen, e.g., for Black Thunder coal base case:

\$10/ton for 8,000 Btu/lb, or

60¢/10⁶ Btu.

Hydrogen, via gasification of coal or natural gas @\$2.50/10⁶ Btu, would cost around \$3.00/10⁶ Btu. The corresponding cost of gasoline is \$3.50/10⁶ Btu.

If all oxygen were removed by carbon rather than with hydrogen, then 6% more carbon as coal would be needed. Overall, about 10% more coal would be fed to the reactor at a cost of \$5 million or 25¢/bbl COE. The corresponding need for hydrogen from the hydrogen plant would be drastically reduced since there is a 2% on coal reduction which is equivalent to 33% on total hydrogen required. Since approximately 40% of the plant capital cost is hydrogen related, this could be a reduction of as much as 13% in capital cost or ~\$2.60/bbl COE.

Corresponding operating costs are also reduced, mainly by reduction in electricity demand, but also in capital cost related items, but not in coal or catalysts which are used unchanged. Savings could easily be 10% on operating costs or ~\$2.00/bbl COE. The overall savings of being able to expel oxygen as CO₂ rather than H₂O would be in excess of \$4.00/bbl COE. A corresponding shift as follows from:

to:

would be worth 25¢/bbl COE. A reasonable objective of increasing oxygen rejection as CO₂ from 25% to 50% is worth \$1.00/bbl COE.

Increased Slurry Time

Increasing the slurry residence time from a minute to one hour at around 300 °C could have an effect of improving yields. This case considers the cost of this option for a slurry flow rate of 1500 tph (1,500 m³/hr). This could be achieved in a single 8 m x 30 m (26 ft x 98 ft) reactor which is equivalent to a typical delayed coker. Assuming a 2 inch wall thickness, which should be rated at ~300 psi, the weight would be ~500 tons. The construction cost would be ~\$4 million based on the previously stated logic, which would be an overly conservative estimate.

Since this case involves addition of a reactor without the full complement of offsites related to a typical liquefaction reactor, the 3x factor for installed cost may be overly conservative. However, since the base design has only a small slurrying reactor with minimal holding time, the use of the full factor is probably necessary. Therefore, the capital cost for achieving a 1 hour slurry residence time is \$12 million which is equivalent to an increase in capital of 0.3%. This would be equal to 6 cents/bbl COE. Based upon a 1% improvement in conversion, this cost would be quite small since previous reports have indicated that a 1% improvement in conversion will reduce overall costs by 0.6%, i.e., 25¢/bbl COE.²² Therefore, an overall net savings of approximately \$0.18/bbl COE would be realized if this level of improvement were realized. Of course, larger improvements would more than multiply this reduction in costs.

Optimization of Coal Grinding

The grind size typically used for power generators is used in the base case for the liquefaction plant, although the standard size is not necessarily optimum for liquefaction. This case examines the cost of supplying a smaller grind size to the plant. If a process advantage could be gained by grinding from a nominal median size of 50 µm to 30 µm, the cost of grinding would double adding 44 cent/bbl COE. If the consequence of feeding the smaller grind size to the 1st-stage reactor was to reduce the volume by 50% due to higher reactivity, then the savings of 20 cents/bbl COE would not

be adequate to cover the grinding cost. Conversely, if 100 μm were small enough, the saving in coal grinding cost would be 20-30 cents/bbl COE.

Other aspects of coal size that need to be quantified are:

- effect on solid-liquid separation (generally the bigger the particles the easier the separation)
- higher slurry concentrations can be handled with larger coal particle sizes if viscosity is the limiting factor
- coarser filter screens can be used with larger grind sizes since bridging occurs more easily.

Other Options to be Considered

1. Shift catalyst from 1st-stage to 2nd-stage or shift portion to 2nd-stage
2. Removing ash and IOM would decrease recycle mass from 2.3/1 to 2.1/1.
3. Lowering pressure
4. Evaluate the effect that hydrogen and oxygen content in coal has on overall hydrogen demand

Summary

Ranking these options by potential for reducing costs;

High	Lower C1-C3	Can give up to \$4/bbl COE; use of low temperature, larger reactors, resid recycle to 2nd-stage reactor.
	Replace 1st-Stage Catalyst	\$1.00-\$1.65/bbl COE; hydrotreat solvent; lower solv/coal ratio.
	Increase residence time	\$1.40/bbl COE;
Medium	Filtration	\$0.40/bbl
	Coal Grinding	\$0.20/bbl
	Increase slurry time	> \$0.18/bbl
Low	CO-Pretreatment	Unknown

References

1. Quarterly Report, Jan.-Mar. 1993, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-25, June 1993.
2. Elliott, D. C.; Sealock, L. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 431.
3. Cugini, A. V.; Utz, B. R.; Krastman, D.; Hickey, R. F. *Prep. Pap. - Amer. Chem. Soc., Div. Fuel Chem.* **1991**, *36 (1)*, 91.
4. Utz, B. R.; Cugini, A. V. U. S. Patent 5,096,570, Mar. 17, 1992.
5. Ni, H. F.; Anderson, R. K.; Givens, E. N.; Stencel, J. M. *Prep. Pap. - Amer. Chem. Soc., Div. Fuel Chem.* **1993**, *38 (3)*, 1107
6. Quarterly Report, Jan.-Mar. 1993, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-25, June 1993, pp. 45-66.
7. P. Courty and C. Marcilly, Preparation of Catalysts, edited by B. Delmon, P. A. Jacobs and G. Poncelet, 1976, Elsevier Scientific; New York; p 191.
8. Scaroni, A. W.; Derbyshire, F. K.; Abotsi, G. M. K.; Solar, J. M. Final Technical Report, DOE/PC/60050, June, 1987.
9. Garg, D.; Givens, E. N. *Fuel Processing Technology*, **1984**, *8*, 123.
10. Andres, M.; Charcosset, H.; Chiche, P.; Djega-Mariadassou, G.; Joly, J. P.; Pregermain, S. *Preparation of Catalysts III*; Elsevier Science; New York, 1983, p 675.
11. Pradhan, V. R.; Tierney, J. W.; Wender, I. *Prep. Pap. - Amer. Chem. Soc., Div. Fuel Chem.* **1992**, *37 (1)*, 254.
12. Quarterly Report, Jan.-Mar. 1993, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-25, June 1993, pp. 45-66.
13. Ni, H. F.; Anderson, R. K.; Givens, E. N.; Stencel, J. M. *Prep. Pap. - Amer. Chem. Soc., Div. Fuel Chem.* **1993**, *38 (3)*, 1107
14. Quarterly Report, Jan.-Mar. 1993, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-25, June 1993, see Table 20, p 51.
15. Quarterly Report, Jan.-Mar. 1993, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-25, June 1993, see Table 22, p 55.
16. Quarterly Report, Jan.-Mar. 1993, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-25, June 1993, see Table 20, p 51.

17. Quarterly Report, Oct.-Dec. 1992, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-21, February 1993, see Table 27, p 89.
18. Quarterly Report, Jan.-Mar. 1993, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-25, June 1993, see Table 22, p 55.
19. Pradhan, V. R.; Tierney, J. W.; Wender, I. *Prep. Pap. - Amer. Chem. Soc., Div. Fuel Chem.* 1992, 37 (1), 254.
20. Quarterly Report, "Advanced Liquefaction Concepts for PETC Generic Units", Feb. 1993, DOE/PC/91040-29, August 1993, Section 4.
21. Taken from Figure 1A, Quarterly Report, "Advanced Liquefaction Concepts for PETC Generic Units", Feb. 1993, DOE/PC/91040-29, August 1993, Section 4.
22. Moore, S. A.; Kimber, G. M.; Gray, M. D. Proceedings, Tenth Annual Pittsburgh Coal Conference, September 1991, p 747

SECTION TWO

CONSOL, Inc.

**QUARTERLY PROGRESS REPORT
FOR THE PERIOD JULY 1 THROUGH SEPTEMBER 30, 1993
SUBCONTRACT No. UKRF-4-25582-92-76**

TASK 1.2 - LABORATORY SUPPORT (CONSOL)

Summary

The samples from Wilsonville Run 255 (Texas lignite) that were received from Amoco were prepared for use in this project. Samples of Martin Lake lignite and Burning Star 2 Illinois No. 6 coal were sent to Sandia.

One package of Martin Lake lignite in use at CONSOL was found to have a relatively low ash content. CONSOL recommended that any samples of this coal found to have ash contents below 13 wt % (MF, SO₃-containing basis) be discarded.

A sample of coker tar, two samples of hydrotreated coker tars and eight hydrogenated distillate samples were received from Sandia. The hydrogenated distillate samples were prepared by hydrotreating samples of V-1074 distillation fractions and dewaxed V-1074 distillation fractions that we sent them.

Evaluation of CAER's microautoclave workup procedure to determine resid conversion is complete. Results will be sent to participants in the near future.

Discussion

The samples from Wilsonville Run 255 (taken during Texas-lignite-only periods of operation in the thermal/catalytic mode at 840 °F) that were received from Amoco and selected for use in this project were prepared for use. The selected samples are:

V-1074	Distillate from End of Run (6/9/88)	# 86454	~1.8 gal
V-131B	Recycle (pasting) solvent (4/25/88)	# 84410	~0.8 gal
V-181	Feed to CSD Unit (4/25/88)	# 84420	~0.8 gal
V-107	Ash concentrate from CSD Unit (4/25/88)	# 84422	~0.8 gal

The results of analyses of these materials are shown in Table 1.

The V-131B recycle solvent from Wilsonville Run 258K (Black Thunder coal, no Mo) was distilled to a 320 °C, 2-torr endpoint (1025 °F atmospheric equivalent). The resid fraction from this distillation was 64.9 wt %. Ash and IOM were determined, in duplicate, on the resid produced from this distillation. This (Mo-free) ashy resid contains 14.2 wt % ash (12.5 wt % SO₃-free ash) and 15.3 wt % IOM (17.4 wt %, SO₃-free ash basis).

A sample of an untreated coker tar and two hydrotreated coker tars were received from Sandia for characterization. These samples are described in Table 2. Eight hydrogenated distillate samples also were received from Sandia. These were prepared by hydrotreating the samples of V-1074 distillate, the light and heavy fractions (from the distillation of V-1074 into approximately equal volume fractions) and the -35 °C acetone/MEK (55/45 vol %) dewaxed V-1074 distillation fractions that we sent them. The V-1074 oil used in this work was from Wilsonville Run 262E (Black Thunder coal). Hydrotreatment conditions for these materials are shown in Table 2.

One package of Martin Lake lignite in use at CONSOL was found to have an unusually low ash content, relative to the other packages used by CONSOL. We sampled one-third of our remaining bags of Martin Lake lignite and found them to be consistent in moisture and ash content. It appears that we do not have a widespread sample heterogeneity problem; instead, only one non-representative bag of coal has been found. No additional work will be needed to insure sample integrity, except to analyze each bag as it is opened for use. We recommend that other participants analyze their Martin Lake lignite samples, and discard any that contain less than about 13 wt % MF ash (SO₃-containing basis). See Task 2.1.2.2 for additional discussion on this issue.

A fresh sample of McKinley coal received from P&M Coal Mining Co. was air-dried overnight, ground, riffled, and sealed in bags. A sample of this coal was submitted for complete analyses (results reported under Task 2.1.2.2).

Four triple-layer bags (25 g each) of Martin Lake Texas Lignite and Burning Star 2 Illinois No. 6 coal were sent to R. Kottenstette at Sandia.

Three samples taken from around the deasher during Wilsonville Run 263J were sent to R. Rathbone of UK/CAER.

Engineering drawings of the PETC generic bench-scale direct liquefaction unit were obtained from DOE and sent to project participants.

Task 2.1.2.1 - Pretreatment Work at CONSOL - Dewaxing

Summary

Resid conversions as high as 30 wt % were obtained by microdistillation of the THF soluble material from microautoclave tests with Black Thunder coal. Resid conversions were found to increase with increasing temperature from 840 to 900 °F (from below 10 wt % to over 30 wt %). Resid conversions were nearly the same when the recycle solvent blend contained untreated V-1074 and hydrogenated-dewaxed V-1074.

Coal and IOM conversions were reduced by about 15 wt % by lowering the cold hydrogen pressure from 1500 psig to 800 psig in microautoclave tests with Black Thunder coal. This result is consistent with the low coal conversions observed by Sandia for tests at lower hydrogen pressures.

Ash and IOM were determined on the ashy resid produced from the Mo-free V-131B recycle solvent from Wilsonville Run 258K. Microautoclave tests were made at our standard conditions (5 min, 824 °F, 1500 psig H₂, S/C = 1.5) with this Mo-free ashy resid substituted for V-1082. Coal conversion was about 10 to 15 wt % lower with the Mo-free resid than when the Mo-containing V-1082 was used in the solvent blend.

Varying the distillate/resid ratio in simulated Wilsonville Run 262E solvent between 0.5 and 1.0 had little effect on the microautoclave coal conversion of Black Thunder coal (5-minutes, 824 °F, 1500 psig H₂, S/C = 1.5). Slightly higher coal conversions were found at the lowest distillate/resid ratio while total IOM conversions were higher at the highest distillate/resid ratio. The lower total IOM conversions at low distillate/resid ratios (higher total resid concentrations) are consistent with our earlier observation that the resid IOM is significantly less reactive than the Black Thunder coal. However, the largest observed difference in conversions, 2.5 wt %, approaches the repeatability of the test.¹

Texas-lignite-derived V-1074 distillate from Wilsonville Run 255 was found to contain about one-third to one-half as much wax as the V-1074 from Wilsonville Run 262E (Black Thunder coal).

The degree of solvent improvement, measured by microautoclave tests, produced by distillate dewaxing alone and by distillate hydrotreatment alone is significantly greater than the incremental improvement attained by hydrotreating dewaxed distillate. There appears to be an optimum level of wax removal (~20 to 25 wt %) at which dewaxed distillate is produced that results in the highest degree of coal conversion in our tests. Dewaxing and/or hydrotreatment appears to be more beneficial for the higher boiling distillate fraction from Wilsonville Run 262E than for the lower boiling distillate fraction. However, the coal conversion obtained with the untreated higher boiling fraction is about 3 wt % less than that observed with the lower boiling fraction and, therefore, the coal conversion measured with either treated (dewaxed, hydrogenated or hydrogenated-dewaxed) distillate fraction is about the same.

Wilsonville preheater simulation tests resulted in ~69 wt % coal conversion and ~4 wt % resid conversion.

A TGA method, based on a similar method used by HRI, is being developed to determine 975 °F⁺ resid on milligram-sized coal-derived liquid samples. Measurement of resid conversions by distillation and TGA is in progress and will be reported later.

Discussion

Resid Conversions

Resid conversions in microautoclave tests can be calculated from the THF solubility determination and the distillation of the THF-soluble product. After a microautoclave run, the product is separated by pressure filtration into THF solubles and insolubles. The THF is stripped from both fractions. Coal and IOM conversions to THF-soluble products are calculated from the THF solubility results. The THF soluble product is then distilled at 320 °C and 2 torr (1025 °F atmospheric equivalent). The non-distillable portion of the THF soluble product is considered to be soluble resid. Two resid conversions are calculated: soluble resid conversion and total resid conversion. Soluble resid conversion

is calculated from the soluble resid determined in the above distillation (soluble resid out) and the soluble resid that was fed in the recycle solvent (soluble resid in). In most cases with coal in the system, the soluble resid conversion is negative because soluble resid is produced from the coal. Total resid conversion is based on product THF insoluble resid (IOM) plus the soluble resid from the distillation of the THF soluble product (total resid out) and coal plus soluble resid plus IOM fed (total resid in). A negative total resid conversion implies a net conversion of distillate to resid.

A 5 g sample of the V-1074 heavy distillate from Wilsonville Run 262E was distilled in the microdistillation apparatus to a 320 °C, 2 torr (1025 °F atmospheric equivalent) endpoint. These are the same conditions used to distill the THF solubles from microautoclave tests for resid conversion calculations. Duplicate microdistillations resulted in 6.6 and 7.0 wt % residual material in the pot after distillation. The mean resid value from these distillations, 6.8 wt %, is used as a correction to our resid conversion calculation; i.e., 6.8% of the V-1074 charged to the microautoclave is treated as soluble resid in the calculations.

The THF-soluble products from recent microautoclave runs were distilled to determine the resid conversions that occurred during these runs. Aliquots from the THF solubles from each run are being saved for TGA analysis by CONSOL and Sandia. The microautoclave resid conversion data from distillations completed through September 1993 are shown in Table 3. These include data from the tests to determine the effect of temperature on coal conversion, the decreased H₂ pressure run (800 vs 1500 psig), five- and 30-minute solvent-only runs, a 30-minute run with ash concentrate, and the runs at 0.5 and 1.0 distillate/resid ratios.

Effect of Temperature on Conversions

A potential benefit of dewaxing and/or hydrogenation of the recycle solvent is the reduction of retrograde reactions at more severe liquefaction conditions. To test this idea, a program was conducted to study the effect of reaction temperature on the conversion of Black Thunder coal in five-minute microautoclave tests. These tests were made at 840 °C, 860 °C, 880 °C and at 900 °C with the original V-1074 and with the Sandia hydrotreated -5 °C acetone dewaxed V-1074

oil, SC1, substituted for the original V-1074 portion of the recycle solvent. All conditions, except for temperature and the distillate used in the solvent blends were the same for each run. The Wilsonville Run 262E solvent composition (42.8 wt % distillate, 6.6 wt % deashed resid and 50.6 wt % ashy resid) was used with a 1.5 solvent/coal (MF) ratio in every run. The results of these tests are given in Table 3 and the measured coal conversion versus temperature is plotted in Figure 1.

Coal conversion with either distillate generally increases with increasing temperature up to 860 °F. At 880 °F, conversion appears to continue to increase for the hydrogenated solvent, SC1, case and to decrease for the untreated V-1074 case. Several repeat determinations were made at 880 °F, Table 3, and the reproducibility of the conversion data from these repeat runs is reflected by the error bars shown for the 880 °F points in Figure 1. If real, the effect of increased conversion at higher temperatures when hydrogenated solvent is used suggests a potential benefit of solvent dewaxing/hydrogenation (i.e., the ability to operate the process at higher temperatures to attain higher single pass conversions than are possible with current solvents).

The heat-up curves for the 880 °F microautoclave runs with V-1074 distillate in the simulated Wilsonville recycle solvent blend were compared to see if better heat-up control could improve reproducibility. The heat-up period for these tests, ~2.5 min, was a significant portion of the total run time. The heat-up data are presented in Figure 2. The curves are nearly identical from 2 minutes to the end of the runs. The spread of temperatures at 1.5 minutes was only 8 °F (839-847 °F). The temperature spread between runs was larger at 1 minute, 36 °F (739-775 °F), but these points are on a relatively steep part of the heat-up curve and the amount of coal conversion at these lower temperatures and short residence times should be minimal. No attempt was made to further improve the heat-up curves.

At 900 °F with Sandia SC1 used as distillate in the simulated Wilsonville recycle solvent, Table 3, the observed coal conversion is even higher than that observed at 880 °F, Run 48, while the coal conversion with V-1074 is about the same as that at 880 °F, Run 47. When the hydrogenated-dewaxed distillate, SC1, is used in the solvent blend, coal conversion steadily increases with increasing

temperature up to 900 °F. When untreated V-1074 distillate is used in the solvent, coal conversion increases with increasing temperature up to >860 °F and then it appears to remain constant. Thus, at more severe operating conditions, i.e., at temperatures >860 °F, the benefit (reflected by coal conversion) of using hydrogenated-dewaxed distillate in the recycle solvent is greater. The reason for the relatively higher coal conversions with SC1 vs V-1074 at the highest temperatures may be reduction of retrograde reactions in the hydrogenated-dewaxed solvent resulting from improved solvent quality.

As with coal and IOM conversions, the resid conversions are found to increase with temperature. Unlike coal and IOM conversions, however, at the liquefaction conditions used, the total resid conversion appears to be little affected by dewaxing and hydrogenating the distillate portion of the solvent. This is illustrated in Figure 3 in which the data from the temperature-effect experiments are plotted. Higher coal and IOM conversions (i.e., insoluble resid conversions) observed with the hydrogenated solvent and similar total resid conversions suggest that soluble resid conversion is lower when hydrogenated solvent is used. The soluble resid conversion data (Table 3) confirm this. The overall implication of these data is that dewaxing and hydrogenating the distillate portion of the solvent leads to increased conversion of coal to THF soluble material that boils above ~1050 °F.

The resid conversions calculated for the duplicate microautoclave tests at 880 °F give an indication of the repeatability of the resid conversion determination. Four determinations were made at 880 °F with V-1074 (Runs 40, 43-45, Table 3). The mean soluble resid conversion for these four determinations was -63.5 ± 2.9 wt % and the mean value of the total resid conversion was 26.0 ± 1.8 wt %. Agreement between the duplicate 880 °F microautoclave runs with the Sandia SC1 distillate (Runs 35 and 42, Table 3) was much worse than that for the four runs with V-1074. When the total resid conversions for these two points are plotted, Figure 3, it appears as if the lower conversion (-109 wt %) point, Run 35, is an outlier. This question may be resolved when the TGA resid conversion determinations are completed.

Effect of Hydrogen Pressure on Microautoclave Conversions

Microautoclave tests were made with Black Thunder coal at our standard conditions (5-minutes, 824 °F, V-1074 distillate in the simulated Wilsonville recycle solvent, S/C = 1.5), except that only 800 psig (cold) H₂ pressure was used (Runs 49 and 57, Table 3). The observed coal and IOM conversions under these conditions were significantly lower than when 1500 psig H₂ is used (76 to 78 wt % vs 88 wt % coal conversion and 64 to 66 wt % vs 75 wt % IOM conversion). This result is consistent with the low coal conversions observed by Sandia for tests at lower hydrogen pressures. Resid conversions have not been determined for our baseline case with Black Thunder coal (5 min, 824 °F, 1500 psig H₂, S/C = 1.5), so direct comparison of the effect of hydrogen pressure on resid conversion cannot be made.

Mo-Free Ashy Resid

Ash and IOM were determined, in duplicate, on the ashy resid produced by distilling the Mo-free V-131B recycle solvent from Wilsonville Run 258K to a 1025 °F atmospheric equivalent endpoint (320 °C, 2 torr). This ashy resid contains 14.2 wt% ash (12.5 wt % SO₃-free ash) and 15.3 wt % IOM (17.4 wt %, SO₃-free ash basis). Both the ash and IOM contents of this material are lower than the ash and IOM contents of the V-1082 ashy resid from Wilsonville Run 262E that we have been using for our standard solvent quality tests (16.0 wt % ash and 21.0 wt % IOM, both on an SO₃-free ash basis).

When this material was substituted for Wilsonville Run 262E Mo-containing ashy resid in a 5-min microautoclave test (Wilsonville Run 262E solvent blend ratio, 1500 psig H₂(cold)), approximately 9 wt % of the IOM in this material was converted to THF solubles (Run 54, Table 3). At the same conditions, ~15 wt % of the IOM in the Wilsonville Run 262E V-1082 ashy resid was converted to THF solubles (Run 50, Table 3). Substitution of hydrotreated dewaxed distillate, SC1, for the V-1074 portion of the solvent blend had little effect on the IOM conversion in either case (Runs 51 and 55, Table 3). When the reaction time was increased to 30 minutes, the IOM conversion increased to ~16 wt % with the Mo-free V-131B resid (Run 56) compared with ~35 wt % with the Mo-containing V-1082 (Run 52).¹ The lower conversion of the Mo-free V-131B IOM may be due to the absence of Mo catalyst in this sample; however, the IOM in the Mo-free V-131B sample also may be less reactive than that in the V-1082 sample.

Substitution of the Mo-free ashy resid for the Wilsonville Run 262E ashy resid (with Mo) in the simulated Run 262E solvent blend in tests with Black Thunder coal (5-min, 824 °F, 1500 psig H₂) resulted in substantial decreases in the coal and IOM conversions. With the baseline V-1074 distillate in the solvent blend, coal conversion was ~73 wt % with the Mo-free ashy resid versus 87.5 wt % with the Mo-containing ashy resid (Runs 63 and 14, Table 3). When the hydrogenated-dewaxed distillate (Sandia SC1) was used with the Mo-free ashy resid, a similar decrease in the coal conversion was observed; ~77 wt % vs 92.1 wt % (Runs 64 and 18, Table 3). As expected, coal conversion with the dewaxed V-1074 and the Mo-free ashy resid (Run 65, Table 3) was between that obtained with untreated V-1074 and that obtained with SC1. Thus it appears that the Mo catalyst played a significant role in all previously reported work with the Wilsonville Run 262E V-1082 ashy resid. In the tests made here with Mo-free ashy resid, some Mo was still introduced in the Run 262E V-130 deashed resid (the deashed resid contains 53 ppm Mo).

In the runs with simulated Wilsonville solvent only (i.e., no coal), Runs 50-56 and 58, Table 3, total resid conversion in the most severe tests (30 minutes) is less than 20 wt %. Resid conversion at thirty minutes was greater in the cases where the Mo-containing ashy resid was used (Runs 52 and 53) than in the case where the Mo-free ashy resid (1025 °F resid from distillation of V131B from Wilsonville Run 258K) was used, Run 56, in the solvent blend (~17 % vs ~11%). As described above for the coal conversion case, dewaxing and hydrogenating the distillate portion of the solvent had little effect on recycle solvent resid conversion (16 wt % total resid conversion when untreated V-1074 was used and 18 wt % total resid conversion when SC1 was used). In the 5-min tests, net total resid conversion was very low in all four cases. The observed differences in the 5-min resid conversions may reflect the reproducibility of the determination.

The observed IOM conversions with no coal and with V-1074 as the distillate portion of the solvent (14 wt% at 5 min, Run 50 and 35 wt % at 30 min, Run 52) are similar to previously measured values where ashy resid was substituted for coal² (15 wt % at 5 min and 37 wt % at 30 min). Apparently, the distillate/resid ratio (0.35 and 0.42 before vs 0.75 in the present case) has little impact on IOM conversion over the range of distillate/resid ratios studied.

Distillate/Resid Ratio

At the Quarterly Review meeting in June 1993, Mike Peluso requested that CONSOL determine the effect of distillate/resid ratio on coal conversion in our 5-min microautoclave test. The distillate/resid ratio for the recycle solvent used in Wilsonville Run 262E (our microautoclave standard solvent) was 0.75. Ratios of 0.5 and 1.0 were tested to determine the effect of this ratio on the conversion of Black Thunder coal to THF solubles. The results of these tests are shown in Table 3. Calculated conversion on an MAF coal basis with either the V-1074 or the hydrogenated-dewaxed V-1074 used in the solvent blend was about 1-2 wt % higher at a distillate/resid ratio of 0.5 than at either of the two higher distillate/resid ratios.

Conversion on a total IOM basis shows a trend opposite to conversion on an MAF coal basis; i.e., a slight decrease in IOM conversion at the lowest distillate/resid ratio. Lower total IOM conversions at low distillate/resid ratios (higher total resid concentrations) is consistent with our earlier observation of decreased total IOM conversions at higher solvent/coal ratios. It results from the fact that the resid IOM is significantly less reactive than the Black Thunder coal. The total IOM in the feed is the sum of the resid IOM and the MAF coal. Since the total resid IOM content increases as the distillate/resid ratio is decreased (the total solvent weight and solvent/coal ratio are kept constant), the less reactive resid IOM becomes a larger percentage of the total IOM as the distillate/resid ratio is lowered. In any event, the observed net effect of distillate/resid ratio on either coal or IOM conversion is near experimental repeatability.¹

The effect of changing the distillate/resid ratio on resid conversions is shown by the data from Runs 59-62, Table 3. It appears that lowering this ratio results in higher soluble resid and total resid conversions. This is consistent with the decrease in total IOM conversion found at the lower distillate/resid ratios discussed in a previous section. As the distillate/resid ratio decreases, the absolute amount of resid IOM increases (coal and total solvent are held constant). Therefore, the ratio of resid IOM to MAF coal increases and the overall IOM conversion decreases due to the relative increase in the less reactive resid IOM. The relative increase in the soluble resid conversion with a decrease in the distillate/resid ratio is also consistent with the low reactivity

of the resid IOM, since a less negative value for soluble resid conversion can imply lower relative production of soluble resid (from resid IOM) as well as increased soluble resid conversion.

Dewaxing Texas-Lignite-Derived Distillate

The V-1074 distillate from Wilsonville Run 255 (Texas lignite) was dewaxed in acetone at -35 °C and -50 °C and in a 55/45 (vol %) acetone/MEK mixture at -35 °C to determine the wax content. The results of these solvent dewaxings are shown in Table 4. The wax content of this distillate, as determined from these experiments, is significantly lower than the wax content of the V-1074 distillate from Wilsonville Run 262E (Black Thunder subbituminous coal) that we have been working with until now. For instance, -35 °C acetone dewaxing of the Run 262E material resulted in approximately 35 wt % wax removal vs about 13 wt % for the Texas-lignite-derived distillate. Similarly, -35 °C dewaxing of the Run 262E distillate in 55/45 (vol %) acetone/MEK removed about 15 wt % wax vs less than 5 wt % removed from the Run 255 distillate at the same conditions. It is not known if the low wax content of the Wilsonville Run 255 distillate reflects inherent coal properties or the specific liquefaction conditions at which the distillate was produced. The collected wax fraction was dark in color and appeared to contain very fine particulate matter. Considerable insoluble matter (3 to 4 wt %) was also collected during the THF filtration of the wax fraction.

The material balances were low for these dewaxing tests. Product recoveries ranged from ~91 to 97 wt % vs over 99 wt % for most of the dewaxing runs with V-1074 from Wilsonville Run 262E. The Texas-lignite-derived distillate is much less viscous at room temperature than the Run 262E V-1074 distillate and contains lower boiling materials that may be removed with the THF and dewaxing solvents during rotary evaporation of the solvents from the product fractions. GC/MS analysis of the feed V-1074 distillate from Wilsonville Run 255 showed the presence of n-paraffins with a carbon number as low as C₁₀ compared with ~C₂₂ for the V-1074 distillate from Wilsonville Run 262E.

Proton distributions for the dewaxed oil and wax from dewaxing the Wilsonville Run 255 V-1074 are shown in Table 5. Dewaxing the Texas-lignite-derived distillate has the expected effect of increasing the aromaticity of the dewaxed oil while producing a highly paraffinic wax. As with the subbituminous-coal-

derived distillate, deeper dewaxing produces a more aromatic dewaxed oil and a less pure, i.e., more aromatic, wax product.

Effect of Distillate Dewaxing and Hydrotreatment on Coal Conversions

Most of the CONSOL work on the evaluation of solvent improvements by dewaxing and/or hydrotreatment was done using the untreated V-1074 heavy distillate from Wilsonville Run 262E, the Sandia-hydrotreated -5 °C acetone dewaxed V-1074, or the -35 °C acetone/MEK (55/45 vol %) dewaxed V-1074. The CONSOL standard modified equilibrium solvent quality test (30 min, 750 °F microautoclave tests with 2:1 ratio of the solvent in question to Indiana V coal) was run for each distillate produced; however, until now the new Wilsonville simulation test (Black Thunder coal, 5-min, 824 °F, 1500 psig H₂, 1.5 S/C) was made for only the untreated V-1074 heavy distillate from Wilsonville Run 262E, and the Sandia hydrotreated -5 °C acetone dewaxed V-1074.

Microautoclave tests (Black Thunder coal, 5-min, 824 °F, 1500 psig H₂, 1.5 S/C), Table 3, were made with -5 °C acetone dewaxed V-1074 (Run 78), -35 °C acetone dewaxed V-1074 (Run 67), -35 °C acetone/MEK dewaxed V-1074 (Run 79), hydrotreated -35 °C acetone dewaxed V-1074 (Sandia #110404, Run 68) and hydrotreated -35 °C acetone/MEK dewaxed V-1074 (Sandia #72302, Run 73, and #72202, Run 83) substituted for the distillate portion of the simulated Wilsonville Run 262E solvent. The results of these experiments are plotted in Figure 4. An estimate of the repeatability of these tests can be obtained from the duplicate points with the -35 °C acetone dewaxed distillate (89.0, Run 16 and 90.4 wt %, Run 67). The three hydrotreated V-1074 distillate samples (Runs 70-72) each were prepared at different temperatures (300 °C, 325 °C and 375 °C, respectively) and under different total pressures (1000, 1400 and 1400 psig, respectively) and are not repeats of each other. The two hydrotreated -35 °C acetone/MEK dewaxed distillate samples (Runs 73 and 83) also were hydrotreated at different temperatures (325 and 375 °C, respectively). The data show that either dewaxing or hydrotreating the distillate portion of the recycle solvent results in higher conversion of the Black Thunder coal to THF solubles. However, it also appears that hydrotreating the dewaxed distillate has a smaller effect on the coal conversion than either dewaxing or hydrotreating alone. These data suggest that there may be an optimum level of dewaxing for the V-1074 from Wilsonville Run 262E that produces the most reactive (as determined by conversion of Black

Thunder coal to THF solubles in our standard 5-min. test) liquefaction solvent. For the conditions used in these tests, this optimum appears to occur at about 20 wt % wax removal which is approximately the degree of dewaxing attained with acetone at -5 °C.

Distillation Fractions of V-1074

Determination of the relative solvent qualities (5-min, 824 °F microautoclave tests with Black Thunder coal and the Wilsonville Run 262E solvent blend) of the hydrotreated distillate materials received last month from Sandia was completed. These samples were produced by hydrotreating the two fractions obtained by distilling the Wilsonville Run 262E V-1074 heavy distillate into approximately equal volume fractions³ and the dewaxed oil produced by dewaxing the light and heavy distillation fractions of the V-1074 at -35 °C in acetone/MEK (45/55 vol %). The results of these hydrogenation tests are shown in Table 3 (Runs 30-33, 74-76 and 84). In the case of the light distillate fraction, the improvement in solvent quality resulting from dewaxing, hydrotreating or combined dewaxing followed by hydrotreating is small. The maximum observed increase in coal conversion was from 87 to 90 wt % for the hydrotreated-dewaxed distillate (Run 76) vs the untreated light distillate fraction (Run 30). A larger improvement (from 84 to 90 wt %) was obtained by hydrotreating either the dewaxed heavy distillate fraction (Run 74) or the untreated heavy distillate fraction (Run 84). For comparison, use of the dewaxed heavy distillate fraction of the V-1074 (without hydrotreatment) in the simulated recycle solvent improved coal conversion from 84 to 89 wt %. These results suggest that a higher boiling cut of the distillate stream is more amenable to solvent quality improvement (by dewaxing, hydrogenation or a combination of the two) than the lighter stream. Thus it may be possible to reduce the required treatment capacity compared with treatment of the entire distillate stream. Resid conversions for these microautoclave tests are being determined and will be reported.

Preheater Simulation

At the Quarterly Review Meeting in June 1993, M. Peluso requested data on the degree of conversion that occurs in the preheater at Wilsonville to get a better understanding of the back-mixed versus plug-flow reactor kinetics comparison. Two microautoclave tests were made to simulate the effect of the preheater at Wilsonville on coal and resid conversions. CONSOL previously recognized and

discussed the importance of coal conversion in the slurry mix tank and preheater at Wilsonville.⁴ The simulated Wilsonville Run 262E solvent, Black Thunder coal and hydrogen were loaded into the microautoclave. The microautoclave then was traced with heating tape and heated to 470 °F (inadvertently about 100 °F above the Wilsonville slurry mix tank temperature). After a residence time of 4 hr at 470 °F, the heating tape was removed and the reactor was placed in a fluidized sand bath and rapidly heated to 824 °F. Upon reaching 824 °F (in approximately 2.5 min) the reactor was removed from the sand bath and quenched. The reactor was continually shaken throughout the run (except while removing the heating tape) to ensure mixing of the components. The results of these tests are shown in Table 3 (Runs 69 and 77).

The conversions calculated for the two runs agree well with each other (68.8 and 69.2 wt % coal conversion). These coal conversions are similar to those obtained in 4-hr soaks at 370 °F followed by 10 min heat-up to 790 °F (68.8 wt %).⁴ The total resid conversion in Run 77 was determined by microdistillation of the THF soluble products and found to be ~4 wt %.

TGA Determination of Resid Conversion

A thermogravimetric analysis (TGA) method for the determination of the equivalent 975 °F* (ASTM 1160) distillation bottoms value, based on a method developed and routinely used at HRI, Inc., was developed for use in-house. The equipment used at HRI is significantly different than that which is available to us at CONSOL R&D. It was, therefore, necessary to modify the HRI method to achieve comparable results.

The CONSOL TGA method uses a DuPont 951 TGA. The control and data acquisition system are PC-based and use software developed by MC-Squared Thermal Systems. The software and data-interface module were supplied by Instrument Specialists, Inc., Antioch, IL.

Conditions established for the TGA experiment are as follows:

2 of 2

<u>Temperature Ramp, °C</u>	<u>Final Actual Temperature, °C</u>	<u>Heating Rate, °C/min</u>	<u>Hold Time, min.</u>	<u>Atmosphere</u>
30-105	110	40	3	N ₂
105-363	375	40	2	N ₂
363-732	732	100	3	O ₂

For each interchangeable furnace, the heating profiles are slightly different. The temperature limits given in the above table may be altered by ± 1 or 2 °C to compensate. The programmed values differ from the actual values achieved because of temperature overshoot which occurs as a result of the furnace design and the relatively high heating rate. The data point for the 975 °F* equivalence is obtained at the beginning of the 2-min hold time, once 375 °C is achieved, as compared to HRI's practice of taking the data point after holding the sample at 375 °C for a number of minutes. The much slower heating rate used here, compared to that which is used by HRI, brings the sample to the 975 °F* equivalent point coincidentally with the achievement of 375 °F. The 2-min hold time is used to line-out the furnace at 375 °F before changing to an O₂ atmosphere. Sample size used for preliminary work was 6 to 10 mg. The method is being standardized on 10.0 mg (± 0.5 mg).

Multiple TGA experiments were run using material supplied by HRI. The values obtained by HRI for the 975 °F* fraction of this material are: 28.80, 28.90, 28.55, 30.43, 27.55, 29.42, 27.73, 29.11, and 29.18 wt %. The mean of these values is 28.85 wt% with a standard deviation of 0.87 wt %. Values obtained using the method detailed above are: 30.9, 27.9, 24.2, 30.4, 30.9, 31.5 wt %. The mean value is 29.3 wt %, with a standard deviation of 2.7 wt %.

In addition to the HRI standard sample, four samples produced at the Wilsonville facility from Runs 258 and 262 were chosen to be standard samples. These four samples of coal-derived materials are two whole oil samples (Wilsonville Run 262 Period E, V1074, and Wilsonville Run 258 Period K, V131B) and two resid samples (Wilsonville Run 262 Period E deashed resid V130, and ashy resid from Wilsonville Run 262 Period E V1082). These materials contain a wide range of ash and resid contents.

All four of these materials were analyzed by HRI Inc. by their well-established TGA method. Two samples were checked by ASTM D-1160 distillation, also performed at HRI. The HRI data are presented in the table below. In addition, we have repeated TGA analyses on these materials using the method which we developed in-house. As can be seen in the table, we reproduce the HRI values fairly well.

Sample (Wilsonville Run Period and Stream)	HRI TGA Value (average of 2 determinations)		HRI ASTM D-1160 Value	CONSOL TGA Value (average of 10 determinations)	
	975 °F+, wt %	Ash, wt %	975 F + wt %	975°F+, wt %	Ash, wt %
262 E, V130	84.34	0.00	84.56	83.76±3.49	1.70±0.35
262 E, V1082	87.51	19.64		90.74±2.29	18.63±0.66
262 E, V1074	1.47	0.01		3.07±1.35	1.19±0.61
258 K, V131B	56.80	10.24	54.47	57.92±2.23	10.01±1.13

Aliquots of these four samples were sent to SRI International for analysis in their large scale (1.5 g sample size) TGA.

These tests confirm the empirical method as adapted for CONSOL's use. The method is now available to the Program on a routine basis.

Task 2.1.2.2 - Pretreatment Work at CONSOL - Agglomeration

Summary

Several Martin Lake lignite agglomeration runs and the float/sink tests reported last quarter initially had high ash balances; the source was identified as heterogeneity of the sample bags of coal in use by CONSOL. Fresh Martin Lake lignite agglomerated with No. 6 fuel oil gave 12 to 28% physical ash rejection, reducing the ash content from 11.0 wt % MF to 8.6 wt % MF (sample 1), or from about 13.5 wt % MF to as low as 9.9 wt % MF (samples 2 and 3).

No significant improvement was obtained over previous physical ash rejection results when two-stage agglomeration of Burning Star 2 coal with No. 6 fuel oil

was used. No significant improvement was obtained over previous physical ash rejection results with Kemmerer coal.

Fresh McKinley Mine (NM) coal agglomerated with No. 6 fuel oil gave 52 to 57 % physical ash rejection, reducing the ash content from 11.7 wt % MF to 4.6 to 5.1 wt % MF. Analyses are reported for McKinley Mine coal. The ash has a very high silica content (60%), which appears to account for its excellent agglomeration performance. In previous work with Martin Lake lignite, evidently much of the rejected mineral matter was silica sand. One unusual feature of the McKinley coal is that the mineral matter rejected from agglomeration is black in color.

The coincidence of high ash SiO_2 contents and high ash rejections in agglomeration in current and previous tests prompted us to explore correlation between the two parameters in several coals. We obtained regressions which allow prediction of agglomeration performance (physical ash rejection) from ash silica content (R^2 = up to 0.77) or from the "free" silica content of the ash (a representation of quartz content, calculated as wt % ash SiO_2 minus 1.25 times the wt % ash Al_2O_3) (R^2 = up to 0.91). The data set consists of nine coal samples, lignite through hvAb. This empirical relation may be useful for screening coals as potential agglomeration feeds.

The CO-pretreated Black Thunder coal slurry supplied by CAER was used in three agglomeration tests. High organic recoveries are obtained when the CO-pretreated Black Thunder coal slurry is agglomerated. There is little physical ash rejection from agglomeration, but a substantial amount of slurry ash dissolution may have occurred prior to or during agglomeration.

Discussion

Martin Lake Lignite and Agglomeration Results

The source of apparently high ash balances reported earlier was identified. The ash content of the sample first used is considerably lower than that of subsequent samples, Table 6 (about 11% MF, vs greater than 13% in recent samples). Thus, use of the earlier ash content in calculations for later runs caused an apparent deficiency in the feed ash content, relative to the recovered product and reject ash. Correction of this caused all of the apparent inconsistencies in the Martin Lake lignite results to disappear (although one agglom-

<u>Temperature Ramp, °C</u>	<u>Final Actual Temperature, °C</u>	<u>Heating Rate, °C/min</u>	<u>Hold Time, min.</u>	<u>Atmosphere</u>
30-105	110	40	3	N ₂
105-363	375	40	2	N ₂
363-732	732	100	3	O ₂

For each interchangeable furnace, the heating profiles are slightly different. The temperature limits given in the above table may be altered by ± 1 or 2 °C to compensate. The programmed values differ from the actual values achieved because of temperature overshoot which occurs as a result of the furnace design and the relatively high heating rate. The data point for the 975 °F* equivalence is obtained at the beginning of the 2-min hold time, once 375 °C is achieved, as compared to HRI's practice of taking the data point after holding the sample at 375 °C for a number of minutes. The much slower heating rate used here, compared to that which is used by HRI, brings the sample to the 975 °F* equivalent point coincidentally with the achievement of 375 °F. The 2-min hold time is used to line-out the furnace at 375 °F before changing to an O₂ atmosphere. Sample size used for preliminary work was 6 to 10 mg. The method is being standardized on 10.0 mg (± 0.5 mg).

Multiple TGA experiments were run using material supplied by HRI. The values obtained by HRI for the 975 °F* fraction of this material are: 28.80, 28.90, 28.55, 30.43, 27.55, 29.42, 27.73, 29.11, and 29.18 wt %. The mean of these values is 28.85 wt% with a standard deviation of 0.87 wt %. Values obtained using the method detailed above are: 30.9, 27.9, 24.2, 30.4, 30.9, 31.5 wt %. The mean value is 29.3 wt %, with a standard deviation of 2.7 wt %.

In addition to the HRI standard sample, four samples produced at the Wilsonville facility from Runs 258 and 262 were chosen to be standard samples. These four samples of coal-derived materials are two whole oil samples (Wilsonville Run 262 Period E, V1074, and Wilsonville Run 258 Period K, V131B) and two resid samples (Wilsonville Run 262 Period E deashed resid V130, and ashy resid from Wilsonville Run 262 Period E V1082). These materials contain a wide range of ash and resid contents.

All four of these materials were analyzed by HRI Inc. by their well-established TGA method. Two samples were checked by ASTM D-1160 distillation, also performed at HRI. The HRI data are presented in the table below. In addition, we have repeated TGA analyses on these materials using the method which we developed in-house. As can be seen in the table, we reproduce the HRI values fairly well.

Sample (Wilsonville Run Period and Stream)	HRI TGA Value (average of 2 determinations)		HRI ASTM D-1160 Value	CONSOL TGA Value (average of 10 determinations)	
	975 °F+, wt %	Ash, wt %	975 F + wt %	975°F+, wt %	Ash, wt %
262 E, V130	84.34	0.00	84.56	83.76±3.49	1.70±0.35
262 E, V1082	87.51	19.64		90.74±2.29	18.63±0.66
262 E, V1074	1.47	0.01		3.07±1.35	1.19±0.61
258 K, V131B	56.80	10.24	54.47	57.92±2.23	10.01±1.13

Aliquots of these four samples were sent to SRI International for analysis in their large scale (1.5 g sample size) TGA.

These tests confirm the empirical method as adapted for CONSOL's use. The method is now available to the Program on a routine basis.

Task 2.1.2.2 - Pretreatment Work at CONSOL - Agglomeration

Summary

Several Martin Lake lignite agglomeration runs and the float/sink tests reported last quarter initially had high ash balances; the source was identified as heterogeneity of the sample bags of coal in use by CONSOL. Fresh Martin Lake lignite agglomerated with No. 6 fuel oil gave 12 to 28% physical ash rejection, reducing the ash content from 11.0 wt % MF to 8.6 wt % MF (sample 1), or from about 13.5 wt % MF to as low as 9.9 wt % MF (samples 2 and 3).

No significant improvement was obtained over previous physical ash rejection results when two-stage agglomeration of Burning Star 2 coal with No. 6 fuel oil

was used. No significant improvement was obtained over previous physical ash rejection results with Kemmerer coal.

Fresh McKinley Mine (NM) coal agglomerated with No. 6 fuel oil gave 52 to 57 % physical ash rejection, reducing the ash content from 11.7 wt % MF to 4.6 to 5.1 wt % MF. Analyses are reported for McKinley Mine coal. The ash has a very high silica content (60%), which appears to account for its excellent agglomeration performance. In previous work with Martin Lake lignite, evidently much of the rejected mineral matter was silica sand. One unusual feature of the McKinley coal is that the mineral matter rejected from agglomeration is black in color.

The coincidence of high ash SiO_2 contents and high ash rejections in agglomeration in current and previous tests prompted us to explore correlation between the two parameters in several coals. We obtained regressions which allow prediction of agglomeration performance (physical ash rejection) from ash silica content (R^2 = up to 0.77) or from the "free" silica content of the ash (a representation of quartz content, calculated as wt % ash SiO_2 minus 1.25 times the wt % ash Al_2O_3) (R^2 = up to 0.91). The data set consists of nine coal samples, lignite through hvAb. This empirical relation may be useful for screening coals as potential agglomeration feeds.

The CO-pretreated Black Thunder coal slurry supplied by CAER was used in three agglomeration tests. High organic recoveries are obtained when the CO-pretreated Black Thunder coal slurry is agglomerated. There is little physical ash rejection from agglomeration, but a substantial amount of slurry ash dissolution may have occurred prior to or during agglomeration.

Discussion

Martin Lake Lignite and Agglomeration Results

The source of apparently high ash balances reported earlier was identified. The ash content of the sample first used is considerably lower than that of subsequent samples, Table 6 (about 11% MF, vs greater than 13% in recent samples). Thus, use of the earlier ash content in calculations for later runs caused an apparent deficiency in the feed ash content, relative to the recovered product and reject ash. Correction of this caused all of the apparent inconsistencies in the Martin Lake lignite results to disappear (although one agglom-

eration run still has a high ash balance). The origin of the problem may have been inadequate mixing of the original sample before it was sealed into bags.

CONSOL sampled one-third of its bags of Martin Lake coal to learn the extent of the sample heterogeneity problem. The moisture and ash content of the lignite samples in all of the bags were consistent with each other, and with those of two bags in previous and current use (Table 6). So far, only one nonrepresentative (low-ash) bag has been identified. Therefore, it appears that one bag was unusual for some unknown reason, but that there is not a general problem of sample heterogeneity. We recommend that other participants analyze their Martin Lake lignite samples, and discard any that contain less than about 13 wt % MF ash (uncorrected for SO_3). No additional work will be needed to insure sample integrity, except to analyze each bag as it is opened for use. One Martin Lake lignite sample is being completely re-analyzed; its analysis (to be reported in the future) will replace the analysis reported in the June 1993 status report and second quarter 1993 technical report.

Agglomeration results (Table 7) for Martin Lake lignite were corrected using the coal analyses appropriate for the sample bag from which the sample originated (Table 6). Tabulated values reported previously for Martin Lake float/sink tests (second quarter 1993) are correct as reported. No agglomeration result with the new sample of Martin Lake lignite has been previously reported.

Seven agglomeration tests were made with Martin Lake lignite and No. 6 fuel oil. No agglomeration occurred in Run A42 in which No. 2 diesel fuel was used at 54 °C and pH 8. Comparison of Run A28 with Run A25 (both sample bag 1, 11.0 wt % MF ash feed) showed that use of the puck-milled feed with an increased oil dose resulted in greater physical ash rejection (19.0 vs 12.5) and lower product ash content (8.6 vs 9.2 wt % MF). Because of the difference in feed coal from sample bag 1 to sample bags 2 and 3 (as reflected in the ash content), these run results are not directly comparable with those of the other runs.

Runs A36 and A48 were replicate runs, one using the bag 2 coal (13.2 wt % MF ash), the other using the bag 3 coal (13.5 wt % MF ash). The runs gave very similar results. Ash balances were slightly high for both, 100 to 108 wt % (typical values are 95 wt % or lower). The runs gave 25 to 28 wt % physical ash

rejection and 99.3 wt % organic recovery. Oil-free ash content of the product was 10.5 to 10.8 wt % MF. Runs A41 and A43 (bag 2 coal feed, 13.2 wt % MF ash) yielded similar results, and a lower product ash content of 9.9 wt % MF. Physical ash rejections were 24 to 27 wt % and ash balances were 96 to 100 wt %. Run A41 used a higher oil dose than Runs A36 and A48, whereas Run A43 used the higher oil dose and the pH was adjusted to 8. Thus, the effect of pH adjustment to 8 on physical ash rejection was small, perhaps slightly negative.

The best agglomeration performance obtained with the new Martin Lake lignite was 24 to 28 wt % physical ash rejection (Runs A36, A41, A43, and A48), lower than was obtained in previous experiments with another sample (about 40 wt %). The bag 1 sample of the current coal produced a lower-ash product, however (Run A28). It has not been determined if a product ash as low as this (8.6 wt % MF) can be obtained from a later sample of the Martin Lake coal (that is, after bag 1). The performance differences between the earlier work and the present work are apparently due to differences in the coal samples. When the old sample was used (Run A22, this program), the physical ash rejection was about 24 %, similar to that obtained with the new sample. Aging of the older sample might account for its lower performance, relative to the original tests completed several years ago.

Agglomeration Tests With Burning Star 2 and Kemmerer Coals

No significant improvement was obtained over previous physical ash rejection results when two-stage agglomeration of Burning Star 2 coal with No. 6 fuel oil was used (Table 7, Runs A45 and A49). Product ash was quite low in Run A45 (6.6 wt % MF), but the ash balance is unusually low (87 wt %), so the results are uncertain. Run A49 was a repeat of Run A45, except that a higher temperature of 65°C was used in Run A49. The Run A49 results are fairly typical of a number of agglomeration runs made with the Burning Star 2 coal. For the two-stage procedure, each run was terminated after initial formation of agglomerates, the agglomerates were washed, reslurried, and a second agglomeration was made. Ash rejections are based on the (mathematically) combined reject from both stages.

Increasing the pH from 6.5 (natural pH) in Run A39 (reported last quarter) to pH 8 (Table 7, Run A44) significantly improved agglomeration of Kemmerer coal with No. 2 diesel fuel at 54°C. However, the results were no better than those

achieved in Run A40 (Table 7, and reported last quarter). Likewise, no significant improvement resulted from increased oil dosage for Kemmerer coal (Table 7, Run A50, vs last month's Run A40). Agglomeration of the same feeds at room temperature with the pH adjusted to 8 gave the same physical ash rejection, but an apparent lower wt % MF product ash content (1.7 in Run A47 vs 2.1 in Run A40). Note that the A47 run also had an unusually low ash balance of 75 wt %, so these results are somewhat uncertain.

McKinley Coal Analysis and Agglomeration Results

The analysis of the sample of McKinley Mine coal received from P&M Coal Mining Co. and used in several agglomeration tests is given in Table 8. The mine is located in McKinley County, New Mexico (Gallup Field, San Juan Basin). At the time the sample was taken, the Blue, Yellow, and Fuschia seams were being mined. The rank of this coal is considered to be near the borderline of bituminous-subbituminous. The silica content of the ash is quite high at 60 wt %. This is the feature of McKinley coal which triggered us to obtain it for agglomeration testing. Our previous work with Martin Lake lignite had shown that most of the mineral matter rejected from it by agglomeration was silica sand. Our supposition that this would be a good agglomeration feed was borne out by the 52 to 57 wt % physical ash rejection results we obtained (discussed below). One unusual feature of the McKinley coal is that the mineral matter rejected from agglomeration is black in color.

Three agglomeration runs with McKinley mine coal (Table 7, Runs A47, A51, and A52) gave 52 to 57 wt % physical ash rejection, 90 to 96 wt % ash balance, 97 to 98% organic recovery, and oil-free product ash contents of 4.6 to 5.1 wt % MF (the feed coal contained 11.7 wt % MF ash). All the tests were made with No. 6 fuel oil; the best one (A51) was made at 54°C with pH adjustment to 8.0 with NaOH, the others were made at 54 or 65°C and a natural pH of 6.8 to 6.9.

Empirical Regressions for Predicting Agglomeration Performance

After obtaining excellent agglomeration results with McKinley coal, we decided to determine if there was a broader relationship between ash silica content and agglomeration performance. It is obvious, of course, that silica content alone could not fully account for coal cleanability. Liberation effects of reducing particle size, the kinds of minerals present, and other factors have a great

impact on coal cleanability. However, any relationship between silica content and agglomeration performance could be useful in screening candidate coals for agglomeration.

We were able to obtain fair-to-good correlation of ash silica content with agglomeration deashing performance for several coals in the current program and in prior work. Four correlations are presented. The data on which the correlations are based are given in Table 9. There are nine samples in the data set, from lignite through hvAb in rank. These are all our agglomeration results for which we could locate feed coal ash elemental data. Two samples are from the same source as two other samples; however, they differ by several years in the time of the sample and of the agglomeration tests. These samples are clean Burning Star 2 samples BS2 and CBS, and Martin Lake lignite samples ML-1 and OML. In the table, "free" SiO_2 is defined as ash SiO_2 content minus 1.25 times the ash Al_2O_3 content. It represents silica that is not part of a clay or other aluminosilicate structure (i.e., quartz). Although the ratio 1.25 was obtained by manual iteration to find the best correlation with agglomeration performance, it is consistent with the real world. First, the silica/alumina ratios measured by CONSOL in several API standard kaolinite clay samples were typically about 1.25. Second, a CONSOL in-house method for estimation of quartz content for other applications uses a silica/alumina ratio of 1.18. This in-house estimation procedure was based on correlation of ash elemental data with quartz mineral content by X-ray diffraction (both data sets from O'Gorman and Walker⁵). Therefore, the optimization of the correlation at a ratio of about 1.25 may not be merely coincidental.

The linear regressions are given below. Equations 1 and 2 are based on linear regression of the entire data set. Equations 3 and 4 are based on the data set minus the RBS (raw Burning Star 2 coal) data. Equations 1 and 3 are regressions of physical ash rejection in agglomeration against ash silica content; equations 2 and 4 are regressions of physical ash rejection in agglomeration against ash "free" silica content. In these equations, AR = wt % physical ash rejection by agglomeration, S = wt % SiO_2 in ash, and F = wt % free SiO_2 in ash ($F = S - 1.25 \times \text{wt \% Al}_2\text{O}_3$ in ash). Each coefficient or intercept is followed by its standard deviation in parentheses.

Data Set: All nine points

$$AR = 1.23 (\pm 0.46) \times S - 20.3 (\pm 14.0), R^2 = 0.503 \quad (1)$$

$$AR = 1.77 (\pm 0.54) \times F - 6.0 (\pm 12.6), R^2 = 0.601 \quad (2)$$

Data Set: Eight points, RBS is omitted

$$AR = 1.22 (\pm 0.28) \times S - 23.6 (\pm 8.4), R^2 = 0.766 \quad (3)$$

$$AR = 1.75 (\pm 0.22) \times F - 9.3 (\pm 5.1), R^2 = 0.914 \quad (4)$$

Equations 2 and 4 give better results than their counterparts (equation 1 and 3). Free silica appears to be able to represent rejectable mineral matter. The best procedure appears to be to use Equation 4 to predict agglomeration performance, realizing that it may underestimate ash rejection in some coals.

The data and regression lines are graphed in Figures 5 and 6.

CO-Pretreated Coal Slurry

The CO-pretreated Black Thunder coal slurry supplied by CAER was agglomerated successfully in three tests with Wilsonville V-1074 heavy distillate (Table 7, Runs B31, B32H, and B33). The physical ash rejection was about 4%. Table 7 shows the results of these runs compared with those of two earlier runs performed with the pretreated coal which was recovered by filtration prior to shipment to CONSOL (Runs B24 and B25H). Runs B24 and B31 were made at the same conditions, except for the form of the pretreated coal. Likewise, Runs B25H and B32H were made at the same conditions, except for the form of the coal. Run B31 has a high ash balance (105%), an unusual occurrence in our experience. The slurry Runs B31 and B32H gave slightly higher physical ash rejections than the filtered coal Runs B24 and B25H (~4% vs 1%), although all were poor. A higher oil dosage in Run B33, relative to Run B31, did not improve physical ash rejection.

Perhaps the relatively low natural pH in B32H and high temperature in B25H and B32H contributes to dissolution of ash in those runs: 11 to 16% ash rejection (including dissolved ash) vs -2 to 5% in Runs B24, B31, and B33. Note that apparent ash dissolution is confounded with the ash-SO₃ error in these results.

The slurry runs (Runs B31 and B32H) gave tiny agglomerates; at equivalent oil dosages, the filtered coal runs (Runs B24 and B25H) gave large agglomerates.

Perhaps this is a physical effect of using the partially-dried coal vs the wet (slurried) coal. Run B33 was made to evaluate a higher oil dose and larger agglomerate size; this resulted in slightly less physical ash rejection.

The product agglomerates were lower in ash in Runs B31, B32H, and B33; however, the slurry coal ash content was only 4.74% MF ash, vs. 6.69 in the parent coal, and 6.30 in the filtered pretreated coal (all contain ash-SO₃). Perhaps the coal stored in slurry form for an extended period lost ash through dissolution prior to agglomeration. To address this possibility, refer to the SO₃-corrected results for Run B32H in Table 7. Based on the untreated coal ash content (5.54% MF), the CO-pretreated coal ash rejection including dissolved ash (assuming that 100% MAF coal is recovered from pretreatment) is 29% for Run B32H. Based on the treated coal ash content (4.43% MF), the ash rejection including dissolution in Run B32H was 11%. Stated another way, agglomeration alone gave 11% ash rejection including dissolution, whereas CO-pretreatment plus agglomeration gave 29% ash rejection including dissolution.

Overall, the results show that high organic recoveries are obtained when the CO-pretreated Black Thunder coal slurry is treated by agglomeration. Physical ash rejection from agglomeration is poor, but a substantial amount of slurry ash dissolution may have occurred prior to or during agglomeration.

Task 2.3.2 - Catalyst Studies (CONSOL)

No work was performed on this task.

Task 2.4.2 - Solids Separation (CONSOL)

No work was performed on this task.

Task 2.6.2 - Coker Overhead Characterization (CONSOL)

A sample of coker tar and two samples of hydrotreated coker tars were received from Sandia for characterization.

Task 3.2 - Economic Evaluation (CONSOL)

No work was performed on this task.

References

1. Project Status Report for July 1993, Subcontract UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040, September 1993.
2. Project Quarterly Technical Progress Report for the Period January 1 - March 31, 1993, Subcontract UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040.
3. CONSOL Inc., Project Status Report for June 1993, Subcontract No. UKRF-4-25582-92-76 to CONSOL Inc. Under DOE Contract No. DE-AC22-91PC91040, July 1993.
4. Brandes, S. D., Lancet, M. S., Robbins, G. A., Winschel, R. A., Burke, F. P., "Coal Liquefaction Process Streams Characterization and Evaluation, Quarterly Technical Progress Report, April 1 through June 30, 1992:, DOE/PC 89883-22, November 1992.
5. O'Gorman, J. V.; Walker, P. L. Jr. "Mineral Matter and Trace Elements in U.S. Coals", U.S. Dept. of the Interior R&D Report No. 61, Contract 14-01-0001-390, 1972.
6. 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.
7. Winschel, R. A.; Burke, F. P. "Oil agglomeration as a pretreatment for coal liquefaction", *Fuel* 1987, 66, 851-858.

TABLE 1
ANALYSES OF WILSONVILLE RUN 255 (TEXAS LIGNITE) SAMPLES

	V-1074 Distillate	V-1318 Pasting Solvent	V-181 Feed to ROSE	V-107 Ash Concentrate
Sample No.	86454	84410	84420	84422
Moisture, wt %	ND	ND	0.1	0.36
<u>Proximate, wt % dry (SO₃-free ash basis)</u>				
Volatile Matter	ND	ND	46.36	32.64
Ash	1.99	13.91	27.10	38.35
Fixed Carbon (diff)	ND	ND	26.54	29.01
<u>Ultimate, wt % dry (SO₃-free ash basis, except as noted)</u>				
Carbon	85.42	71.64	60.77	48.78
Hydrogen	9.5	6.96	4.28	2.89
Nitrogen	0.68	0.8	0.81	0.92
Sulfur	0.35	1.2	2.45	3.23
Oxygen (diff)*	2.06 (1.81)	5.49 (2.86)	4.59 (-0.93)	5.83 (-0.47)
Ash*	1.99 (2.24)	13.91 (16.54)	27.10 (32.62)	38.35 (44.65)
<u>Ash Elementals, wt %</u>				
Na ₂ O	1.36	1.28	1.24	1.25
K ₂ O	0.50	0.44	0.45	0.47
CaO	19.39	14.35	13.69	14.21
MgO	4.34	3.60	3.42	3.52
Fe ₂ O ₃	20.45	17.40	17.16	17.66
TiO ₂	1.30	1.10	1.05	1.07
P ₂ O ₅	0.27	0.18	0.17	0.18
SiO ₂	26.52	31.65	31.54	32.15
Al ₂ O ₃	14.98	12.97	12.44	13.72
SO ₃	11.10	15.93	16.91	14.10
Total	100.21	98.90	98.07	98.33

ND = Not Determined

* Analyses on an SO₃-containing ash basis are given in parentheses.

TABLE 2
HYDROTREATED MATERIALS RECEIVED FROM SANDIA

Sample No.	Description	Hydrotreatment Conditions	
		Temp, °C	Pressure, psig
42201	Coker Tar from CAER	400	1500
42301,2	Coker Tar from CAER	350	1500
72301	V-1074 (Wilsonville Run 262E)	325	1400
72201	V-1074 (Wilsonville Run 262E)	375	1400
72302	-35 °C Acetone/MEK Dewaxed V-1074	325	1400
72202	-35 °C Acetone/MEK Dewaxed V-1074	375	1400
81701	V-1074 Heavy Distillate	377	1400
72803	V-1074 Light Distillate	375	1400
72701	-35 °C Acetone/MEK Dewaxed V-1074 Heavy Distillate	375	1400
72801	-35 °C Acetone/MEK Dewaxed V-1074 Light Distillate	375	1400

TABLE 3
RESULTS OF MICROAUTOCLAVE TESTS

Run No.	Distillate	Resid	Soluble Resid Conv., wt %	Total Resid Conv., wt %	Coal Conv., wt %	IOM Conv., wt %	Comments
36	SC1	V-1082	-113.3	7.8	94.0	80.7	840 °F
38	SC1	V-1082	-80.4	20.1	94.0	80.6	860 °F
35	SC1	V-1082	-109.1	11.8	98.3	84.4	880 °F
42	SC1	V-1082	-64.0	27.7	96.6	82.9	880 °F
48	SC1	V-1082	-52.5	31.3	99.2	84.4	900 °F
37	V-1074	V-1082	-87.2	15.9	91.0	78.1	840 °F
40	V-1074	V-1082	-60.2	25.3	89.6	76.9	860 °F
43	V-1074	V-1082	-63.1	27.7	96.0	82.4	880 °F
44	V-1074	V-1082	-67.1	23.9	91.8	78.8	880 °F
45	V-1074	V-1082	-63.9	26.8	94.9	81.5	880 °F
47	V-1074	V-1082	-45.7	30.9	93.7	79.8	900 °F
49	V-1074	V-1082	-86.7	6.6	77.9	66.3	800 psig H ₂
57	V-1074	V-1082	-69.0	12.1	75.5	64.2	800 psig H ₂
50	V-1074	V-1082	-3.2	-4.0	No Coal	14.2	Solvent Only; 5 min
51	SC1	V-1082	-3.3	-3.6	No Coal	16.7	Solvent Only; 5 min
54	V-1074	Mo-free	7.0	5.7	No Coal	9.0	Solvent Only; 5 min
55	SC1	Mo-free	-0.5	-0.8	No Coal	8.4	Solvent Only; 5 min
52	V-1074	V-1082	15.6	16.0	No Coal	35.2	Solvent Only; 30 min
53	SC1	V-1082	18.2	18.1	No Coal	34.7	Solvent Only; 30 min
56	V-1074	Mo-free	11.5	10.8	No Coal	16.6	Solvent Only; 30 min
58	SC1	Mo-free	12.3	11.7	No Coal	18.1	Solvent Only; 30 min
39	SC1	V-107	-345.4	-20.9	No Coal	54.2	Ash Concentrate in SC1
59	V-1074	V-1082	-99.1	11.9	87.8	76.1	1.0 Distillate/Resid Ratio
60	SC1	V-1082	-99.9	14.1	92.2	79.9	1.0 Distillate/Resid Ratio
61	V-1074	V-1082	-75.3	12.7	90.1	74.9	0.5 Distillate/Resid Ratio
62	SC1	V-1082	-64.6	18.6	93.1	77.4	0.5 Distillate/Resid Ratio
69	V-1074	V-1082			68.8	58.6	Pre-heater Simulation 470 °F for 4 hr
77	V-1074	V-1082	-82.0	3.6	69.1	58.8	Pre-heater Simulation 470 °F for 4 hr
14	V-1074	V-1082			87.5	74.6	Base Case
18	SC1	V-1082			92.1	78.6	Base Case with SC1
63	V-1074	Mo-free	-93.7	0.3	77.9	66.3	Mo-free V-131B as Ashy Resid
64	SC1	Mo-free			77.2	67.6	Mo-free V-131B as Ashy Resid
65	-35°C AMDW	Mo-free	-104.6	-3.4	74.4	65.1	Mo-free V-131B as Ashy Resid
66	None	Mo-free	11.6	35.3	74.2	63.1	Whole V-131B (No Distillate)
16	-35°C ADW	V-1082			89.0	76.0	-35 °C Acetone Dewaxed V-1074
67	-35°C ADW	V-1082	-107.4	5.3	90.4	76.9	-35 °C Acetone Dewaxed V-1074
68	S-110404	V-1082	-103.7	7.4	91.6	77.9	Hydrotreated -35 °C Acetone DW V-1074 (#110404)
78	-5°C ADW	V-1082	-85.8	14.8	92.6	78.8	-5 °C Acetone Dewaxed V-1074
79	-35°C AMDW	V-1082	-91.5	11.9	91.3	77.6	-35 °C Acetone/MEK Dewaxed V-1074
73	S-72302	V-1082	-78.7	16.4	90.4	76.9	Hydrotreated -35 °C Acetone/MEK DW (#72302)
83	S-72202	V-1082	-101.1	8.5	91.7	78.0	Hydrotreated -35 °C Acetone/MEK DW V-1074 (#72202)
30	V-1074 Light	V-1082			86.8	74.5	V-1074 Light Distillate
31	V-1074 Heavy	V-1082			84.0	72.1	V-1074 Heavy Distillate
32	DW Light	V-1082			87.6	75.2	-35 °C Acetone/MEK DW Light Distillate
33	DW Heavy	V-1082			89.4	76.7	-35 °C Acetone/MEK DW Heavy Distillate
70	S-82804	V-1082	-83.8	14.0	89.6	76.2	Hydrotreated V-1074 (#92804) - not dewaxed
71	S-72301	V-1082			89.3	76.0	Hydrotreated V-1074 (#72301) - not dewaxed
72	S-72201	V-1082	-71.1	19.4	90.6	77.1	Hydrotreated V-1074 (#72201) - not dewaxed
74	S-72701	V-1082	-110.3	4.2	90.4	76.9	Hydrotreated -35 °C Acetone/MEK DW Heavy (#72701)
75	S-72803	V-1082	-73.2	17.3	88.1	75.0	Hydrotreated Light (#72803) - not dewaxed
76	S-72801	V-1082	-85.4	13.7	90.2	76.8	Hydrotreated -35 °C Acetone/MEK DW Light (#72803)
84	S-81701	V-1082			90.5	77.0	Hydrotreated Heavy (#81701) - not dewaxed

TABLE 4

DEWAXING CONDITIONS AND YIELDS FOR WILSONVILLE RUN 255 V-1074 DISTILLATE

Solvent	Temp, °C	Yields, wt %			
		Dewaxed Oil	Wax	THF Insolubles	Total Recovery
Acetone	-35	76.0	12.9	3.9	92.8
Acetone	-50	69.4	24.0	3.7	97.1
55 vol % Acetone/45 vol % MEK	-35	83.2	4.7	3.3	91.2

TABLE 5

PROTON DISTRIBUTIONS OF PRODUCTS
FROM DEWAXING WILSONVILLE RUN 255 V-1074 DISTILLATE

Solvent	Temp, °C	Material	¹ H-NMR Proton Distribution, %						
			Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alkyl	Cyclic Beta	Alkyl Beta	Gamma
---	---	V-1074 ¹	11.4	5.8	17.3	10.2	18.4	23.9	13.0
A (2)	-35	Dewaxed Oil	14.4	6.7	18.5	11.0	17.9	18.1	13.5
A (2)	-35	Wax	1.5	1.2	4.3	4.0	14.0	50.2	24.8
A (2)	-50	Dewaxed Oil	15.2	7.9	18.6	11.2	17.4	16.9	12.8
A (2)	-50	Wax	3.1	2.1	7.5	5.6	16.9	42.2	22.5
A/M (3)	-35	Dewaxed Oil	12.6	5.4	18.4	10.2	18.6	20.9	13.9
A/M (3)	-35	Wax	1.3	1.2	4.6	4.2	9.4	64.8	14.6

(1) = Heavy distillate, V-1074, from Wilsonville Run 255 with Texas Lignite.

(2) = Acetone

(3) = 55 vol % Acetone/45 vol % MEK

TABLE 7

THIRD QUARTER 1993 AGGLOMERATION RESULTS

Run (a)	Coal	Oil	Oil Dosage, wt % MF Coal	pH, Agent	Temp., °C	Product Ash, wt % Oil-Free	Organic Recovery, wt %	Ash Rejection (b) (Dissolved and Physical), wt %	Physical Ash Rejection (c), wt %	Ash Balance (d), wt %
A25 (e)	ML-1	P1	9.2	6.5, None	50	9.2	99.7	18.1	12.5	94.3
A28 (f)	ML-1	P1	27.6	6.5, None	50	8.6	99.7	23.9	19.0	95.1
A36	ML-2	P1	16.7	6.5, None	54	10.8	99.3	20.1	28.2	108.1
A41	ML-2	P1	33.0	6.5, None	54	9.9	99.5	27.7	27.2	99.5
A42 (g)	ML-2	P3	45.5	8.0, NaOH	54	NA	NA	NA	NA	NA
A43	ML-2	P1	33.2	8.0, NaOH	54	9.9	99.2	28.0	24.1	96.1
A48	ML-3	P1	16.9	6.8, None	54	10.5	99.3	24.9	25.3	100.3
A45	BS2	P1	24.8	8.0, NaOH	54	6.6	98.7	46.0	32.9	86.9
A49	BS2	P1	25.7	8.0, NaOH	65	7.5	99.0	38.4	31.3	92.8
A40 (h)	KM	P3	26.0	5.6, None	23	2.1	99.9	44.3	30.4	86.0
A44	KM	P3	30.6	8.0, NaOH	54	2.3	99.8	37.4	30.4	92.9
A47	KM	P3	51.1	8.0, NaOH	27	1.7	97.9	54.7	29.8	75.0
A50	KM	P3	33.0	5.5, None	23	2.3	99.9	39.6	27.8	88.1
A46	MK	P1	22.5	6.8, None	54	5.1	98.2	59.8	55.4	95.6
A51	MK	P1	23.5	8.0, NaOH	54	4.6	97.8	64.1	56.7	92.6
A52 (i)	MK	P1	23.5	6.9, None	65	4.7	96.9	62.7	52.3	89.6
B24 (j)	PBT	C1	14.1	6.0, None	50	6.05	99.7	4.3	2.34	98.1
B25H (j,k)	PBT	C1	16.1	5.5, None	175	5.34	99.8	16.1	0.47	84.4
B31	PBTS	C1	16.5	5.0, None	50	4.83	99.8	-2.0	3.28	105.3
B32H (k)	PBTS	C1	18.5	4.0, None	175	4.23	98.6	11.2	4.08	92.9
B33	PBTS	C1	27.8	5.0, None	50	4.52	99.8	4.8	0.39	95.6
SO ₂ -Free Ash Basis, CO-Pretreated Feed Coal from Slurry = 4.43% MF Ash (Filter Cake Ash Assumed to be SO ₂ -Free)										
B32H (k)	PBTS	C1	18.5	4.0, None	175	3.95	98.6	11.2	4.36	93.2
SO ₂ -Free Ash Basis, Untreated Feed Coal = 5.54% MF Ash (Filter Cake Ash Assumed to be SO ₂ -Free)										
B32H (k)	PBTS	C1	18.5	4.0, None	175	4.00	98.6	29.0	3.49	74.5

Coals: ML-x = Martin Lake (new sample), x = sample bag no.; BS2 = Burning Star 2 (new sample); KM = Kemmerer (old sample); MK = McKinley (new sample); PBT = CO-pretreated Black Thunder; PBTS = CO-pretreated Black Thunder slurry.

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

- (a) Run numbers with prefix A were made in the large vessel, those with prefix B were made in the small vessel.
- (b) Based on feed ash which was not recovered in the product.
- (c) Based on feed ash which was recovered in the solid reject (filter cake).
- (d) Ash balance does not include dissolved ash.
- (e) Cresylic acid (1.06 wt % MF coal) was added as a promoter prior to oil addition.
- (f) Feed coal was puck-milled. Cresylic acid (1.75 wt % MF coal) was added as a promoter prior to oil addition.
- (g) No agglomeration occurred.
- (h) Results reported last month.
- (i) A small amount of filter cake (reject) ash was lost during analysis.
- (j) Results reported previously in the Fifth Quarterly Report.
- (k) Agglomerated at 97°C, reactor was then sealed and heated to 175°C for continuation of the run.

Note: No SO₂ ash correction was made.

TABLE 8
ANALYSIS OF MCKINLEY MINE COAL

	McKinley Mine Coal
Moisture, wt % As-Determined	13.03
Ash, wt % MF, Including SO ₃	12.00
<u>Proximate, wt % MF, SO₃-Free Ash Basis</u>	
Ash, SO ₃ -Free	11.56
Volatile Matter	40.66
Fixed Carbon	47.78
<u>Ultimate, wt % MF, SO₃-Free Ash Basis</u>	
Carbon	68.21
Hydrogen	4.85
Nitrogen	1.21
Sulfur	0.47
Chlorine	<0.010
Oxygen (by diff)	13.70
Ash, SO ₃ -Free	11.56
<u>Sulfur Forms, wt % (MF)</u>	
Pyritic	0.04
Sulfate	<0.01
Organic (by diff)	0.43
<u>Ash Elementals, Oxide Wt % of Ash</u>	
Na ₂ O	1.54
K ₂ O	1.31
CaO	3.41
MgO	1.10
Fe ₂ O ₃	5.29
TiO ₂	0.96
P ₂ O ₅	0.04
SiO ₂	60.04
Al ₂ O ₃	20.43
SO ₃	3.64
Total	97.76
HHV, Btu/lb (MF)	12,029
<u>Particle Size by Laser Diffraction, Vol %</u>	
D ₁₀	5.8 μm
D ₅₀	33.5 μm
D ₉₀	130.7 μm

TABLE 9
DATA SET FOR AGGLOMERATION PERFORMANCE REGRESSION

Coal Code	Comments	wt % SiO ₂ in Ash	wt % Al ₂ O ₃ in Ash	wt % Free SiO ₂ in Ash	wt % Physical Ash Rejection in Best Agglomeration Test
OML	Raw, Martin Lake, Previous Work ⁶	50.1	13.5	33.23	42.50
WY	Raw, Clovis Pt. Wyodak, Previous Work ⁶	28.9	13.3	12.28	10.70
ML-1	Raw, 1st Bag Martin Lake, This Work	31.13	12.02	16.11	18.99
MK	Raw, McKinley Coal, This Work	60.04	20.43	34.50	56.69
BS2	Plant-Cleaned, Burning Star 2, Illinois 6 Seam, This Work	46.71	18.84	23.16	35.71
BT	Raw, Black Thunder, This Work	31.48	15.76	11.78	14.48
BA	Plant-Cleaned, Low- Ash CONSOL Pittsburgh Seam, Unreported Work	50.18	23.67	20.59	19.80
CBS	Plant-Cleaned Burning Star 2, Previous Work ⁷	49.8	19.2	25.80	37.60
RBS	Raw, Burning Star 2, Previous Work ⁷	43.8	17.1	22.43	62.70

Note: Ash is on an SO₃-containing basis.

Figure 1. Effect of Reaction Temperature on the Conversion of Black Thunder Coal in Five-Minute Microautoclave Tests.

Figure 2. Microautoclave Heat-Up Curves for 880 °F Runs with V-1074.

Figure 3. Resid Conversion vs Temperature.
(Black Thunder Coal, 1500 psig H₂, S/C = 1.5)

ADW = Acetone Dewaxed
AMDW = Acetone/MEK Dewaxed

Figure 4. Black Thunder Coal Conversion.
(5-min, 824 °F, 1.5 S/C, 1500 psig H₂, 262E Ratios)

Corr. of Ash SiO₂/Agglom. Deashing

Figure 5. Regressions of Ash Rejection with Ash Silica Content.

Corr. of Ash SiO₂/Agglom. Deashing

Figure 6. Regressions of Ash Rejection with Ash "Free" Silica Content.

SECTION THREE

SANDIA NATIONAL LABORATORY

ADVANCED DIRECT LIQUEFACTION CONCEPTS for PETC GENERIC UNITS
QUARTERLY PROGRESS REPORT for JULY 1993 through SEPTEMBER 1993

SANDIA NATIONAL LABORATORIES

Subtask 1.3 Laboratory Support

Results from the TGA experiments with mixtures of V1074 heavy distillate and V1082 ashy resid were discussed in the April 1993 to June 1993 quarterly progress report. The TGA results were used to approximate the amount of resid in products from microautoclave tests (a necessary measurement to determine resid conversion). This quarter, experiments were performed to evaluate resid content of mixtures with a high resolution gas chromatograph (HRGC). Samples of previously analyzed resid/heavy distillate mixtures were diluted in a known volume of solvent (THF) and injected into a HRGC using a 30 meter capillary column with the injector temperature at 260°C. Since the HRGC has an adsorbent material in the injector liner which acts as a trap for nondistillable material, it is possible that the detector response from the HRGC may be inversely correlated with resid content and directly correlated with distillate content of the mixtures. Results from previous analyses using the TGA method and current results using the HRGC are shown in Table 1. The values for resid, ash, and distillate were determined using the TGA method with the original V1082 ashy resid and the V1074 heavy distillate as standards and applying gravimetric corrections to the respective mixtures. The area counts from the chromatogram are the net area counts from the HRGC corrected for solvent peak areas and sample dilutions.

TABLE 1 Distillate Content of Resid/Distillate Mixtures Using TGA and HRGC Methods

SAMPLE	Expected Resid (%)	Expected Ash (%)	Expected distillate (%)	HRGC Area Counts
V1082	61	21	18	10490
75% V1082 : 25% V1074	47	16	37	39560
67% V1082 : 33% V1074	43	14	43	41370
50% V1082 : 50% V1074	34	11	55	74340
39% V1082 : 61% V1074	24	8	68	112150
20% V1082 : 80% V1074	12	4	84	140080
V1074	6	0	94	217760

The "expected" values for the distillate quantities in Table 1 are derived from TGA results and have not been independently measured by distillation. For this reason the HRGC correlation depends on the veracity of the TGA results. A correlation coefficient of 0.96 is obtained when a linear regression is performed on the "expected" distillate vs. the area counts for the mixtures. In general the HRGC test seems reliable for approximating resid content of mixtures.

To test the HRGC method, four thermal coal liquefaction runs were performed with Black Thunder subbituminous coal and the Wilsonville Recycle Oil (WRO) using either V1074 or Hexahydropyrene (H₆Py) as the distillate component of the recycle oil. The reactors were pressurized to 1400 psig of hydrogen and heated to 440°C. Samples of the THF soluble products from the microautoclave tests were analyzed using the TGA method and were also diluted in a known volume of solvent (THF) and injected into the HRGC. Results from the TGA and HRGC methods are shown in Table 2. The values for resid and distillate were determined using the TGA method, reading the resid content at the 375°C (707°F) plateau in the program. Since there is no ash in the THF soluble products from the liquefaction runs, the distillate was assigned a value of 100 minus the resid content for purposes of Table 2. The area counts from the chromatogram are the net area counts from the HRGC corrected for solvent peak areas and sample dilutions.

TABLE 2 Distillate Content of THF Soluble Liquefaction Products Using TGA and HRGC Methods (440°C, 1400 psig H₂)

SAMPLE	Time (min.)	Solvent	THF conv. (%maf coal)	TGA Resid (%)	TGA distillate (%)	HRGC Area Counts
080301	30	H ₆ Py	102	20	80	49800*
080401	5	H ₆ Py	97	30	70	14960*
080501	30	V1074	83	32	68	101110
080502	5	V1074	76	40	60	64743

* Area counts adjusted for initial H₆Py in sample.

Area counts for the experiments which used H₆Py as the "distillate" source for liquefaction are lower since the discrete H₆Py product peak areas were subtracted from the total area. Since future efforts to quantify the resid yields will include process derived solvents and standards, the differences between the model solvent and the V1074 will not be an issue. In general the HRGC test shows significant sensitivity to resid conversions and could be used for approximating resid content of mixtures. Interestingly the "net" difference between the five minute and thirty minute

tests is about the same for the H₆Py and V1074 tests (appx. 35K counts). Future experiments should include standards that are well characterized by distillation and will approximate the resid/distillate concentration from a liquefaction test. Along with better standards, future tests could be aimed at reducing analysis time (the current analysis time is approximately two hours per sample).

Subtask 2.1.3 Solvent Pretreatment

CONSOL has sent samples from a distillation done on V1074 heavy distillate. The products from the original distillation were split and a portion of the "light" and "heavy" distillate were dewaxed in 45/55 (vol%) MEK/Acetone at -35°C. The distillations were done to supply Sandia with a "light" and "heavy" distillate solvent for hydrogenation with a supported catalyst in a microautoclave test. Table 3 has the sample descriptions.

Table 3 Run 262E Distillate Samples from CONSOL

Sample	wt% on distillation	Sample Description
1621-22-5G	46.1	Light from V1074 distillation
1621-22-5H	53.4	Heavy from V1074 distillation
1621-22-5G-1	NA	Dewaxed (1621-22-5G) light from distillation
1621-22-5H-1	NA	Dewaxed (1621-22-5H) heavy from distillation

The dewaxed oil yields from these dewaxings were 84.5% and 82.5% for the light fraction and the heavy fraction respectively. Each of the samples were hydrogenated in batch microautoclaves using 1400 psig of hydrogen at 375°C for 60 minutes. Comparison tests were run using a sample of V1074 and a sample of V1074 that had been dewaxed in 45/55 (vol%) MEK/Acetone at -35°C. Proton NMR results for the original and hydrotreated nondewaxed solvents are shown in Table 4.

Table 4 Proton NMR Results for Original and Hydrotreated Nondewaxed Distillation Products

Sample	Hydrotreating TEMP°C	Cond Arom	Uncond Arom	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
V1074	NA	11.3	3.6	14.7	7.6	15.8	34.6	12.3
V1074	325	9.2	2.9	14.8	7.0	17.2	36.0	12.8
V1074	375	8.4	3.4	14.0	6.7	18.3	36.0	13.2
1621-22-5G	NA	9.4	2.6	13.0	6.6	16.7	37.4	14.3
1621-22-5G	375	8.4	2.8	13.2	6.4	18.2	36.9	14.1
1621-22-5H	NA	13.1	2.7	15.0	6.7	16.0	34.6	11.9
1621-22-5H	375	10.2	3.1	16.9	7.2	17.8	33.5	11.3

Column two of Table 4 shows the hydrotreating temperature used with the listed samples. Initial tests at two temperatures (325°C and 375°C) with the "whole" V1074 indicated more extensive hydrogenation at 375°C. For this reason the distillation samples were hydrotreated at 375°C. In general, the "light distillate" had a lower initial aromatic hydrogen concentration than the original V1074 and hydrogenation increased its cyclic alpha and beta hydrogen content from 29.7% to 31.4%. The "heavy distillate" had a higher initial aromatic hydrogen content than the original V1074 and hydrogenation increased its cyclic alpha and beta protons from 31% to 34.7%. Results from proton NMR spectroscopy analysis of the dewaxed V1074 and the dewaxed distillate cuts from the V1074 are shown in Table 5.

Table 5 Proton NMR Results for Original and Hydrotreated Dewaxed Distillation Products

Sample	Hydrotreating TEMP°C	Cond Arom	Uncond Arom	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
-35°C Dewax	NA	15.3	3.5	18.8	8.3	19.0	23.2	11.8
-35°C Dewax	325	12.8	3.6	19.4	8.8	19.8	23.4	12.2
-35°C Dewax	375	10.3	3.9	18.6	8.8	21.3	24.3	12.8
1621-22-5G-1	NA	13.2	3.0	16.6	8.4	19.3	25.5	14.1
1621-22-5G-1	375	10.8	4.0	16.7	8.2	20.4	25.8	14.2
1621-22-5H-1	NA	17.2	3.6	20.2	9.3	18.1	20.9	10.6
1621-22-5H-1	375	14.5	3.0	22.0	8.2	20.5	20.9	10.8

The "light distillate" had a lower initial aromaticity (before hydrotreating) than the dewaxed whole V1074 and therefore had smaller hydroaromatics content after hydrotreating. Hydrogenation increased the cyclic alpha and beta hydrogen content from 35.9% to 37.1%. Hydrotreating the "Dewaxed V1074 heavy" increased the cyclic alpha and beta hydrogen content from 38.1% to 42.5%.

If one looks at the improvement in solvent quality over the original "waxy" V1074 we can see an increase in cyclic alpha and beta hydrogen content from 30.5% to 42.5% after treatment by distillation, dewaxing and hydrotreating (hydrotreated 1621-22-5H-1). Microautoclave tests will be necessary to see how these proton distribution changes affect coal dissolution with the Black Thunder coal. These samples were submitted to CONSOL for this purpose.

Subtask 2.1.3 Solvent Pretreatment

CONSOL sent a 500g sample of V1074 heavy distillate dewaxed in 45/55 (vol%) MEK/Acetone mixture at -35°C in February 1993. This material was used this quarter to evaluate hydrogenation conditions with two different types of hydrotreating catalysts. The two catalysts used were a platinum hydrous titanium oxide catalyst (HTO) and a sulfided nickel molybdenum catalyst supported on alumina (Shell 324). Proton NMR results for the original and dewaxed V1074 solvents are shown in Table 6.

Table 6 Proton NMR Results for V1074 Heavy Distillate Samples

Sample	% H	Cond Arom	Uncond Arom	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
V1074	9.9	11.3	3.6	14.7	7.6	15.8	34.6	12.3
Dewaxed V1074a	8.9	14.5	5.4	16.9	9.0	17.1	23.5	13.5
Dewaxed V1074b	8.1	17.3	6.2	20	10.3	17.1	17.9	11.2

a) Dewaxed at -35°C with 45/55 (vol%) MEK/Acetone mixture. b) Dewaxed at -35°C with acetone; used for tests with 0903 prefix.

Column two of Table 6 shows the hydrogen content of the samples and the other columns show how the hydrogen is distributed in the samples. Hydrotreating studies this quarter evaluated the

effects of increased hydrogen pressure, reaction temperature and liquid hourly space velocity using dewaxed heavy distillate.

Test results for the platinum HTO catalyst

The platinum catalyst had a platinum content of 5.5 wt% and was prepared by calcining at 300°C in air followed by reducing with hydrogen in situ at 200°C. Previous results with the platinum catalyst indicated that a high degree of solvent hydrogenation is possible with this catalyst in a "hydrogen only" atmosphere (see first quarter 1992 report). This catalyst was tested at 320°C and 360°C using 1000 psig H₂. Elemental organic analyses were performed on the products and results are shown along with run conditions in Tables 7. Results in Table 7 are from two consecutive days of operation and demonstrate some degree of catalyst deactivation over time.

Table 7 Results from Hydrotreating Experiments with Platinum HTO Catalyst

SAMPLE	TEMP (°C)	WHSV (hr ⁻¹)	VHSV* (hr ⁻¹)	Nitrogen ppm	Carbon wt%	Hydrogen wt%
FEED	320	NA	NA	5000	89.3	8.9
81702	320	1.1	0.8	2740	89.6	10.0
81703	320	0.9	0.7	2900	ND	ND
81704	320	0.9	0.7	3340	ND	ND
81705	320	0.8	0.6	3330	ND	ND
81706	320	0.7	0.5	3520	89.6	9.6
81707	320	0.8	0.6	3500	ND	ND
81802	360	1.0	0.7	2770	90.0	9.6
81803	360	1.1	0.8	3080	ND	ND
81804	360	1.0	0.7	3350	ND	ND
81805	360	1.0	0.7	3500	ND	ND
81806	360	1.0	0.7	3710	89.2	9.3
81807	360	1.0	0.7	3830	ND	ND

ND = Not Determined. * Assume density of packed catalyst is 0.76 g/cm³ and that of feed is 1.05 g/cm³.

In general the solvent hydrogen content increased by approximately 0.7% at 320°C on the first day of testing. The increase in nitrogen content of the product with time shows a decrease in catalyst activity as the catalyst ages. On the second day of testing the catalyst shows increased activity at 360°C but again catalyst deactivation is noted with time on line. The results of these two days of testing indicate that the platinum catalyst does in fact deactivate significantly with the dewaxed heavy distillate. Proton NMR spectroscopy will be performed on selected samples next quarter to get a clearer picture of catalyst deactivation and its effect on hydroaromatic content of the solvent.

Test results for the NiMo on alumina (Shell 324) catalyst

This nickel molybdenum catalyst (Shell 324) had a nickel content of 2.8% and a molybdenum content of 12.4% and was prepared by sulfiding with a 9% H₂S in hydrogen gas mixture at 400°C for four hours in situ. Testing with this catalyst involved a first day of testing at 320°C followed by a second day of testing at 360°C. The liquid hourly space velocity was adjusted at midday during the second day to investigate the effect of increased space velocity upon the hydrogenation of the heavy distillate. Analysis by LDP Associates has indicated that increased throughput to the hydrotreater could potentially allow the hydrotreating step to be done with fewer reactor units and thus decrease capital expense for hydrotreating. System hydrogen pressure was maintained between 1300 and 1400 psig for these experiments. Elemental organic analysis was performed on the products and are shown along with run conditions in Tables 8 and 9. Table 8 gives results obtained at 360°C with a more aromatic feed and with space velocity increased as indicated above. Proton NMR spectroscopy will be performed on selected samples next month.

Table 8 Results from Hydrotreating Experiments with NiMo Catalyst at 320°C

SAMPLE	TEMP (°C)	WHSV (hr⁻¹)	VHSV* (hr⁻¹)	Nitrogen ppm	Carbon wt%	Hydrogen wt%
FEED	320	NA	NA	5000	89.3	8.9
90202	320	0.8	0.7	2700	ND	ND
90203	320	1.0	0.8	3090	ND	ND
90204	320	1.0	0.8	3490	89.6	9.3
90205	320	1.2	1.0	3630	ND	ND

ND = Not Determined. * Assume density of packed catalyst is 0.86 g/cm³ and that of feed is 1.05 g/cm³.

Results from the first day of hydrotreating indicated that the catalyst activity decreased with time on line as indicated by the increasing nitrogen content of the product. After a four hour induction time the product hydrogen increase was 0.4%. This increase is approximately equal to previously observed catalyst activity for the Shell 324 catalyst.

Table 9 Results from Hydrotreating Experiments with NiMo Catalyst at 360°C

SAMPLE	TEMP (°C)	WHSV (hr⁻¹)	VHSV* (hr⁻¹)	Nitrogen ppm	Carbon wt%	Hydrogen wt%
FEED	360	NA	NA	6300	89.6	8.1
90302	360	0.8	0.6	2700	ND	ND
90303	360	0.9	0.7	3090	90.1	8.8
90306	360	1.5	1.2	3630	ND	ND
90307	360	1.4	1.1	4390	90.0	8.5
90308	360	1.4	1.1	3800	ND	ND

ND = Not Determined. * Assume density of packed catalyst is 0.86 g/cm³ and that of feed is 1.10 g/cm³.

At 360°C the amount of hydrogen was 0.7 wt% higher than the feed (sample 90303). This hydrogen uptake was improved over the steady state sample at 320°C (sample 90204 at 0.4%). When the volume hourly space velocity was increased by over 50% to 1.1 hr⁻¹ the net hydrogen uptake was 0.4 wt%. Proton NMR and coal liquefaction tests on these solvents should give better information to gauge the effectiveness of solvent hydrogenation at the higher liquid flow rates. These experiments are forthcoming.

Subtask 2.3.3 Catalyst Studies

A platinum hydrous titanium oxide (HTO) catalyst was formulated this quarter. The 50 gram batch was pelletized and sized to -10/+20 mesh, calcined at 300°C before being packed in the trickle bed reactor. The platinum content was 5.5% after calcining.

Catalyst deactivation was noted for the Pt HTO catalyst as well as the Shell 324 NiMo catalyst tested this quarter. Table 10 shows the elemental analyses for catalysts that were removed at different bed depths in the packed tube reactor. The samples were taken from top (where the feed entered the reactor) to the bottom (where the feed exited the packed bed).

Table 10 Post Reaction Catalyst Analysis

Catalyst	Bed Position	Carbon(%)	Nitrogen (ppm)	Sulfur (ppm)
Pt HTO	1(top)	6.7	1220	1260
Pt HTO	2	4.3	1020	910
Pt HTO	3	2.4	370	1100
Pt HTO	4	1.8	130	1190
Pt HTO	5	1.6	150	1180
Pt HTO	6(bottom)	1.5	100	1150
NiMO (Shell)	1(top)	7.7	1400	ND
NiMO (Shell)	2	6.7	1660	ND
NiMO (Shell)	3	6.3	1540	ND
NiMO (Shell)	4	5.7	2030	ND
NiMO (Shell)	5	5.0	2400	ND
NiMO (Shell)	6(bottom)	4.5	2500	ND

ND = Not Determined

Both of the catalysts had high carbon deposits on the feed end of the reactor, however the Shell 324 catalyst had much more carbon deposition at lower portions of the reactor. The alumina support is much more acidic than the bulk HTO support so the increased coke deposition may be expected. This observation indicates that the HTO substrate may be desirable for applications such as donor solvent hydrogenation where hydrocracking is not required. In addition, the nitrogen laydown was much more significant for the alumina supported Shell catalyst. It is unclear however, why the nitrogen content increases from feed end to exit end of the reactor for the alumina supported catalyst.

SECTION FOUR

LDP ASSOCIATES

LDP ASSOCIATES

Michael Peluso, Proprietor
908-752-5581

603 Fairview Ave.
Piscataway, N.J. 08854

November 17, 1993

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

Dear Ed:

Subject: QUARTERLY PROGRESS REPORT FOR JULY TO SEPTEMBER 1993

During the quarter ending September 30, 1993 the following subcontract services (UKRF-4-25582-92-75) were performed in support of the DOE Advanced Concepts Program (DE-AC22-91PC91040):

BASELINE ECONOMIC ASSESSMENT

The baseline economic assessment, based on Wilsonville Run # 263J, serves as the reference against which the results of this program will be compared.

The sensitivity of the Required Gasoline Selling Price (RGSP) to the Total Plant Cost (TPC) for the Revised Base Case was investigated. As expected the RGSP is a strong function of the TPC. A 25% reduction in the TPC reduces the RGSP by 18.2% at a 10% discount rate or 16.1% at a 5% discount rate.

FLUID COKING

The full set of Bechtel's reports (8 volumes) on their baseline and improved baseline designs (Illinois #6 coal) was received from PETC. A quick review of the fluid coking option study indicates that none of the very heavy fluid coker overhead product was used as recycle solvent. Since the latter is the intent in our program, further evaluation is required.

NEW MOLY-FREE PROCESS SOLVENT

Process solvent from Wilsonville Run # 258K will be used in future autoclave tests to eliminate the effect of recycle moly contained in the resid portion of the original process solvent sample from WR # 262E. The properties of the distillate portions of these two solvents differ significantly. WR # 258K was conducted with almost fresh second stage catalyst in the batch deactivation mode of operation at a relatively low second stage temperature of 760°F. As a consequence, the proton NMR distribution of the 258K distillate has a significantly lower concentration of

alkyl beta protons versus the corresponding 262E material (25.0 vs 34.6%). The difference between the two distillates is also reflected in the results of CONSOL's modified-equilibrium solvent quality test (89% for 258K vs 59% for 262E). Therefore, in order to determine the true effect of eliminating the recycle moly it was recommended that upcoming tests be run by combining the distillate from Run # 262E with the moly-free ashy resid from Run # 258K.

DEWAXED OIL HYDROTREATING

Sandia has and will continue to run hydrotreating tests on Dewaxed V-1074 distillate samples made at CONSOL. In order to fully evaluate this hydrotreating step it is necessary to generate baseline information on coal distillate hydrotreating. An appropriate choice for such a baseline is the distillate solvent hydrotreating work done at Exxon during the development of their EDS process. A copy of the report, "EDS Wyoming Coal Bottoms Recycle Study Design Addendum Interim Report" was obtained and reviewed. While some of the relevant technical and economic data for the EDS solvent hydrotreating section are not explicitly disclosed, enough information was available to permit reasonable estimates of key parameters such as LHSV.

A memo was prepared for Sandia (Peluso to Kottenstette, 9/14/93) outlining the key features of the EDS design for its commercial Wyoming coal-based solvent hydrotreater. It was recommended that Sandia conduct screening type hydrotreating tests at high space velocities ($LHSV \geq 1$) in order to allow an assessment of performance at reduced capital cost levels.

CONSOL MICROAUTOCLAVE TESTS WITH DWO's

Data from tests where Dewaxed Oil (DWO) and hydrotreated DWO were substituted for the as-is V-1074 in recycle solvent blends were analyzed. The DWO was obtained from dewaxing at -35°C with an MEK, acetone mixture, while the HT-DWO originated from a more severe dewaxing at -5°C with acetone followed by hydrotreatment at Sandia. When the HT-DWO was used, better coal conversion resulted. CONSOL had also produced a DWO using acetone at -35°C which had a significantly lower alkyl beta content than either of the above materials. It was therefore recommended that CONSOL run microautoclave tests with this most severely dewaxed material as-is and after hydrotreatment since these materials might further improve coal conversion. CONSOL agreed to conduct such tests.

SEPARATE DEWAXING OF V-1074 FRACTIONS

CONSOL distilled the distillate process solvent (V-1074) into two approximately equal fractions and then dewaxed each separately. The data indicate that the DWO yields and properties differ only slightly between the light and heavy portions. This means that the waxy components are almost evenly distributed throughout the V-1074 stream boiling range.

STEADY STATE SOLVENT DEWAXING UNIT BALANCE

Work was completed on a steady state balance for a commercial scale Solvent Dewaxing unit. A steady state balance is necessary because the properties of the distillate recycle solvent change significantly once a dewaxing unit is used in the process scheme. CONSOL's paper on net wax yield in the liquefaction of sub-bituminous coals was reviewed and a net wax make of 4% on MAF coal was chosen as a basis for the steady state balance. Data on the buildup of wax in the distillate recycle stream (V-1074) during Wilsonville Runs # 262 and # 263 were also analyzed. During Run # 263 the wax level of the V-1074 stream was approximately constant. Therefore, at the particular conditions employed, the wax cracking and production rates were approximately equal. This information was used to set a wax cracking rate of 22% of total wax circulating for the steady state simulation. DWO and slack wax proton NMR data from CONSOL's three major dewaxing runs were analyzed to verify that proton NMR balances could be used as a suitable surrogate for material balances in the steady state simulation.

An important requirement of the calculation technique is the prediction of DWO properties versus dewaxing severity. A simplified process simulation was used to study the effect of treating 25%, 50%, 75% and 100% of the available feed versus the resultant paraffinic content (i.e. alkyl beta proton concentration) of the distillate recycle solvent. Dewaxing only 25% of the available feed reduced the alkyl beta content from 32.9% to 25.5%. Dewaxing 100% of the feed further reduced the alkyl beta content to 21.4%.

ECONOMIC ASSESSMENT OF DEWAXING

Defining the incremental benefit-cost relationship of lowering the alkyl beta content of the recycled distillate solvent from 32.9% thru 21.4% will set the amount of feed sent to the proposed Dewaxing unit. A key factor in determining the benefit-cost relationship is the value of the wax recovered in the Dewaxing unit. If all the recovered wax can be sold as fully refined paraffin wax at current U.S. price levels, then the byproduct revenue will be sufficient to offset Dewaxing unit costs. However, if the current domestic market would be over saturated by wax production from a reasonable number of commercial scale production plants (3 to 5), then byproduct revenues would be significantly lower (e.g. slack wax as FCC feed). In order to properly value the slack wax feed as FCC feed, FCC yields were estimated based on slack wax properties and R. E. Maples book entitled, "Petroleum Refinery Process Economics". The valuation of the Dewaxing unit byproduct wax should be completed in November.

The latter market situation might also make the use of catalytic dewaxing a more attractive alternative to the current solvent dewaxing process.

DOE CONTRACTORS CONFERENCE & WORKSHOP

The above conference was attended on September 28 and 29. At the September 27 Workshop session on Focused Research for Improved Economics, a presentation was made on, "Economic Assessment of Solvent Dewaxing and Hydrotreating the Distillate Recycle Solvent in the Liquefaction of Sub-Bituminous Coal". A hardcopy of this presentation is attached.

Very truly yours,

A handwritten signature in black ink, appearing to read "Michael Peluso", with a stylized flourish at the end.

Michael Peluso
LDP Associates

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

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

**PRESENTED AT DOE WORKSHOP ON
"FOCUSED RESEARCH FOR IMPROVED LIQUEFACTION ECONOMICS"
PITTSBURGH, SEPTEMBER 27,1993**

**BY LDP ASSOCIATES
ADVANCED DIRECT LIQUEFACTION CONCEPTS
DOE CONTRACT DE-AC22-91PC91040**

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

WEIGHT RATIO TO MF COAL :	0.858
ESTIMATED SPECIFIC GRAVITY :	1.04 (4.6°API)
ESTIMATED ELEMENTAL ANALYSIS, Wt. %	
- Carbon	89.28
- Hydrogen	9.49
- Oxygen	0.76
- Nitrogen	0.44
- Sulfur	0.03
BOILING RANGE, °F :	650 to 1,000
ESTIMATED WATSON "K" FACTOR :	10.5
PROTON NMR DISTRIB'N (CONSOL), %:	
- Condensed Aromatics	13.9
- Uncondensed Aromatics	4.4
- Cyclic Alpha	14.3
- Alkyl Alpha	8.2
- Cyclic Beta	14.5
- Alkyl Beta	32.9
- Gamma	11.8
SOLVENT QUALITY* (CONSOL):	70.9

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

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

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

TABLE 2
DEWAXING OF DISTILLATE PORTION OF PROCESS SOLVENT
DEWAXING UNIT SEPARATION MODEL

OBJECTIVES:

**MAKE A PRELIMINARY ESTIMATE OF COMMERCIAL UNIT
STEADY STATE PERFORMANCE INCLUDING:**

- (1) THE AMOUNT OF FEEDSTOCK TO BE PROCESSED**
- (2) THE RESULTANT DEWAXED OIL & SLACK WAX
PROPERTIES INCLUDING PROTON NMR DISTRIBUTIONS**

KEY ASSUMPTIONS:

- USE OF A SOLVENT TYPE DEWAXING PROCESS**
- VALIDITY OF THE PROTON NMR BALANCE**
- "WAX" PRODUCED FROM COAL TO LIQUEFACTION**
- WAX CRACKING RATE IN LIQUEFACTION**
- PROTON NMR DISTRIBUTION OF "WAX" PRODUCT**
- OIL CONTENT OF "WAX"**
- ACCURACY OF SEPARATION FACTORS USED**

TEXACO DEVELOPMENT CORPORATION

TWO STAGE SOLVENT DEWAXING UNIT WITH INCREMENTAL DILUTION

FIGURE 2A

TEXACO DEVELOPMENT CORPORATION

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

FIGURE 2B

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

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

FIGURE 3
EFFECT OF DEWAXING UNIT BYPASS

TABLE 4
SLACK WAX UPGRADING VIA CAT CRACKING
POTENTIAL ADVANTAGES & DISADVANTAGES
Vs
FULLY REFINED PARAFFIN WAX PRODUCTION

Advantages

- MARKET CAN READILY ABSORB TRANSPORTATION FUELS & PRECURSORS PRODUCED FROM MANY SLACK WAX UPGRADING UNITS
- BETTER PRODUCT FIT; MAIN PRODUCT FROM LIQUEFACTION PLANT IS ALSO TRANSPORTATION FUELS
- LOWER DEWAXING UNIT INVESTMENT
- HIGH OCTANE OXYGENATE PRECURSORS PRODUCED IN SIGNIFICANT QUANTITIES

Disadvantages

- VALUE OF TRANSPORTATION FUELS & PRECURSORS IS SIGNIFICANTLY LESS THAN FULLY REFINED PARAFFIN WAX

FIGURE 4
EDS SOLVENT HYDROTREATER

TABLE 5
DISTILLATE SOLVENT HYDROTREATER
DESIRED OPERATING PARAMETERS

HYDROGEN PARTIAL PRESSURE :	$\geq 1,500$ psig
TEMPERATURE :	$< 750^{\circ}\text{F}$
LHSV :	≥ 1.0
HYDROGEN UPTAKE :	1% of Feed
TIME BETWEEN CATALYST REGENERATIONS	> 6 Months

TABLE 6
DEWAXING & HYDROTREATING
OF DISTILLATE PORTION OF PROCESS SOLVENT
KEY FACTORS IN ECONOMIC EVALUATION

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

CURRENT & PLANNED ACTIVITIES

- STUDY WAX MARKET & ASSESS IMPACT OF ABOVE PROJECT
- DETERMINE DEWAXER BYPRODUCT VALUE
- USE TEXACO DATA to ESTIMATE DEWAXING UNIT CAPITAL &
OPERATING COSTS
- USE EXXON EDS DATA to ESTIMATE HYDROTREATER UNIT
CAPITAL & OPERATING COSTS
- QUANTIFY LIQUEFACTION SYSTEM BENEFITS vs DEGREE OF
SOLVENT QUALITY IMPROVEMENT
- DETERMINE BEST PROCESS SCHEME (i.e. Maximum "Benefit - Cost")
- DETERMINE SENSITIVITY to WAX YIELDS
- INVESTIGATE USE of CATALYTIC DEWAXING TECHNOLOGY

DATE

FILMED

6 / 9 / 94

END