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

**Quarterly Technical Progress Report
for Period April 1993 through June 1993**

by

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

Sandia National Laboratories

CONSOL Inc.

LDP Associates

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SUMMARY

TASK 1.1 LABORATORY SUPPORT (UK/CAER)

Samples of a dewaxed heavy distillate and two samples of hydrotreated dewaxed heavy distillate that were received from Sandia were evaluated in coal liquefaction with Black Thunder coal using Wilsonville derived recycle oil from Run 262. These runs were made by substituting the dewaxed and hydrotreated dewaxed samples for the V-1074 heavy distillate portion of the recycle oil solvent. These data were calculated using the method that has been used up to now in our lab, i.e., no ash SO_3 correction was used. These data are discussed relative to the method of hydrotreating and are included in the Sandia report Section 3, pages 11-13. Subsequently, these data were recalculated on a SO_3 -free ash basis, the first data treated by this method in our lab. To complete the data set, these SO_3 -free ash data are included in this section for comparison with data shown in Section 3. Generally, on a SO_3 -free ash basis, oils and PA + A decrease by 2-3%, IOM increases by ~5%, and hydrocarbon and carbon oxide gases remain essentially unchanged.

TASK 1.2 LABORATORY SUPPORT (CONSOL)

The V-131B pasting solvent from Wilsonville Run 258K was chosen as the source of Mo-free ashy resid material for future work. A sample of this material was received and distilled at 1025 °F atmospheric equivalent end point to obtain the ashy resid sample.

Samples of Burning Star No. 2 Mine (Illinois 6) coal, and Martin Lake Mine (Texas lignite) were received and analyzed. The Burning Star No. 2 Mine coal appears to be typical. The Martin Lake Mine lignite is lower in ash content than our previous sample. Both coals were distributed to the other program participants.

Lignite-derived process liquids (Wilsonville Run 255) were obtained and pertinent samples of these were selected for use in this project.

Project participants were provided with Wilsonville's description of the ash- SO_3 correction

method applied to Run 246. Wilsonville did not correct for ash SO_3 in any subsequent run.

TASK 1.3 LABORATORY SUPPORT (SANDIA)

Methods development work proceeded on the thermogravimetric analysis (TGA) technique to determine resid concentrations in microautoclave products. It was found that the thermogram could be made more distinct if the ramp rate was slowed to $50^\circ\text{C}/\text{min}$ from $200^\circ\text{C}/\text{min}$. Resid concentrations have been measured with the modified method on mixtures of V1082 ashy resid and V1074 heavy distillate. The method has also been applied to two different coal liquefaction tests. Preliminary results indicate that filtering the liquefaction products with THF followed by THF evaporation may enhance sampling reproducibility.

TASK 2.1.1 CO PRETREATMENT (UK/CAER)

In continuation with our effort to demonstrate the effectiveness of CO pretreatment of coal, we report in this quarter further results from liquefaction experiments of pretreated and untreated coal. The effect of pretreatment time and CO/H_2 partial pressures were evaluated. In addition, a sample of Texas Lignite was pretreated under established reaction conditions and compared with previous results obtained from Clovis Point and Black Thunder Wyodak subbituminous coal. An evaluation and discussion on the chemistry of the water-gas shift reaction is also presented.

TASK 2.1.2.1 PRETREATMENT / DEWAXING - (CONSOL)

Wilsonville Run 262E V-1074 was distilled into two fractions and dewaxed as outlined in the action item list from the last quarterly meeting. Dewaxing improved the solvent quality of both fractions; however, the effect was significantly larger for the higher boiling fraction. Increasing the temperature in microautoclave tests, up to 880°F , was found to increase the coal and IOM conversions with hydrotreated dewaxed V-1074. A significant portion of the organic matter rejected from the ROSE unit in the ash concentrate stream was found to be convertible to THF solubles.

TASK 2.1.2.2 PRETREATMENT / AGGLOMERATION - (CONSOL)

Agglomeration of an old sample of McKinley Mine coal (New Mexico) with No. 6 fuel oil resulted in about 25 wt % physical deashing.

A series of agglomeration runs was begun to optimize results with mine-cleaned Burning Star 2 Mine coal and Martin Lake Mine Texas lignite, and to explore the agglomeration potential of Kemmerer coal, a low-ash (3.7 wt % MF) subbituminous coal that we tested on a limited basis in previous work.

Agglomeration of the clean Burning Star 2 Mine coal gave 32 wt % physical ash rejection at several oil dosages and pHs, and 36 wt % ash rejection with a micronized feed; additional optimization is in progress. A repeat of the best agglomeration test in earlier work indicated that the current sample may not be as cleanable as the one used previously, which gave up to 41 wt % ash rejection.

An old sample of Kemmerer subbituminous coal gave an ash rejection of 30 wt % when agglomerated with No. 2 diesel fuel at ambient temperature, reducing the MF ash from 3.7 wt % in the feed to 2.1 wt % in the product (not corrected for ash-SO₃).

Results from recent Martin Lake Mine Texas lignite agglomeration tests will be presented in a future report, after completion of the ash analyses.

We conducted float/sink tests on three agglomeration feed coals (Martin Lake Mine lignite, Black Thunder Mine coal, Burning Star 2 Mine coal). The float/sink test method used is not strictly applicable to fine coal or to low-rank coal. Overall, the results indicate that agglomeration performed substantially better than the determined washability curve predicts for Burning Star 2 Mine coal and Martin Lake Mine lignite, and about the same as predicted for Black Thunder Mine coal.

TASK 2.1.3 SOLVENT PRETREATMENT (SANDIA)

A sample of overhead (tar) from the fluidized coker at CAER was hydrogenated in batch microautoclave tests. The hydrogen content of the tars increased from 7.9 wt% to 9.7 wt% and 10.2 wt% in two different tests. Proton NMR results indicated an increase in hydroaromatic nature of the tars. The samples were sent to CAER for liquefaction tests and will be sent to CONSOL for further characterization.

Liquefaction experiments performed at Sandia with Black Thunder Coal and Wilsonville Recycle Oil at low (1.5:1) solvent to coal ratios give coal conversion results that are lower than results from similar experiments performed at CONSOL. When solvent to coal ratios are raised to 2.3:1 the conversion discrepancies are significantly reduced. Presently, the discrepancies are thought to be due to gas-liquid mass transfer problems. Experiments will be performed to evaluate this hypothesis.

Results from liquefaction experiments with hydrotreated dewaxed heavy distillate substituted into the Wilsonville Recycle Oil increased coal conversions from 99% to 107% (conversion based on maf coal basis) for 30 minute runs at 415°C. Experiments performed at 415°C for 60 minutes showed that the combination of dewaxing and mild hydrotreatment of heavy distillate increased coal conversions, but more significantly increased the oil yield (as determined by pentane solubility) from 51% to 66%.

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS (UK/CAER)

Sulfated hematites and molybdenum, tungsten, cobalt, and nickel promoted sulfated hematites were produced by an aqueous precipitation technique. Synthesis involved adding the metal containing compound to a iron alum / urea solution. Molybdenum was added as ammonium molybdate, tungsten as ammonium tungstate, cobalt as the sulfate, and nickel as ammonium nickel sulfate. The addition of more than one promoter metal was also investigated through the use of combinations of these compounds. Using this technique the combinations of molybdenum with nickel, cobalt, and tungsten have been investigated. The promoter loading on the iron catalyst was controlled by varying the amount of compound added to the solution. Molybdenum

concentrations up to 10 wt %, with respect to iron, have been produced allowing the effect of molybdenum loading on the particle parameters to be evaluated.

Particles were analyzed using a variety of techniques, including XRD, BET nitrogen adsorption, SEM/TEM, and elemental analysis. The major phase for the as formed particles was identified as α -FeOOH (goethite) although traces of α -Fe were present. After calcination the particles were α -Fe₂O₃ (hematite) with some α -Fe being present. The average particle diameter was estimated to be 10-25 nm. The addition of promoter metals had no apparent effect on the phase of the iron oxide. The precipitated particles contained sulfur at 2-6 wt% loading and calcining had little effect of the absolute sulfur content. Sulfur may serve to inhibit the particle growth and agglomeration as well as increase the super acidity of the catalyst. The addition of molybdenum results in a decrease of sulfur on the catalyst. TEM micrographs showed that the particles exist as elongated cylinders of ~ 10 nm in diameter and ~ 50 nm in length. Figure 10 shows an example of the TEM micrograph of these particles.

Liquefaction of the Black Thunder subbituminous coal in tetralin was determined with these materials. The catalyst was added at an iron loading of 1 wt% with respect to maf coal. Sulfated hematite resulted in a substantial increase in total conversion with no substantial change in oil yield. The addition of 1 wt % molybdenum, which corresponds to a 100 ppm molybdenum loading, caused only a modest effect while increasing the promoter concentration to 5 wt% molybdenum (500 ppm on coal) increased conversion by 4%. At 1000 ppm molybdenum, conversion increased by 6% and oil yield by 14% compared to the sulfated hematite. Molybdenum promoted sulfated hematite displayed the highest activity and selectivity to oils of the single metal promoted catalysts.

Cobalt /molybdenum and tungsten/molybdenum promoted sulfated hematites demonstrated considerable catalytic activity. However, addition of 0.9 wt% molybdenum/0.7 wt% nickel resulted in marginally higher total conversion. More importantly, the selectivity to oils was higher than obtained for 5 wt% molybdenum on sulfated hematite. This indicates a synergistic effect between the nickel and molybdenum.

A kinetic model was developed based upon data developed in this program. Results at 415°C in both tetralin and full range Wilsonville Recycle Oil (WRO) were used to assess the model which comprises a series of ordinary, first order, linear differential equations to describe the reaction rates for five reactants and products: coal+IOM, PA+A, oils, carbon oxide gases, and hydrocarbon gases. In this model, IOM is converted to PA+A (k1), oils (k3) and CO_x(k5), and PA+A is converted to oils (k2) and both PA+A and oils are converted to HC gases (k4). An unreactive IOM fraction, I_ω, is included to define the IOM remaining at maximum coal conversion in a specific solvent at a particular reaction temperature.

Data taken at 7½, 15, 30, or 60 minutes were used to develop the simultaneous solution of this set of equations for which R² values were calculated.

In tetralin an R² value of 0.941 was obtained which was improved by using a I_ω value taken from the 60 minute IOM measurement. Using the I_ω value improved the fit giving an R² value of 0.994. The k1 rate constants obtained for an IW-impregnated Fe coal showed a 46% increase over a non-catalyzed case with smaller changes being observed in the other rate constants

In Wilsonville Recycle Oil (WRO) from Run 262 the best fit was obtained using an I_ω value of 7.9. This gave an R² of 0.977. Runs with 1.0 wt% added Fe as SFIO gave an R² value of 0.991. Since a portion of the IOM is immediately soluble in the WRO process solvent after 15 minutes at 300°C, the effect of adjusting the IOM and PA+A concentrations on the rate constants was determined. The biggest change was in the values of k2 and k3 which increase and decrease by 20%, respectively, along with a 5% increase in k1. The fit of the adjusted case appears to be little changed.

TASK 3.2 ECONOMIC EVALUATION (CONSOL)

We calculated the maximum possible yield of net product (gasoline containing 13.5% H) and the required hydrogen consumption for Black Thunder coal. Two cases were examined. In Case I, all oxygen is removed from the coal as CO₂. In Case II, all oxygen is removed as H₂O. The results, detailed in Table 8, show the maximum gasoline yield increases from 77.9% to 86.1% MAF in going from Case I to Case II. Hydrogen consumption simultaneously increases

from 5.8% to 9.3% MAF. The hydrogen efficiencies are 13.4 and 9.3, respectively.

Analysis of a V-107 ash concentrate sample from Period J of Wilsonville Run 263 was obtained and reported. The ash elemental composition supports the validity of the ash-SO₃ correction for the baseline economic assessment made by LDP Associates. The ash concentrate analysis also is discussed in relation to options for use of the liquefaction bottoms, such as deashing and/or recycling.

TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP ASSOCIATES)

A revision of the baseline economic assessment based upon Wilsonville 263J was completed to account for the change to an SO₃-free ash basis. The baseline provides a reference against which the results of the program will be compared. The revision was necessary since none of the material and elemental balances for Wilsonville subbituminous coal runs were done on a SO₃-free ash basis. Because of this it was necessary to revise the base case assessment which had been previously completed.

One important reason for revising the base case is the overstatement of maf coal conversion when using non-SO₃-free corrected ash balances. The revised conversion based on SO₃-free ash is 92.0% compared to 93.6% calculated earlier. New resid conversions for the 1st and 2nd stage reactors were determined to be 22.4% and 17.1% versus the earlier 23.2% and 17.6%, respectively.

The improved coal conversion case was recalculated on an SO₃-free ash basis. This case contains an increased coal conversion of 96.0% versus the earlier calculated 93.4%. Economic assessment of this change has a \$93.4 million capital advantage and a \$10.1 million/year operating cost advantage.

SECTION ONE

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

WORK PERFORMED

TASK 1.1 LABORATORY SUPPORT (UK/CAER)

Liquefaction in Dewaxed and Hydrotreated Dewaxed Solvent

Samples of both dewaxed and hydrotreated dewaxed samples received from Sandia were evaluated in coal liquefaction with Black Thunder coal using Wilsonville derived recycle oil from Run 262. In addition to liquefaction runs being made with the Run 262 heavy distillate, runs were made with hydrotreated Run 262 V-1074 heavy distillate, -5°C dewaxed V-1074 heavy distillate, and two samples of hydrotreated -5°C dewaxed V-1074 heavy distillate.

Reconstituted Solvents - Liquefaction runs were made using solvents reconstituted from the individual fractions produced at Wilsonville in Run 262 by substituting the above distillates for the V-1074 in the Run 262 reconstituted recycle oil. The solvents used in these runs were combinations of V-1082 ashy resid, V-130 deashed resid and V-1074 heavy distillate or a substitute using one of the -5°C dewaxed V-1074 heavy distillate derived materials. The composition of the Run 262 individual components and the reconstituted oil is shown in Table 1. All of these liquefaction feeds contained residual iron and molybdenum which accumulated in the recycle oil in Run 262. In that run the plant was adding 2 wt% iron oxide and 100 ppm molybdenum as Molyvan L. Since the iron and molybdenum was concentrated in the ashy resid and deashed resid fractions, concentrations in the composite solvents were all 1.7 wt% and 156 ppmw, respectively.

Solvents for each liquefaction run were separated into THF insolubles, THF soluble-pentane insolubles, and pentane solubles (Table 2). These included each component in the Wilsonville Run 262 recycle solvent, hydrotreated heavy distillate, -5°C dewaxed heavy distillate, and hydrotreated -5°C dewaxed heavy distillate. The THF insoluble IOM concentrations in dewaxed heavy distillate and the hydrotreated distillates were slightly higher than for the original V-1074 assuming the very small concentration of ash was removed during hydrotreating in the trickle-bed reactor.

Table 1. Wilsonville Run 262 Solvent Composition, wt%				
	Heavy Distillate V-1074	Deashed Resid V-130	Ashy Resid V-1082	Composite Solvent V-131B
Concentration	42.7	6.6	50.7	100
1050°F Distillate	100	16.0	2.5	43.8
Cresol Soluble Residue	0	83.9	58.8	36.6
Cresol Insolubles	0	0.01	18.3	9.2
Ash	0	0.11	20.4	10.4
Iron	not determined	100	3.3	1.7
Mo, ppmw	2	53	300 ^a	156 ^a
a. Calculated from component fraction analysis				

Table 2. Solvent Characterization of Wilsonville Run 262 Recycle Solvent Components

Solvent Separation Results		Oils	PA + A	IOM	Ash
Heavy Distillate	V-1074	95.91	0.74	3.09	0.26
Deashed Resid	V-130	63.51	32.63	3.43	0.43
Ashy Resid	V-1082	29.78	31.89	18.31	20.03
Hydrotreated Heavy Distillate		95.0	0.1	4.9 ^a	
-5°C Dewaxed Heavy Distillate		91.3	5.5	3.2 ^a	
Hydrotreated Dewaxed Heavy Distillate		93.6	0.8	5.6 ^a	
a. Sum of IOM plus Ash (Total THF Insolubles)					

Liquefaction Procedure - The liquefaction procedure and product analysis scheme are the same as those being used throughout this program. All runs were made using 3 g as-received coal, 5.4 g solvent, and 1000 psig H_2 cold, and were conducted in 50 mL microautoclaves at 415°C. SFIO was added, where noted, at a level equivalent to 1.8 wt% Fe_2O_3 on dry coal. Gaseous products were analyzed by gas chromatography and solid products were separated into THF insoluble (IOM), THF soluble-pentane insoluble (PA + A), and pentane soluble fractions. Added iron is presumed to convert to pyrrhotite ($Fe_{0.9}S$) and report to the ash fraction. Based upon the assumption of complete ash recovery, the oil values, which were calculated by difference, include water. The yield (or loss) of each fraction, on a SO_3 -free ash basis, is calculated by subtracting, for each fraction, the amount in the feed from the amount in the product, the sum of which equals the coal in the feed less moisture and SO_3 -free ash.

Liquefaction Results - The Wilsonville Run 262 recycle oil contained 8.3 wt% SO_3 -free ash, 11.3 wt% THF-insoluble organic matter (IOM), and 43.8 wt% 1050°F⁻ distillate. Iron and molybdenum concentrations in the feed coal slurry were 4.1 wt% Fe and 370 ppmw Mo on a dry coal basis. The iron is predominantly present as pyrrhotite while the molybdenum is presumably in the sulfide form.

The effect of these V-1074 dewaxed and hydrotreated dewaxed distillates on coal liquefaction were determined by substituting them for the 1050°F⁻ distillate fraction in WRO. Product distributions from both 30 and 60 minute liquefaction runs on as-received coal are compared with runs in which the recycle oil contained treated distillates (Table 3).

Oil yields and THF conversions (100-IOM) were higher by a sizable margin for each of the treated distillates compared to the base WRO distillate. Conversions for the 30 and 60 minute runs uniformly increased by 4-8% for each of the treated distillates relative to the untreated distillate. All of the hydrotreated samples had higher conversions at 30 minutes than the heavy distillate or the dewaxed heavy distillate.

Table 3. Product Distribution from Liquefaction of Wyodak Coal at 415°C
(wt% maf coal, SO₃-free ash basis)

	1050°F Distillate Source				
	WRO ^a	HT-WRO	DW-WRO	HT DW-WRO Sandia 20502 ^b	HT DW-WRO Sandia 20405 ^c
30 minute runs					
HC Gases	1.1	1.2	1.2	1.3	1.4
CO+CO ₂	5.0	5.1	4.8	5.1	4.7
Oils	34.3	53.1	41.5	51.0	42.8
PA+A	53.4	40.5	50.0	44.0	51.4
IOM	6.3	0	2.5	-1.5	-0.4
THF Conversion	93.7	100	97.5	101.5	100.4
mg H ₂ /g maf coal	42.7	43	42.1	44.4	56.2
Run Number	2-167-2	3-159-1	3-161-3	3-159-3	3-174-2
60 minute runs					
HC Gases	1.9	1.8	2.0	2.1	-
CO+CO ₂	5.0	5.6	5.5	5.7	-
Oils	48.9	62.5	57.5	63.4	-
PA+A	45.7	36.1	42.0	35.2	-
IOM	-1.4	-6.0	-7.0	-6.4	-
THF Conversion	101.4	106.0	107.0	106.4	-
mg H ₂ /g maf coal	56	51	48.9	48.2	-
Run Number	-	3-158-3	3-165-1	3-159-2	
a. WRO - Wilsonville Recycle Oil from Run 262 b. Hydrotreated in 1000 psig H ₂ . c. Hydrotreated in 1000 psig 1:1 H ₂ O/CO.					

At 60 minutes the conversions of all the treated distillates were comparable, all being higher than the untreated distillate.

At 30 minutes all of the treated solvents had higher oil yields than the Run 262 heavy distillate. The oil yields for the hydrogen-hydrotreated solvents were both significantly higher than for the CO/H₂O treated dewaxed solvent or the dewaxed solvent itself. The oil yields from the hydrotreated solvents had a margin over WRO at 30 minutes of 17-19% while at 60 minutes the range was 13-14%. The smaller differential for the dewaxed distillates of 8 and 9 wt% were observed versus WRO distillate at 30 and 60 minutes, respectively. The decrease in the differential between the 30 and 60 minute data at these longer residence times reflects the likely onset of retrogressive reactions.

Nanometer Iron Oxide Catalysts - In the Run 262 composite solvents, superfine iron oxide (SFIO) had been shown to be highly catalytic toward liquefaction. This is shown for 30 minute runs in Table 4 where the addition of SFIO equivalent to 1.8 wt% Fe₂O₃ increased conversion from 93.7 wt% to 99.5 wt%. Oil yields increased from 34.3 wt% to 42.9 wt%.

Addition of SFIO to each of the treated distillate runs resulted in higher conversion in three out of four of the cases than the SFIO WRO run. The exception was the 1000 psig H₂ hydrotreated dewaxed WRO which had a conversion comparable to the SFIO catalyzed WRO. Oil yields also were higher than the SFIO-WRO in three out of four of the cases. The exception was the dewaxed WRO which had an oil conversion slightly lower than for the base SFIO catalyzed WRO. Both of the hydrotreated dewaxed WRO samples had significantly higher oil yields with the water-gas shift hydrotreated dewaxed WRO increasing to 52.8 wt% relative to the base SFIO catalyzed case of 42.8%.

Comparing the results from addition of the SFIO in Table 4 with those without the added catalyst in Table 3 indicates the increase in yield by addition of SFIO is not quite as high as observed for the treated solvents without added SFIO except for the CO/H₂O hydrotreated dewaxed WRO. In this latter case the oil yield was 52.8 wt% versus the 42.8 wt% in the

absence of SFIO. Generally, THF conversion appears to have increased in the presence of the SFIO. Otherwise, oil yields in these modified distillates do not appear to be affected by catalysts.

Table 4. Effect of 1 wt% Fe as SFIO on Product Distribution, 30 min at 415°C
(wt% maf coal, SO₃-free ash basis)

	1050°F Distillate Source					
	WRO ^a no Fe	WRO	HT-WRO	DW-WRO	HT DW-WRO Sandia 20502 ^b	HT DW-WRO Sandia 20405 ^c
Fe, wt% ^d	0	1.0	1.0	1.0	1.0	1.0
HC Gases	1.1	1.7	1.7	1.9	1.6	2.1
CO+CO ₂	5.0	4.9	5.2	5.0	4.6	6.0
Oils	34.3	42.9	45.4	40.3	47.3	52.8
PA+A	53.4	50.0	53.9	57.1	46.9	44.7
IOM	6.3	0.5	-6.2	-4.2	-0.4	-5.6
THF Conversion	93.7	99.5	106.2	104.2	100.4	105.6
mg H ₂ /g maf coal	42.7	-	45.6	60.6	48.3	66.4
Run Number	2-167-2	3-074-1	3-168-1	3-173-3	3-160-4	3-173-4
a. WRO - Wilsonville Recycle Oil from Run 262 b. Hydrotreated in 1000 psig H ₂ . c. Hydrotreated in 1000 psig 1:1 H ₂ O/CO. d. Sulfur added as Dimethyldisulfide at S/Fe atomic ratio of 2.6-2.9/1.						

Task 2.1.1 CO PRETREATMENT (UK/CAER)

In continuation of our effort to demonstrate the effectiveness of CO pretreatment of coal, we report in this quarter further results from liquefaction experiments of pretreated and untreated coal. The effect of pretreatment time and CO/H₂ partial pressures were evaluated. In addition, a sample of Texas Lignite was pretreated under established reaction conditions and compared with previous results obtained from Clovis Point and Black Thunder Wyodak subbituminous coals. An evaluation and discussion on the chemistry of the water-gas shift reaction is also presented.

Effect of Process Variables on CO-Pretreatment

Limited studies on the effect of additional process variables were started during this period. Preliminary results are presented in this report.

Effect of Pretreatment Time - Pretreatment was examined at longer run times to determine the effect on the pretreated product. The reaction conditions were:

3.0 g Black Thunder coal (as received),
5.4 ml. of 0.33 M NaOH solution,
800 psig CO cold,
300°C,
30-90 min.

THF solubility of CO-pretreated product increased from 28% at 30 minutes to 36% at 90 minutes. The change in solubility after the initial 30 minutes decreases significantly. Additional results will be reported when they become available.

Effect of CO/H₂ Partial Pressure - In plant application, it may not be practical to use pure CO for the pretreatment process. Thus a study on the use of synthesis gas mixtures was performed. Substituting 100% of the initial CO partial pressure with H₂ reduced the recovery of water-insoluble product to 86.8% based on moisture and ash-free coal from the 89.7 wt% recovery

in 100% CO. A total of 4 wt% humic acids were produced in H₂ in addition to the 9.2 wt% oils+gases+water. THF solubility of the water-insoluble product also decreased in H₂ from 20% to 4%, with all of the solubles being pentane insoluble material in both cases.

Later data that are still incomplete indicate that the yield of water-insoluble product increases as the CO concentration in the synthesis gas increases. Improvement was observed both at 25% and 50% CO in H₂. It appears that the CO partial pressure must be at least 400 psig cold in order to obtain a reasonable THF solubility in the water-insoluble product and retard the humic acid formation.

CO-Pretreated Product Characterization

Morphology of Pretreated Coals - The maceral composition in Wyodak coal is predominantly huminite featuring remnant woody cell structures and layering (Figure 1a). Only minor changes in the coal structural morphology occurred for coals treated in the absence of CO in nitrogen (Figure 1b) or hydrogen. The particles retained their angular shapes similar to the original coal, but became ragged indicating some disintegration had occurred. In addition, some of the particles retained the botanical structures and layering features found in the original coal. Coal treated at 1.48 MPa CO in aqueous NaOH gives a product that is similar to that produced when nitrogen or hydrogen is used. Most of the coal particles retain their angular outlines but have developed rounded edges indicating some melting had occurred. Treatment at 2.86 MPa led to more extensive reaction of the huminite macerals (Figure 1c). A preponderance of large, rounded, porous particles are formed which retain none of the botanical structures and layering features found in the original coal. Finally, at 5.62 MPa CO, the huminite structure completely melts and agglomerates to form large, coherent, porous masses (Figure 1d). Some of the pores appear to be filled with a solid, homogeneous bitumen-like material that exhibits a low reflectance and is fluorescent under ultraviolet irradiation. Such optical properties are displayed by hydrogen-rich liptinite macerals in coal and kerogen. Under these conditions, the liptinite and, particularly, the inertinite macerals were relatively unaffected.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 1. All photomicrographs obtained in reflected white light at a magnification of 625X.

(a) Subbituminous coal with huminite (H) and liptinite (L) macerals indicated. Note the botanical structures in the larger huminite particle. Dark gray background is epoxy resin.

(b) Coal treated with 5.62 MPa nitrogen. Many coal particles retain distinct, angular outlines, occasionally observed with botanical structures (B), whereas others appear partially disintegrated (D).

(c) Coal treated with 2.86 MPa CO. Note rounded particles, often containing large pores (P).

(d) Coal treated with 5.62 MPa CO. Majority of coal has melted and agglomerated forming larger masses with numerous pores (P). Liptinite (L) and inertinite (I) macerals are essentially intact.

(e) Coal treated with 5.62 MPa CO without added base. Coal particle outlines are rounded, indicative of partial melting, although botanical (B) and layering features are still observed.

(f) Coal treated with 5.62 MPa CO with NaHCO_3 . Note areas with "smooth" (S) microtexture within material exhibiting a porous, specular appearance.

Although macropores are readily evident in the optical microscope, mercury porosimetry indicates the macropore volume almost disappeared, dropping from 0.67 cc/g in the starting coal to 0.03 cc/g in the pretreated product. Since the specimen preparation procedure for optical microscopy presents a cross section through the particles, many of the observed macropores may not be available to immediate intrusion by the mercury in the porosimetry evaluation. The three-fold increase in the mesopore volume of the CO-treated sample (0.096 cc/g) versus the raw coal (0.037 cc/g) may be a result of a breakthrough of the mercury into the inner particle void volume at the higher mercury pressures that appear as an increase in the mesopore volume. Nitrogen-BET measurements indicate that neither the original coal nor the pretreated water-insoluble materials showed any indication of microporous structure.

The absence of NaOH has a moderate effect on the reaction only in that less transformation appears to have occurred (Figure 1e). The particles become rounded and do not retain their angular shapes, but occasionally show some botanical structural and layering features. Treatment at 250°C indicates no significant structural changes have occurred. The product, which retained the original coal microstructure, comprises angular particles, similar in appearance to the residue produced at 300°C in nitrogen.

Na₂CO₃ produces a material that is ostensibly similar in appearance to that produced using NaOH. However, with NaHCO₃, the extent of melting and agglomeration varied; some areas were completely agglomerated, while others were melted and only loosely agglomerated (Figure 1f). The loosely agglomerated areas had a smooth microtexture which presumably was melted huminite, similar in appearance to the 2.86 MPa CO treated residue (Figure 1c), while other areas were porous-looking, similar to the high pressure CO reaction product (Figure 1d).

Reflectance Measurements - The mean reflectance of the water-insoluble products has been measured for each of the experiments under study and the results appear to be dependent on the degree of pretreatment (Table 5). Coals treated in the absence of CO or at low CO pressures have the highest reflectance while those treated at the highest CO pressures have the lowest values. In addition, the corresponding hydrogen to carbon atomic ratios of these pretreated

Table 5. Reflectance Data						
Pretreatment Conditions					R _o % ^a	H/C, atomic ratio ^b
Coal ^c	Gas	Pressure MPa	Temperature °C	Base		
BT	-	-	-	-	0.39	0.84
CP	-	-	-	-	0.40	0.83
CP	N ₂	5.62	300	NaOH	0.67	0.72
BT	H ₂	5.62	300	NaOH	0.65	0.78
CP	CO	1.48	300	NaOH	0.65	0.75
CP	CO	2.86	300	NaOH	0.58	0.83
CP	CO	5.62	300	NaOH	0.43	0.92
BT	CO	5.62	310	Na ₂ CO ₃	0.43	0.84
CP	CO	5.62	300	NaHCO ₃	0.47	0.81
BT	CO	5.62	300	NaHCO ₃	0.48	n.a. ^d
CP	CO	5.62	300	none	0.50	0.80
BT	CO	5.62	250	NaOH	0.45	0.75
BT	CO	5.62	310	NaOH	0.40	0.90
a. R _o is huminite reflectance in immersion oil. b. Water-insoluble product from Method A. c. BT - Black Thunder; CP - Clovis Point d. n.a. - not available						

materials decreases linearly with their increasing reflectance values (Figure 2). Not unexpectedly, the sample prepared at 250°C deviates the most from this correlation. Since all of these samples have similar oxygen concentrations, and their O/C contents are very similar, reflectance is obviously not related to oxygen content. This correlation is directionally in agreement with previous studies on coal liquefaction residues which showed that preferred product slates accompany residues having low reflectance.¹

Figure 4 - Reflectance of water-insoluble product versus H/C Ratio.

Liquefaction Results

Earlier it was shown that pretreating Wyodak coals from the Clovis Point and Black Thunder mines with CO/H₂ and base gave better conversion and product yields than the corresponding untreated coal.² Further, total hydrogen consumption from the gaseous and solvent phases were significantly reduced.

Derbyshire et al.³ showed that a thermally staged pretreatment at 350°C of subbituminous and bituminous coals in the presence of a dispersed sulfided Mo catalyst gave better conversions and product yields than untreated coal when liquefied at 425°C for 10 min. In this study, the effect of coal pretreatment in the absence of CO, i.e., N₂ and H₂, but in the presence of aqueous base is evaluated relative to its impact on liquefaction at 400°C for an hour in the presence of tetralin. The results are presented in Table 6.

The N₂/NaOH and 200 psig CO/NaOH pretreated coals both gave slightly lower THF conversions (ca. 5 wt%) than untreated coal. The higher conversion of the untreated coal versus the N₂ and 200 psig CO pretreated coal can be attributed almost exclusively to the differences in the CO+CO₂ yields. The PA+A and oil+water yields for the untreated and 200 psig CO pretreated coal are very similar. On the other hand, the N₂ pretreated coal gave larger (by ca. 10 wt%) PA+A yield and correspondingly smaller oil yield. More significantly, both pretreated coal reactions consumed more hydrogen during the reaction. This supports unequivocally the results presented in previous reports that thermally treated coals in the absence of a suitable hydrogen donor gave a product which has undergone undesirable retrogressive reactions. The material has become intractable and not conducive to hydrogenation under liquefaction conditions.

The conversion data calculated on raw coal is shown in Figure 3. The THF conversion values increase significantly relative to the raw coal. The oil values, which includes the oil+gas +water yield, also increase. The nitrogen pretreatment result on a parent coal basis is the same as the raw coal for both THF conversion and oil yield. The high CO pretreatment

Table 6. Liquefaction of Raw and CO Pretreated Clovis Point Wyodak Coal				
Reactant	Raw Coal	800 psig CO ^a	200 psig CO ^a	800 psig N ₂ ^a
Time, min	60	60	60	60
THF Conv, wt% maf coal	75	83	71	70
Products, wt% maf coal				
PA + A	43	42	44	52
Oils ^b	26	39	24	15
CO + CO ₂	5	2	2	2
HC Gases	0.3	0.6	0.5	0.5
H ₂ Gas Consumed ^c	17	18	29	30
Total Hydrogen Consumed ^d	32	26	42	42
a. Pretreated 60 min with 0.33 M NaOH at indicated initial pressure. Water-insoluble product. b. Includes water c. H ₂ Gas Consumed (mg/g maf coal) = $[H_{2\text{ in}} - H_{2\text{ out}}]/\text{coal}$; excludes H ₂ consumed from tetralin. d. Includes both gaseous hydrogen and hydrogen from tetralin.				

result clearly stands out relative to the raw coal result. Hydrogen consumption data shown in Figure 4 also show a clear cut advantage of the CO-pretreated coal over the raw coal, being 2.4 wt% versus 3.2 wt%, on an maf coal basis. This includes the hydrogen consumed from the tetralin solvent.

Comparable data from the catalyzed liquefaction of the CO-pretreated coal is shown in Figures 5 and 6. Both Shell 324 and Nanocat iron oxide show improved oil yield over the raw coal runs. As for the noncatalyzed cases, hydrogen consumption is also reduced for the pretreated case relative to the raw coal.

Figure 3

Liquefaction of Raw and (CO/NaOH)
Pretreated Coals at 400 °C with H₂/Tetralin

Figure 4

Hydrogen Consumption from the Reaction of Raw and Pretreated coal

Figure 6

Hydrogen Consumption from Reactions of Raw and Pretreated Coal

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS (UK/CAER)

Production, Characterization, and Testing of Promoted Sulfated Hematites

Introduction - A variety of iron based catalysts have been investigated and reported in the literature to possess varying degrees of catalytic activity⁴. It has been shown that, regardless of the phase of the precursor, in the presence of sufficient sulfur under liquefaction conditions iron based catalysts transform to a sulfide phase. A reduction in the size of the catalyst particles may increase activity due to the increased ratio of surface to internal iron available for reaction. However, the use of oil soluble precursors, such as iron pentacarbonyl, which start with a maximum dispersion, result in the rapid formation of fairly large crystallites, decreasing the dispersion and inhibiting the catalytic activity⁵. One study found that iron aerosols maintained a higher dispersion than the iron carbonyl precursor during coal liquefaction.

Another recent study related the hydrogenation activity of nanoscale iron based catalysts to the surface area, or diameter, of the particles⁶. Using iron carbide, iron sulfide, and iron oxide, this study also concluded that the factor limiting the conversion was bond cleavage rather than availability of labile hydrogen. Therefore, further increases in total conversion require the use of a catalyst with hydrocracking activity. While iron based catalysts are generally associated with hydrogenation, modifications by addition of promoter species may increase the cracking activity of these particles.

The production of sulfated iron oxides has been reported by several groups^{7,8}. These particles consist of sulfate groups chemisorbed on the surface of the iron oxide substrate, denoted as $\text{Fe}_2\text{O}_3 \cdot \text{SO}_4^{2-}$. The superacidity associated with the sulfate group on the surface of the particles may increase the cracking ability of the catalyst. Further, the presence of the sulfate may be responsible for the increased dispersion and reduction in growth and agglomeration of the particles during the reaction.

Sulfated iron oxides, produced by several techniques, have been reported to exhibit significant

catalytic effect for the liquefaction of coal and the coprocessing of coal with a Maya resid⁹. The addition of the promoter metals molybdenum and tungsten has been reported to further enhance the activity of the particles for the liquefaction of both bituminous and subbituminous coals.¹⁰ It has been reported that these particles maintain their high dispersion for long reaction times, even after conversion to pyrrhotite.

The use of various promoter metals in association with the sulfated hematites has been utilized in an attempt to increase the catalytic activity of the particles. The metals studied for this purpose include molybdenum, tungsten, cobalt, and nickel.

Production - The sulfated hematites and metal promoted sulfated hematites were produced by an aqueous precipitation technique. In this process 17.5 g of iron alum (ferric ammonium sulfate hydrate) and 25 g of urea were mixed in 500 ml of distilled deionized water. The solution was stirred and heated to $\sim 95^{\circ}\text{C}$ for ~ 2 hours. During this period the pH of the solution increased from ~ 2 to ~ 7 indicating completion of the reaction. The precipitate was separated by vacuum filtration, washed to remove unbound sulfate groups, and dried in an air flow oven at 100°C overnight. The particles were then vacuum dried at 70°C for 2 hrs. A muffle furnace was used to calcine the catalyst at 475°C for ~ 15 minutes.

The promoted sulfated hematites were produced by addition of a metal containing compound to the iron alum / urea solution. Molybdenum was added as ammonium molybdate. The promoter loading on the iron catalyst was controlled by varying the amount of compound added to the solution. Using this method molybdenum concentrations up to 10 wt %, with respect to iron, have been produced. This enabled the investigation of the effect of molybdenum loading on the particle parameters as well as the catalytic activity. Higher loadings are not considered to be economically viable and were therefore not produced.

Similarly, other metals may be added to the sulfated hematites. Tungsten was incorporated by addition of ammonium tungstate to the solution. The use of cobalt sulfate and ammonium nickel sulfate allowed the incorporation of cobalt and nickel into the catalyst, respectively. The

addition of more than one promoter metal was also investigated through the use of combinations of these compounds. Using this technique the combinations of molybdenum with nickel, cobalt, and tungsten have been investigated.

Characterization - The particles produced in this study were analyzed using a variety of techniques including XRD, BET nitrogen adsorption, SEM/TEM, and elemental analysis. The major phase of the particles as well as the average crystallite diameter were determined from XRD data. The major phase for the as formed particles was identified as α -FeOOH (goethite), although traces of α -Fe were present in most samples. As can be seen in Figure 7, the as formed particles showed poor crystallinity in the XRD pattern, making phase identification and particle diameter estimation difficult.

After calcination the XRD pattern of the particles was clearly identified as α -Fe₂O₃ (hematite) as shown in Figure 8, although some α -Fe was clearly present. The particle size of the calcined particles were estimated using a Debye-Scherrer relationship. The average particle diameter was estimated by this technique to be in the range of 10-25 nm. The addition of promoter metals had no apparent effect on the phase identified from XRD pattern. Similarly, little impact on the particle size estimated from XRD was observed as a function of promoter addition. These results are summarized in Table 7. As an example, the pattern for the nickel and molybdenum promoted sulfated hematite particles, shown in Figure 9, clearly indicate that all peaks correspond to either hematite or α -Fe.

Elemental analysis of the catalysts was used to determine the amount of sulfur associated with the particles. The precipitated particles contained sulfur at 2-6 wt% loading. Calcining the particles had little effect of the absolute sulfur content, although the concentration of sulfur rose slightly, reflecting the decrease in weight of the sample due to water loss during calcination. The effect of sulfur may serve to inhibit the particle growth and agglomeration as well as increase the superacidity of the catalyst. The addition of other metals results in a decrease of sulfur on the catalyst. It has been reported that, for similar

Figure 7. XRD Spectra of Uncalcined Catalyst, Goethite and Alpha Iron

Figure 8. XRD Spectra of Calcined Catalyst, Hematite and Alpha Iron

particles, the majority of the molybdenum is on the surface, thereby displacing the sulfur.⁷ This finding agrees well with the data obtained by elemental analysis which shows that the sulfur content decreases as the molybdenum concentration increases.

Table 7. Effect of Promoter Metal on Particle Phase and Size

Promoter	Major Phase	Diameter, nm
No Promoter	Hematite	19 $\pm$ 2
1 wt% Molybdenum	Hematite	14 $\pm$ 3
5 wt% Molybdenum	Hematite	21 $\pm$ 4
10 wt % Molybdenum	Hematite	21 $\pm$ 3
1.4 wt % Nickel	Hematite	14.2 $\pm$ 2
2.5 wt % Cobalt	Hematite	17 $\pm$ 4
4 wt % Tungsten	Hematite	18 $\pm$ 3

SEM micrographs of the particles show that they exist as a loose agglomeration of particles below the resolution of the machine (e.g. <50 nm). TEM micrographs were taken to determine the particle morphology and size. These pictures showed that the particles exist as elongated cylinders of ~ 10 nm in diameter and ~ 50 nm in length. Figure 10 shows an example of the TEM micrograph of these particles.

Nitrogen adsorption is being carried out to determine the surface area of the particles. Preliminary results indicate that the surface areas range from 100-200 m²/g. Since TEM indicates no porosity associated with these particles, the entire surface area should be available for reaction with the coal.

Figure 9. XRD Spectra of Mo/Ni Promoted Catalyst, Hematite and Alpha Iron

Figure 10. TEM Micrograph of Calcined Particles

The use of nickel, cobalt, and tungsten as promoter metals on the sulfated hematite was also investigated. The nickel and cobalt were not as easily attached to the sulfated hematite as the molybdenum and tungsten using this precipitation technique. For the calculated value of 5 wt% metal loading on iron, the nickel concentration, determined by elemental analysis, was only 1.4 wt %. Similarly, for the same calculated value, the cobalt concentration was measured at only 2.5 wt %. However, the molybdenum and tungsten showed the similar values for both calculated and measured metal concentration. This indicates that a portion of the nickel and cobalt were not incorporated in the catalyst and were removed with the filtrate and wash water.

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

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

The use of the sulfated hematite resulted in a substantial increase in total conversion over the blank thermal baseline run. The increase in conversion was due entirely to an increase in PA&A yield, as shown in Figure 11, with no substantial change in oil or gas yield. This conversion

compares favorably with the results obtained using the super fine iron oxide (SFIO) catalyst at similar iron loadings. This, despite the fact that the SFIO has smaller diameter (3 vs 19 nm) and higher surface area (190 vs 100 m²/g) than the sulfated hematite. The gas yield was unaffected by any of the catalysts utilized in this study.

The addition of 1 wt % molybdenum as a promoter metal to the sulfated hematite resulted in no significant increase in total conversion. However, as shown in Figure 12, there is a slight increase in selectivity to oils. The molybdenum concentration of 1 wt% with respect to iron corresponds to a 100 ppm molybdenum loading on an maf coal basis. At this low loading the effect of molybdenum is very modest.

Increasing the promoter concentration to 5 wt% molybdenum on iron results in a significant increase in total conversion to 92% compared to 88% for the sulfated hematite. Further, an increase in oil yield and a decrease in PA&A yield is also observed for this catalyst compared to the sulfated hematite. This indicates a significant improvement in the activity and selectivity of the sulfated hematite at a molybdenum loading of only 500 ppm on maf coal.

Increasing the promoter concentration to 10 wt% molybdenum on iron results in a further increase in both conversion and selectivity. As shown in Figure 13, the increase in total conversion results from an additional increase in oil yield and a decrease in PA&A yield. The net result of the 1000 ppm molybdenum on maf coal loading is an overall increase in total conversion of 6% and an increase in oil yield of 14% compared to the sulfated hematite. Figure 14 shows the effect of molybdenum concentration on the conversion of the Black Thunder coal in tetralin.

The addition of 1.4 wt % nickel on the sulfated hematite resulted in a slight increase in total conversion over the sulfated hematite. This increase was due entirely to an

Figure 11. Effect of 1 wt % Fe as Sulfated Hematite on Conversion

Figure 12. Effect of 1 wt% Mo Promoter on Conversion

Figure 13. Effect of 10 wt% Molybdenum on Conversion

Figure 14. Effect of Molybdenum Loading on Conversion

increase in PA&A yield as the oil yield remained constant, within experimental error, as shown in Figure 15. This represents the most significant increase in total conversion and the lowest selectivity to oils of each of the promoter metals, excluding molybdenum. The addition of 2.5 wt % cobalt resulted in negligible increase in total conversion compared to the sulfated hematite but a slight increase in oil yield. The effect of 4 wt % tungsten yielded the same results as the 2.5 wt % cobalt, within experimental error. This indicates that 500 ppm tungsten and 250 ppm cobalt on maf coal have very similar catalytic activity for coal liquefaction, while 140 ppm nickel on maf coal had slightly higher activity for total conversion but lower selectivity to oils.

The results of this study clearly indicate that the molybdenum promoted sulfated hematite displays the highest activity and also the greatest selectivity to oils. Further, both the activity and selectivity of the catalyst increase with increasing molybdenum concentration. However, due to the significant cost associated with molybdenum, a loading of 1000 ppm on maf coal would be prohibitively expensive. Therefore the use of other promoters in combination with the molybdenum was explored.

The use of a cobalt /molybdenum promoted sulfated hematite demonstrated considerable catalytic activity. As shown in Figure 16 the addition of 1 wt % molybdenum and 0.5 wt % cobalt to the sulfated hematite increased the total conversion substantially. The total conversion was close to that obtained with 5 wt% molybdenum, and greater than that obtained with 2.5 wt % cobalt on sulfated hematite. This appears to indicate a synergistic effect between the molybdenum and the cobalt promoters. The oil yield was increased to 40%, only slightly higher than the oil yield obtained for 1 wt % Mo. This indicates that at a promoter concentration of 100 ppm molybdenum and 50 ppm cobalt on maf coal, the activity of the catalyst for total conversion approaches that of 500 ppm molybdenum, although the selectivity to oils is somewhat lower.

Similar results were obtained for the combination of molybdenum with tungsten as promoter metals on sulfated hematite. The addition of 1 wt% molybdenum and 0.8 wt % tungsten

Figure 15. Effect of Various Promoter Metals on the Activity of Sulfated Hematite

Figure 16. Effect of Molybdenum and Cobalt on the Activity of Sulfated Hematite

resulted in an increase in total conversion to 92 % and an increase in oil yield to 40%. Figure 17 shows the comparison of this catalyst with the 5 wt% molybdenum and with 4 wt% tungsten on sulfated hematite. These results show the similar effect of cobalt and tungsten when added with molybdenum to the sulfated hematite.

The combination of nickel and molybdenum yielded somewhat better results. The use of 0.9 wt % molybdenum and 0.7 wt% nickel as promoters on sulfated hematite resulted in marginally higher total conversion compared to the cobalt/molybdenum and tungsten/molybdenum promoters shown previously. More importantly, however, is the fact that the selectivity to oils is higher for this sample than for the previous samples. As shown in Figure 18, the oil yield is higher than that obtained for 5 wt% molybdenum on sulfated hematite. This indicates a synergistic effect between the nickel and molybdenum which results in the high selectivity for oils. The combination of 90 ppm molybdenum, 70 ppm nickel, with 1 wt% iron on maf coal resulted in the highest selectivity to oils of the multi-promoted catalysts tested.

The promising results of these studies have prompted further interest in these catalysts. By varying the concentration of promoter metals it may be possible to obtain higher conversions or, more probably, to increase the selectivity to oils. Studies are currently underway to optimize the catalyst concentration to maximize catalytic activity and selectivity.

Figure 17. Effect of Molybdenum and Tungsten on the Activity of Sulfated Hematite

Figure 18. Effect of Molybdenum and Nickel on the Activity of Sulfated Hematite

Reaction Model Development

The decision to develop a simple kinetic model for coal liquefaction was made with four objectives in mind:

1. to better understand the reaction context and dynamics.
2. to allow a new, more comprehensive platform to compare experimental data.
3. to estimate the results of changes in reaction parameters across a narrow range.
4. to evaluate the relative effect of hydroliquefaction catalysts developed under this section.

Results at 415°C in both tetralin and full range Wilsonville Recycle Oil (WRO) were used to assess the suitability of the proposed model, with results at higher temperatures and energy of activation calculations to be presented in a subsequent report.

Model Structure

The structure of this model was influenced by other researchers in the coal liquefaction area, as well as by our own laboratory observations. As early as 1951, Weller¹¹ and his coworkers, working with bituminous coal anthraxylon (or vitrain) and with process derived asphalt, suggested that the following first order reaction sequence using broad product classifications could be useful in considering coal liquefaction reaction kinetics:

Their work also identified a "refractory organic material which is not liquefied, even at long reaction times." This quantity was accounted for in the rate equation by reducing the amount of moisture and ash free coal present at zero time.

Later, Curran et al.¹², working with a bituminous Pittsburgh seam coal and tetralin in the 324

to 440°C range, developed a rate expression for the dissolution of coal. The coal was dissolved by solvent extraction in air in batch microautoclaves. Conversion was measured by extracting the products with xylenol at 220°F. Here the authors identified three coal fractions: labile, refractory and unreactive. These were incorporated into a rate expression as shown below, where γ represents the fractional part of labile coal in the overall reactive portion of the coal and k_1 and k_2 are the corresponding rate constants for the labile and refractory portions of the coal.

$$C_T - C = \gamma C_T e^{-k_1 t} + (1 - \gamma) C_T e^{-k_2 t}$$

The unreactive fraction is implicit in the C_T term, which represents the ultimate possible conversion of the coal (in this case 91%).

In 1979, Brunson¹³, using data from a 50 lb/day integrated donor solvent pilot plant operating on Illinois No. 6 coal in the range of 370 to 480°C, developed a kinetic model in terms of an empirical classification of four reactive coal constituents: γ , α , β , ω . The first fraction, γ , converts instantaneously and is determined by carbonizing a sample of feed coal in a distillation procedure. The α and β fractions correspond roughly to typical preasphaltene and asphaltene fractions, while the ω fraction is unreactive. This last fraction includes ash and is determined by petrographic analysis of the coal.

Cronauer and Ruberto¹⁴, using Belle Ayr subbituminous coal at 400 to 470°C in hydrogenated anthracene oil (and in other oils) proposed the following kinetic model with six pseudo first order, irreversible rate constants:

This model is similar to others previously reported, except that gases and a portion of the asphaltenes are assumed to be formed directly from coal. This model also includes an unconvertible weight fraction of coal, C_{un} .

Pradhan, et al.,¹⁵ proposed a kinetic model to evaluate finely divided catalysts using Wyodak coal in tetralin. This model was similar to the one of Cronauer and Ruberto, but did not have as many lumped product fractions. Gases were not analyzed and were calculated by difference. While allowing both series and parallel conversion pathways to oils, they also incorporated parallel catalytic pathways. Again, an unreactive maf coal fraction was included for each temperature in a particular solvent.

A more detailed review of coal liquefaction modelling is found elsewhere¹⁶.

Kinetic Model - The model proposed here is similar to the one proposed by Cronauer and Ruberto with the following exceptions; the preasphaltenes and asphaltenes are treated collectively (PA+A), the carbon oxide gases (CO and CO₂) are assumed to be formed directly from the coal, and the hydrocarbon gases (CH₄ to C₂H₆) are formed from conversion of PA+A and oils together. As shown in Figure 19, IOM is converted to oils, PA+A and CO_x and its disappearance is proportional to rate constants k_1 , k_3 , and k_5 . Since PA+A is converted to other products it goes through a maximum. Its rate of formation is a function of k_1 and the concentration of IOM and its disappearance is proportional to rate constants k_2 and k_4 . Note that oils are formed from PA+A as well as directly from IOM. Hydrocarbon gases are formed from PA+A and oils and their concentration is proportional to rate constant, k_4 .

In the model presented here, an unreactive IOM fraction, I_w , is included which is defined by the IOM remaining at maximum coal conversion in a specific solvent at a particular reaction temperature. For example, I_w is a fixed value for reactions at 415°C in tetralin, regardless of the catalyst used, but is different for reactions in Run 262 Wilsonville Recycle Oil (WRO)

Figure 19

Coal Dissolution Kinetic Model

I_{ω} = unreactive coal fraction

at 415°C. Listed below are values of $I\omega$ for three reaction systems at 415°C.

Reaction systems	$I\omega$
Coal in tetralin, wt% maf coal	10.1
WRO without coal, wt% total feed	7.9
Coal in WRO, wt% maf coal	5.6

This parameter is important since it determines the agreement of the IOM model with the data at 60 minutes reaction time, which is about 8 half-lives with respect to the disappearance of IOM.

In short, the model will appear successful if it provides:

- ▶ Agreement with experimental data at short reaction times, since we have considered both labile and the more refractory IOM fractions as one.
- ▶ Agreement with gas yield data.
- ▶ Good agreement with experimental yields in general, in view of considering each fraction, regardless of source (e.g., PA+A freshly derived from coal and that exposed to severe hydroliquefaction conditions), as having the same reactivity.

Treatment of Data - Using the kinetic model shown in Figure 19, a system of ordinary, first order, linear differential equations was formulated to describe the reaction rates for five reactants and products: IOM, PA+A, oils, hydrocarbon gases, and CO+CO₂. Each reaction step is irreversible and assumed to be first order with respect to reactant concentration. The concentration of each reactant as a function of time is provided through integration and

rearrangement of these five rate equations. Each of these five equations is thus one component of the model for the overall system. An example of one of these individual product fraction equations in the model is the one for IOM, which is a function of k_1 , k_3 , and k_5 , but not k_2 or k_4 . Using the outcome of a liquefaction experiments conducted for a series of prescribed times (e.g., 7½, 15, 30, or 60 minutes), simultaneous solution of this set of equations yields a set of rate constants, $k_1 \dots k_5$.

Ideally, in the absence of experimental error and with a perfect model, each experiment would provide the same value of $k_1 \dots k_5$. However, in practice the k 's vary, and each time period yields k 's that fit a particular time period best. A constrained non-linear regression analysis was used to minimize the residual sum of squares (RSS), which were the sum of residuals squared $(Y_{\text{model}} - Y_{\text{exp}})^2$ for each individual product fraction, to give the best overall fit. Total residuals were considered at a minimum when any individual element of the model began to fit poorly, for example, if a "multiple correlation coefficient squared value" began to deviate below 0.85 (the "constraint"). This was required since the minimum RSS value was found without regard to the smaller gas fractions, which do not contribute much to the overall "total sum of squares".

The "multiple correlation coefficient squared value" of the model, or R^2 , was calculated as one minus the ratio of the "sum of the residuals squared" to the "total sum of squares". This value indicates the deviation about the mean which can be accounted for by the kinetic model. Initial concentrations of each reactant/product are included in this calculation, since the fit of the model to the initial conditions is an important aspect of the overall model correlation.

Results

Liquefaction in Tetralin - Table 8 shows the results of coal liquefaction experiments at 415°C using Black Thunder coal in tetralin without any added catalyst or sulfur.

- .. Experiments were conducted at 7½, 15, 30 and 60 minutes. Figure 20a shows the results of a regression analysis of the data for both IOM and PA + A concentrations as a function of

time. The PA+A model provides good agreement with the experimental data. However, the IOM model does not provide a good fit to the short run-time data. Further, I_w is somewhat low for thermal runs without catalyst, which is apparent in the 60 minute conversion data. However, the overall R^2 value for the model is 0.941, indicating good agreement for all fractions. Predicted and experimental values for oils are shown in Figure 20b, while the corresponding data for CO+CO₂ and HC gases are given in Figure 20c.

Table 8. Thermal Liquefaction of Black Thunder Coal in Tetralin ^a Products of Reaction				
Reaction temp, °C	415	415	415	415
Reaction time, min	7.5	15	30	60
Catalyst added	none	none	none	none
Products, wt% maf Coal				
HC Gases	0.3	0.4	0.7	1.0
CO+CO ₂	3.9	4.2	4.4	4.9
Oils	21.7	20.7	28.0	43.4
PA+A	28.2	41.0	43.6	35.8
IOM	45.9	33.7	23.3	14.9
THF Conv	54.1	66.3	76.7	85.1
mg H ₂ /g maf Coal	31.3	30.0	28.0	36.2
Run number	3-76-1	2-154-2	2-154-1	2-160-2
a. 3 g Black Thunder coal, 5.4 g tetralin, 6.89 MPa H ₂ cold.				

Liquefaction results on a 0.77 wt% iron incipient-wetness impregnated as-received coal, that were run under the same conditions as the thermal case in Table 8, are shown in Table 9. The liquefaction results with this impregnated coal were improved over the coal itself, as was

Figure 20a

IOM and PA + A yields from liquefaction of Black Thunder Coal in tetralin at 415°C

Rate constants, 1/min

$$k_1 \cdot 1000 = 50.278$$

$$k_2 \cdot 1000 = 8.3$$

$$k_3 \cdot 1000 = 22.826$$

$$k_4 \cdot 1000 = 0.336$$

$$k_5 \cdot 1000 = 4.477$$

RSquared = 0.941

IOM and PA + A yields (wt% maf coal) from thermal liquefaction of Black Thunder Coal in tetralin at 415 C, versus time.

Figure 20b

Oil yield from liquefaction of Black Thunder Coal in tetralin at 415°C

Figure 20c

Gas yield from liquefaction of Black Thunder Coal in tetralin at 415°C

discussed previously.¹⁷ A model was developed using a I_w value taken from the 60 minute IOM value. The overall fit of the model is much improved over the first case discussed above having an overall R^2 of 0.994. The fit of the data to the model are shown in Figure 21. In Figure 21a the fit of the IOM is quite good at 60 minutes with the 30 minute data showing some departure. Oil yields are excellent with PA+A deviating at 30 minutes. The data for gases shown in Figure 21b are in good agreement with the experimental data.

Table 9. Fe Catalyzed Liquefaction of Black Thunder Coal at 415°C in Tetralin ^a Products of Reaction			
Reaction time, min	15	30	60
Added Fe, wt% dry Coal ^b	0.77	0.77	0.77
Added S, wt% dry Coal	1.62	1.63	1.64
S/Added Fe, m/m	3.69	3.69	3.71
Products, wt% maf Coal			
HC Gases	0.8	1.1	1.3
CO+CO ₂	3.3	3.4	3.4
Oils	18.6	28.5	38.9
PA+A	49.4	48.6	46.1
IOM	27.9	18.4	10.3
THF Conv	72.1	81.6	89.7
mg H ₂ /g maf Coal	37.3	39.6	44.6
Run number	2-226-1	2-227-1	2-226-2
a. 3 g Black Thunder coal, 5.4 g tetralin, 6.89 MPa H ₂ cold. b. 0.77 wt% Fe in FeOOH, prepared by incipient wetness/ precipitation.			

Comparing the rate constants for the thermal and the IW-impregnated Fe coal showed a 46% increase for the value for k_1 for the IW-impregnated Fe coal (see Table 10), while much smaller changes were observed in the other rate constants, which may be an artifact of the curve fitting procedure.

Figure 21a

IOM, PA+A and oil yields from liquefaction of IW-impregnated
Fe on Black Thunder Coal in tetralin at 415°C

Rate constants, 1/min

$k_1 \cdot 1000 = 73.234$
 $k_2 \cdot 1000 = 6.979$
 $k_3 \cdot 1000 = 23.694$
 $k_4 \cdot 1000 = 0.432$
 $k_5 \cdot 1000 = 4.491$

— IOM model
 □ IOM
 — Oils model
 ◇ Oils
 — PA + A model
 × PA + A

Figure 21b

Gas yields from liquefaction of IW-impregnated
Fe on Black Thunder Coal in tetralin at 415°C

RSquared = 0.994

— CO/CO2 model
 □ CO/CO2
 — HC gas model
 + HC gases

Conversion of Wilsonville Recycle Oil - The model has been applied to liquefaction of coal in Wilsonville Recycle Oil (WRO) taken from Run 262 when running with Black Thunder coal. Both iron oxide and Molyvan L were added at Wilsonville during the run. First, the reactivity of the WRO under liquefaction conditions in the absence of coal and any added catalysts was determined. Data for reactions conducted for 3¼, 7½, 15, 30, and 60 minutes are shown in Table 11.

Table 10. Summary of Rate Constants ^a k x 1000, min ⁻¹		
	Thermal/ tetralin	0.77% IW Fe/ tetralin
k1	50.3	73.2
k2	8.30	6.98
k3	22.8	23.7
k4	0.34	0.43
k5	4.48	4.49
I _ω	10.1	10.1
a. k's were calculated from regression analysis.		

A model was developed for reaction of the WRO in the absence of coal. Figure 22 shows the experimental data as it compares with the model. Since the initial conversion of the IOM reaches 23% within 3¼ minutes and increases further to only 33% after 60 minutes, this model fails to provide a good fit to the IOM plot shown in Figure 22a. Likewise, the model fails to accurately describe the behavior of the PA+A fraction. In fact, the actual data passes through a minimum rather than a maximum as predicted by the model. Oppositely, the oils model predicts a steady increase, as seen in Figure 22b, rather than the observed rapid increase followed by the subsequent decrease after 10 to 15 minutes, presumably via retrogressive reactions. There is, however, good agreement between predicted values and actual concentrations of the gas fractions as shown in Figure 22c. Note here that CO and CO₂

approach their final concentration (0.07% maf WRO) at the shortest reaction time. However, the uniform though small hydrogen consumption over this entire range of reaction times indicates that hydrogen consumption occurs at the shortest times and then fails to increase any further. Overall, the model provides a very poor fit to the observed concentrations of the various fractions, which means that it fails to describe the reactions that are occurring here.

Table 11. Thermal Liquefaction of WRO at 415°C ^a						
Reaction time, min	-	3¼	7½	15	30	60
	Reactants	Products	Products	Products	Products	Products
wt% maf WRO						
HC Gases	0.0	0.03	0.04	0.09	0.15	0.31
CO+CO ₂	0.0	0.07	0.06	0.07	0.10	0.07
Oils	67.2	72.7	74.5	74.7	72.8	69.7
PA+A	20.8	17.9	16.4	16.4	18.2	21.8
IOM	12.1	9.3	9.0	8.7	8.8	8.1
THF Conv	87.9	90.7	91.0	91.3	91.2	91.9
mg H ₂ /g maf WRO	-	10.2	9.0	12.3	11.7	12.8
% IOM Conversion	-	23.3	25.2	28.1	27.4	32.7
Run number		3-188-2	3-188-1	3-188-3	2-155-2	2-140-1
a. No coal, 5.4 g WRO, 6.89 MPa H ₂ cold.						

The very rapid IOM conversion at these short reaction times suggests that these changes are not related to conversion of coal macerals, but appear to be related to a rapid solubilization of a significant portion of the IOM fraction of the WRO. This transformation does not appear to be related to hydroliquefaction. In order to determine whether this phenomena is a mere resolubilization of predissolved coal macerals, tests were run at lower temperatures for 15 min in N₂ and H₂ and compared with results at 415°C (see Table 12).

Figure 22a

IOM and PA+A yields from heating WRO at 415°C

$$k1 = 49.6$$

$$k2 = 9.656$$

$$k3 = 0.192$$

$$k4 = 0.054$$

$$k5 = 1.556$$

Figure 22b

Oil yield from heating WRO at 415°C

Figure 22c
Gases yield from heating WRO at 415°C

IOM decreased in nitrogen at 300°C, almost to the same extent as in hydrogen at 415°C, which was discussed above. In hydrogen at 300°C the IOM remaining at 300°C was the same as observed at the higher temperature. The only difference in these two runs was a higher oil yield at the higher temperature. There was also a slightly higher oil yield in hydrogen versus nitrogen at the lower temperature.

Table 12. Thermal Liquefaction of WRO at 15 minutes ^a				
Gas	-	H2	N2	H2
Temperature, °C		300	300	415
	Reactants	Products	Products	Products
wt% maf WRO				
Gases	0.0	0.02	0.04	0.15
Oils	67.2	71.0	68.3	74.7
PA+A	20.8	20.0	22.0	16.4
IOM	12.1	9.0	9.7	8.8
Run number		3-189-1	3-200-1	3-188-3
a. No coal, 5.4 g WRO, 6.89 MPa gas cold.				

Conversion of Coal in WRO - Results from coal liquefaction in the absence of any added catalysts in Wilsonville Recycle Oil from Run 262 are presented in Table 13. As mentioned previously, the concentrations of iron and molybdenum in the ashy resid were quite high. The concentration of iron was 4.4 wt% maf coal and the concentration of molybdenum was 404 mg/kg maf coal. The best fit using the model with an $I\omega$ value of 7.9 was determined and is compared with the experimental data (see Figure 23). It is apparent that the mixture of coal and WRO provides good agreement with the experimental data for IOM, PA+A and oils as shown in Figure 23a. R^2 was calculated to be 0.977. The model provides a good fit for the gas fractions as shown in Figure 23b.

Table 13. Thermal Liquefaction of Black Thunder Coal in WRO^a

	Reactants	Products	Net Coal Yield ^b	Reactants	Products	Net Coal Yield ^b	Reactants	Products	Net Coal Yield ^b
Reaction Time, min	-	15	15	-	30	30	-	60	60
Wt% maf mixture/ (Coal)									
HC Gases	0.0	0.2	(0.5)	0	0.3	(1.1)	0	0.61	(1.9)
CO+CO ₂	0.0	1.4	(4.5)	0	1.5	(5.0)	0	1.5	(5.0)
Oils	46.3	52.9	(21.3)	46.5	57.7	(36.4)	46.6	62.3	(51.3)
PA + A	14.3	32.2	(57.6)	14.4	31.7	(56.2)	14.4	29.2	(48.4)
IOM	39.4	13.3	(16.1)	39.2	8.7	(1.3)	39.0	6.4	(-6.6)
Total	100.0	100.0	(100.0)	100.0	100.0	(100.0)	100.0	100.0	(100.0)
THF Conv	60.6	86.7	(83.9)	60.8	91.3	(98.7)	61.0	93.6	(106.6)
Run number	2-148-2	2-148-2	2-148-2	2-167-2	2-167-2	2-167-2	2139-1 2167-1 2337-1	2139-1 2167-1 2337-1	2139-1 2167-1 2337-1

a. 415°C, 3 g Black Thunder coal, 5.4 g WRO, 6.89 MPa H₂ cold. No catalyst or sulfur added.

b. [Fraction, wt%] = 100 x [Wt. Fraction in Product - Wt. Fraction in feed]/[Wt. Coal, maf]

Figure 23a

IOM, PA+A and oil yields from liquefaction of Black Thunder coal in WRO at 415°C

Rate constants, 1/min

$$\begin{aligned} k_1 \cdot 1000 &= 55.835 \\ k_2 \cdot 1000 &= 4.023 \\ k_3 \cdot 1000 &= 22.751 \\ k_4 \cdot 1000 &= 0.124 \\ k_5 \cdot 1000 &= 4.225 \end{aligned}$$

— IOM model
□ IOM
— Oils model
◇ Oils
— PA + A model
× PA + A

Figure 23b

Gases yields from liquefaction of Black Thunder coal in WRO at 415°C

RSquared = 0.977

Data on liquefaction of Black Thunder coal with added catalyst are summarized in Table 14. In these runs 1.0 wt% Fe contained in superfine iron oxide (SFIO) on as-received coal in WRO to which was added 2.6 mol S/mol Fe as DMDS. At 60 minutes, total conversion is 1.3% higher and oils yield is 5.4% higher on an maf coal basis than in the case without added SFIO and sulfur. These experimental data provide an excellent fit to the model as shown in Figure 24 giving an R^2 value of 0.991.

Adjustment of Solubility Fractions

Since a portion of the IOM is immediately soluble in the process solvent at reaction temperature, the IOM and PA + A concentrations in the starting material were adjusted to reflect this change. IOM concentration in the starting solvent was adjusted downward to a level based upon the final IOM concentration observed in nitrogen after 15 minutes at 300°C. PA + A was adjusted upward by an equal amount. Rate constants for the thermal liquefaction of Black Thunder coal in WRO were determined based upon this revised feed composition. From these values, corresponding values providing a best fit were calculated. The experimentally observed values are shown in Figure 25 along with the k values providing the best fit.

The revised k values versus the unadjusted case are shown in Table 15. The biggest changes are in the values of k_2 and k_3 which increase and decrease by 20%, respectively. By increasing the initial concentration of PA + A the corresponding rate of disappearance of PA + A, k_2 , decreases. An explanation for the decrease in k_3 is less straightforward but may be intertwined with the apparent shift of oils formation through the PA + A fraction. The 5% increase in k_1 reflects the lower initial IOM conversion. The fit of the IOM data in the adjusted case in Figure 25a appears to be little changed from the earlier case in Figure 23a. There does, however, appear to be a slightly better fit of the PA + A and oils in the adjusted case in Figure 25a versus the non-adjusted case in Figure 23a.

Table 14. Liquefaction of Black Thunder Coal with SFIO in WRO^a

	Reactants	Products	Net Coal Yield ^b	Reactants	Products	Net Coal Yield ^b	Reactants	Products	Net Coal Yield ^b
Reaction Time, min		15			30			60	
Catalyst Added		SFIO			SFIO			SFIO	
Added Fe, wt% Coal		1.0			1.0			1.0	
Added S, wt% Coal		1.5			1.5			1.6	
S/Added Fe m/m		2.6			2.6			2.7	
Wt% maf mixture/(Coal)									
HC Gases	0.0	0.4	(1.2)	0.0	0.5	(1.7)	0.0	0.4	(1.2)
CO+CO ₂	0.0	1.3	(4.1)	0.0	1.5	(4.9)	0.0	1.6	(5.0)
Oils	46.2	55.5	(29.7)	46.2	60.3	(45.1)	46.4	63.9	(56.7)
PA+A	14.3	31.3	(54.4)	14.3	30.7	(52.6)	14.3	28.3	(45.0)
IOM	39.5	11.6	(10.6)	39.5	7.0	(-4.3)	39.3	5.8	(-7.9)
Total	100.0	100.0	(100.0)	100.0	100.0	(100.0)	100.0	100.0	(100.0)
THF Conv	60.5	88.4	(89.4)	60.5	93.0	(104.3)	60.7	94.2	(107.9)
Run number	3-74-2	3-74-2	3-74-2	3-74-1	3-74-1	3-74-1	2-272-1	2-272-1	2-272-1

a. 415°C, 3 g Black Thunder coal, 5.4 g WRO, 6.89 MPa H₂ cold.

b. [Fraction, wt%] = 100 x [Wt. Fraction in Product - Wt. Fraction in feed]/[Wt. Coal, maf]

Figure 24a

IOM, PA+A and oil yields from liquefaction of Black Thunder coal in WRO at 415°C with 1.3 wt% Fe in SFIO

Rate constants, 1/min

$k_1 \cdot 1000 = 66.181$
 $k_2 \cdot 1000 = 5.755$
 $k_3 \cdot 1000 = 24.071$
 $k_4 \cdot 1000 = 0.09$
 $k_5 \cdot 1000 = 5.282$

— IOM model
 □ IOM
 — Oils model
 ◇ Oils
 — PA + A model
 × PA + A

Figure 24b

Gases yields from liquefaction of Black Thunder coal in WRO at 415°C with 1.3 wt% Fe in SFIO

RSquared = 0.991

Table 15. IOM Adjusted Rate Constants ^a k x 1000, min ⁻¹		
	Thermal/ WRO	
	IOM Non-Adjusted	IOM Adjusted
k1	55.8	58.6
k2	4.02	4.8
k3	22.8	18.2
k4	0.12	0.12
k5	4.2	4.3
I _ω	5.6	5.6
a. k's were calculated from regression analysis.		

Overview

Each of the rate constants is summarized in Table 16. In going from tetralin to WRO, the values for k1 increases from $50 \times 10^{-3} \text{ min}^{-1}$ to $56 \times 10^{-3} \text{ min}^{-1}$, which may be, in part, a response of the model to account for the rapid solubilization of the portion of the WRO IOM that was found to dissolve, even at temperatures as low as 300°C. With added SFIO, k1 further increases to $66 \times 10^{-3} \text{ min}^{-1}$, which reflects a catalytic effect on the conversion of the coal macerals, since the WRO IOM is not particularly affected by the SFIO.

Also, k2 is 43% higher in WRO for the SFIO catalyzed reaction. Interestingly, k3 (for direct conversion of IOM to oils) is not only about the same for coal liquefaction in WRO, but is also about the same value for all reaction systems. It also appears to be an important pathway for the production of oils. The rate constant for hydrocarbon gas production, k4, decreased significantly moving from the tetralin to the WRO system. This was primarily the result of the diluting effect of the PA+A and oils added in the WRO which did not produce as much gas as did the freshly formed PA+A and oils formed from the coal in the tetralin reaction system. Finally, the rate constant for CO and CO₂ production remained about the same for all reaction systems.

In both tetralin and WRO, k_1 increased upon addition of iron. In tetralin, the k_3 value for the IW-impregnated Fe case increased by 45% over the base thermal case while in WRO the addition of particulate SFIO resulted in an 18% increase over the base thermal case. This is strong evidence for the catalytic effect of iron on the dissolution step, whereas the influence on the k_2 value is not consistent in both of these systems.

Table 16. Summary of Rate Constants ^a k x 1000, min ⁻¹				
	Thermal/ tetralin	.77% IW Fe/ tetralin	Thermal/ WRO	1.3% Fe in SFIO/ WRO
k ₁	50.3	73.2	55.8	66.2
k ₂	8.30	6.98	4.02	5.76
k ₃	22.8	23.7	22.8	24.1
k ₄	0.34	0.43	0.12	0.09
k ₅	4.48	4.49	4.23	5.28
I _ω	10.1	10.1	5.6	5.6
a. k's were calculated from regression analysis.				

Figure 25a

IOM, PA+A and oil yields from liquefaction of Black Thunder coal in WRO at 415°C

Modified for WRO IOM partial solubility

Figure 25b

Gases yields from liquefaction of Black Thunder coal in WRO at 415°C

Modified for WRO IOM partial solubility

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SECTION TWO

CONSOL, INC

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

TASK 1.2 - LABORATORY SUPPORT (CONSOL)

Summary

The V-131B pasting solvent from Wilsonville Run 258K was chosen as the source of Mo-free ashy resid material for future work. A sample of this material was received and distilled at 1025 °F atmospheric equivalent end point to obtain the ashy resid sample.

Samples of Burning Star No. 2 Mine (Illinois 6) coal, and Martin Lake Mine (Texas lignite) were received and analyzed. The Burning Star No. 2 Mine coal appears to be typical. The Martin Lake Mine lignite is lower in ash content than our previous sample. Both coals were distributed to the other program participants.

Lignite-derived process liquids (Wilsonville Run 255) were obtained and pertinent samples of these were selected for use in this project.

Project participants were provided with Wilsonville's description of the ash-SO₃ correction method applied to Run 246. Wilsonville did not correct for ash SO₃ in any subsequent run.

Discussion

The need for a Mo-free ashy recycle solvent as the baseline solvent for this project was discussed at the Quarterly Project Review Meeting in Albuquerque on March 25-26. We considered two candidate materials produced from Black Thunder Mine coal.

Candidate oil A is the end-of-run inventory of V-1067 oil from Wilsonville Run 260 (sample dated 11/14/90). Approximately three-fourths of one drum of this material is available at CONSOL; two gallons were sent to CAER previously. V-1067 is the bottoms stream from the atmospheric flash. It is fed to the vacuum distillation tower from which the recycled heavy distillate, the ashy resid (feed to deasher), and deashed resid (i.e., all the components of the recycle solvent) are derived. During Run 260, three periods of thermal/catalytic, high/low

temperature operation were followed by three periods of catalytic/thermal, low/high temperature operation. In Table 1 discussed below, the previously analyzed V-1067 solvent from period 260F is used as a surrogate for candidate oil A.

Candidate oil B is the V-131B recycle solvent from Wilsonville Run 258, period K (dated 10/25/89). Approximately four drums of this material is available at CAER. Run 258 was operated in the thermal/catalytic mode at a high/low temperature sequence. The V-131B has all the recycle components blended together in the appropriate proportions for period 258K.

We recommend that candidate oil B be used as the Mo-free oil for this project. The 1050 °F⁺ content of the solvent (requested by Ed Givens) is listed in Table 1; note, however, that this is based on the blend specification, and not the actual analysis. The actual 1050 °F⁺ content of the solvent may be available from Wilsonville.

A comparison (see Table 1) was made of the properties of the V-131B recycle solvent from period 263J (the period to be simulated), candidate oil A, and candidate oil B. We used recent analyses of the oils, or analyses on file for oils from adjacent periods in cases for which no sample was readily available for analysis. Many of the properties of candidate oil B are similar to those of the 263J recycle solvent. Relative to candidate oil A, the 263J recycle solvent and candidate oil B contain more 850 °F⁻ distillate, slightly less THF-soluble resid, lower concentrations of phenolic -OH, they are more aromatic, and they have significantly higher donor solvent qualities as measured by a standard test. However, candidate oil B and the 263J recycle solvent differ in a few significant areas: the 263J oil contains 2 wt % more ash than does candidate B, which also gives the 263J oil 2 wt % more total insolubles (21 wt % vs 19 wt %); the 263J oil is slightly less aromatic, and is more paraffinic than candidate B; and candidate oil B may have a significantly higher donor solvent quality index than the 263J oil (89.1 vs 77.1 for the distillate-only test; the whole candidate B oil gave 76.9; the whole 263J oil was not tested).

Also included in this table for comparison is V-131B recycle solvent data for periods D and E of Wilsonville Run 262. Our current Mo-containing baseline

recycle oil is blended from individual Run 262 components from 9/16/91, which fell between periods D and E but was operated at period E conditions. Relative to the desired 263J V-131B simulated solvent, our current solvent is low in aromaticity, high in paraffinicity, and low in donor solvent quality.

We received one gallon of V-131B Mb-free recycle solvent from Wilsonville Run 258K from UK/CAER. Approximately 1700 g of this sample was distilled at 320°C and 2 torr (1025 °F atmospheric pressure equivalent) to produce a Mb-free simulated V-1082 ashy resid sample. Under these conditions, 34.8 wt % of the V-131B material was collected as distillate and 64.9 wt % remained in the distillation pot as 1025 °F⁺ resid. The overall material balance was 99.7 wt %.

We received Amoco's entire inventory of oils from Wilsonville Run 255. We selected materials from this inventory that are appropriate for use in this project as lignite-derived oils and will composite these to make a master batch for the project when we know the quantity of sample required by CAER and Sandia.

We received 15 gal of Burning Star 2 Mine coal from HRI to replace the atypical sample they previously sent. The new Burning Star 2 Mine coal sample was riffled and sealed under partial vacuum in triple-layer bags. The Martin Lake Mine Texas lignite sample received last quarter was air-dried, ground to -100 mesh, riffled, and sealed in triple-layer bags under partial vacuum. A 20 lb sample of Black Thunder Mine coal and 8 lb each of Burning Star 2 Mine coal and Martin Lake Texas lignite were shipped to Ed Givens at UK/CAER. The chemical analyses of the Burning Star coal and Texas lignite are shown in Table 2. The Burning Star 2 Mine coal appears to be a typical plant product. The new sample of Martin Lake Mine lignite contains less ash than anticipated (8.4 wt % vs 13.3 wt % MF SO₃-free in the previous sample). Four triple-layer bags, 25 g each, of both; Burning Star No.2 coal and Texas lignite were prepared for shipment to Sandia.

Sandia's original sample of Black Thunder Mine coal (~1 lb) was divided into ~50 g portions and repackaged by CONSOL as requested by R. Kottenstette. This material was returned to Sandia.

We were informed of Sandia's alternative feedstock requirements, and are awaiting similar information from CAER.

We informed project participants that Wilsonville performed no ash-SO₃ corrections after Run 246. We described the correction and its effects when Wilsonville applied it to their Run 246 results (see Task 3.2). Information provided to project participants is included as Appendix 1.

We received a fresh 70 lb sample of McKinley Mine (NM) coal from the P&M Coal Mining Co. This coal, whose rank is near the bituminous/subbituminous border, will be used for agglomeration testing. It was selected because available information suggests that it may be cleanable by oil agglomeration (unlike our baseline Black Thunder Mine coal).

Task 2.1.2.1 - Pretreatment Work at CONSOL - Dewaxing

Summary

Wilsonville Run 262E V-1074 was distilled into two fractions and dewaxed as outlined in the action item list from the last quarterly meeting. Dewaxing improved the solvent quality of both fractions; however, the effect was significantly larger for the higher boiling fraction. Increasing the temperature in microautoclave tests, up to 880 °F, was found to increase the coal and IOM conversions with hydrotreated dewaxed V-1074. A significant portion of the organic matter rejected from the ROSE unit in the ash concentrate stream was found to be convertible to THF solubles.

Discussion

Coal Conversion with Mo-free Solvent

A microautoclave test (5 min, 824 °F, 1500 psig cold H₂), Run 29, Table 3, was made with a 1.5:1 ratio of Wilsonville Run 260EOR V-1067:Black Thunder Mine coal. The purpose of this run was to eliminate the catalytic effect of the Mo present in the Wilsonville Run 262 ashy resid (V-1082). The coal conversion in this run was 67 wt %. This is significantly lower than the conversion of this coal at the same conditions in the blended Wilsonville Run 262E solvent that contained Mo catalyst (87 wt %). Although the Run 260EOR V-1067 sample differs considerably from the Run 262E solvent, the large difference in observed coal conversions strongly suggests that the Mo catalyst present in the Run 262E V-1082 ashy resid played an important role in our previous microautoclave tests. Similar studies will be made with the Mo-free ashy resid prepared from Wilsonville Run 258K

V-131B pasting solvent, described under Task 1.2, that more closely resembles the Run 262 and Run 263 materials.

Distillation and Dewaxing of V-1074

An action item from the last quarterly technical review meeting was to distill the Wilsonville Run 262E V-1074 heavy distillate into two fractions and to separately dewax each fraction. If any of these materials are found to be more conducive to conversion or more easily upgraded via hydrogenation, a significant reduction in solvent pre-treatment cost may result from reducing the quantity of material requiring treatment.

Approximately 400 mL (430 g) of V-1074 heavy distillate from Wilsonville Run 262E was distilled at 833 °F atmospheric equivalent (293 °C pot temp, 258 °C column temp, 5 torr) into two, approximately equal, fractions. Each of these fractions was dewaxed in 45/55 (vol %) MEK/Acetone at -35 °C via the method described for acetone dewaxing in Reference 1. The yields from the distillation/dewaxing of the V-1074 heavy distillate from Wilsonville Run 262E are shown in Table 4. The dewaxed oil yields from these dewaxings, 84.6 and 82.6 wt % for the lower boiling fraction and the higher boiling fraction, respectively, were nearly the same as that obtained for the whole V-1074 distillate material, 82.4 wt %. The ¹H-NMR proton distributions of the two distillation fractions, 833 °F⁻ and 833 °F⁺, and the dewaxed oil and wax from each fraction are shown in Table 5. The higher boiling component is somewhat more aromatic than either the lower boiling fraction or the original V-1074 material. As expected, the dewaxed material is more aromatic than the respective dewaxing feed, and the slack waxes are nearly free of aromatic protons.

The coal conversions measured in our standard microautoclave test (5 min, 824 °F, Black Thunder Mine coal) with all four of these materials and with the V-1074 feed are given in Table 3. Dewaxing appears to improve the solvent quality toward conversion in every case. However, this improvement was slight for the cases of the original V-1074 and the lower boiling fraction, which gave 1.5 and 0.8 wt % increases in the measured coal conversions, respectively. The observed coal conversion with the dewaxed higher boiling fraction of the V-1074 was 5.4 wt % higher than that of the non-dewaxed higher boiling fraction.

Samples of each distillation fraction and of the dewaxed oils derived from these fractions were sent to Sandia for hydrogenation treatment. Proton NMR analyses and microautoclave tests will be conducted at CONSOL on the hydrogenated samples returned by Sandia.

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, the effect of reaction temperature on the conversion of Black Thunder Mine coal was evaluated in microautoclave tests. Tests were made 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. Microautoclave runs were made at 880 °C, 860 °C and 840 °C. All conditions, except for temperature and the distillate portion of the solvent, 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 conversions are plotted versus temperature in Figure 1.

Coal conversion with either distillate generally increases with increasing temperature up to 860 °F. At 880 °F, conversion continues to increase with the hydrogenated solvent, SC1, and appears to decrease with the untreated V-1074. 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. Differences in the heat-up curves in the 5-min microautoclave tests, in which the ~2.5 min heat-up is a significant portion of the total run time, may have affected the repeatability of these tests. The heat-up curves from these tests will be examined to further explore this possibility. If real, the effect of increased conversion at higher temperatures when hydrogenated solvent is used suggests one 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).

Ash Concentrate

The ash concentrate from the ROSE unit contains a significant amount of organic material. Although the ash content of this material is high, >30 wt %, the ash concentrate is moisture-free, it has a low oxygen content and its specific energy content can be higher than that of the feed coal. Thus, from a hydrogen consumption standpoint, the ash concentrate has some advantages as a liquefaction feedstock compared to subbituminous coal. Two microautoclave runs (Runs 34 and 39, Table 3) were made to estimate the potential for conversion of this material to THF solubles.

The THF solubility of the V-107 ash concentrate from Wilsonville Run 263J was determined to be 9.1 wt % (14.8 wt % MAF) by pressure filtration and 18.9 wt % (30.7 wt % MAF) by overnight Soxhlet extraction. In the first run, the Run 263J V-107 ash concentrate was substituted for coal in a microautoclave test, Run 34 (5-min, 824 °F, S/C = 2.3), with our simulated Wilsonville Run 262E simulated recycle solvent. "Coal" conversion (one minus {"non-solvent" IOM recovered divided by ash concentrate IOM fed}) for this run was 47 wt % and the total IOM conversion was 33 wt %. Since the microautoclave work-up procedure uses THF filtration, the IOM in V-107 that was determined by pressure filtration (not Soxhlet extraction) was used in these calculations. Black Thunder Mine coal conversion under the same conditions was ~89 wt %.

A second run (Run 39) was made for 30 min in a 2.0:1 mixture of Sandia SCl solvent (-5 °C dewaxed/hydrogenated V-1074) and V-107 with no added resid to determine the nominal maximum convertibility of the ash concentrate. Under these conditions, 54.2 wt % of the IOM in the ash concentrate was converted to THF solubles. These tests show that a significant portion of the organic matter rejected from the ROSE unit is convertible and suggest that further investigation of potential utilization of this stream is warranted.

Task 2.1.2.2 - Pretreatment Work at CONSOL - Agglomeration

Summary

Agglomeration of an old sample of McKinley Mine coal (New Mexico) with No. 6 fuel oil resulted in about 25 wt % physical deashing.

A series of agglomeration runs was begun to optimize results with mine-cleaned Burning Star 2 Mine coal and Martin Lake Mine Texas lignite, and to explore the agglomeration potential of Kemmerer coal, a low-ash (3.7 wt % MF) subbituminous coal that we tested on a limited basis in previous work.

Agglomeration of the clean Burning Star 2 Mine coal gave 32 wt % physical ash rejection at several oil dosages and pHs, and 36 wt % ash rejection with a micronized feed; additional optimization is in progress. A repeat of the best agglomeration test in earlier work indicated that the current sample may not be as cleanable as the one used previously, which gave up to 41 wt % ash rejection.

An old sample of Kemmerer subbituminous coal gave an ash rejection of 30 wt % when agglomerated with No. 2 diesel fuel at ambient temperature, reducing the MF ash from 3.7 wt % in the feed to 2.1 wt % in the product (not corrected for ash-SO₃).

Results from recent Martin Lake Mine Texas lignite agglomeration tests will be presented in a future report, after completion of the ash analyses.

We conducted float/sink tests on three agglomeration feed coals (Martin Lake Mine lignite, Black Thunder Mine coal, Burning Star 2 Mine coal). The float/sink test method used is not strictly applicable to fine coal or to low-rank coal. Overall, the results indicate that agglomeration performed substantially better than the determined washability curve predicts for Burning Star 2 Mine coal and Martin Lake Mine lignite, and about the same as predicted for Black Thunder Mine coal.

Discussion

Alternative Feedstocks

A report on washabilities of U.S. coals² gave data which suggested that coal from the McKinley Mine in New Mexico may be cleanable by oil agglomeration. This coal is of borderline bituminous/subbituminous rank. We located a small sample of McKinley coal in our inventory and agglomerated it with No. 6 fuel oil. The run was repeated because some conditions deviated from those planned. Agglomeration of McKinley Mine coal (Runs B29 and B30, Table 6) with No. 6 fuel oil resulted in about 25 wt % physical deashing.

Initial agglomeration runs (A24, A26, A27, see Table 6) of clean Burning Star 2 Mine coal with No. 6 fuel oil gave only about 20% physical ash rejection. Runs A26 and A27 were made with a puck-milled micronized feed, but A24 used the conventional (-100 mesh) feed. With additional tests, the best result obtained with this coal and oil was 36 wt % physical ash rejection with a wet ball-milled micronized Burning Star 2 Mine coal feed (Run A29, Table 6). Several runs (A31-A35, A37, A38, Table 6) with the conventional (-100 mesh) feed gave about 32 wt % ash rejection. Oil dosage (15 to 35 wt % of MF coal) and pH (7.4 to 10.0) had no significant effect on ash rejection of the -100 mesh feed. Agglomerate product ash content (MF, oil-free basis) was 7.0 wt % in the micronized coal run and about 7.5 wt % in several of the -100 mesh coal runs. Burning Star 2 Mine coal was agglomerated at 54 °C and 85 °C to test the effect of temperature on the performance (Runs A37 and A38, Table 6; most other runs were made at 65 °C). The deashing performance seems to be marginally better at the higher temperatures. Ash rejections were 33 wt % at 65 °C and 85 °C, vs. 31 wt % at 54 °C. Product MF ash contents (oil-free) were 7.4 wt % at 65 °C and 85 °C, vs. 7.9 wt % at 54 °C.

In order to compare agglomeration performance of old and new Burning Star 2 Mine coal sample with that of the coal tested 11 years ago, we duplicated one set of the original test conditions with the new coal sample (Run A30, Table 6). The physical ash rejection was 28% with the new sample, lower than the 41% achieved in the original test. This seems to result from differences in the two samples of the Burning Star 2 Mine coal.

An old sample of Kemmerer subbituminous coal gave an ash rejection of 30 wt % when agglomerated with No. 2 diesel fuel at ambient temperature (Run A39, Table 6), but only 9 wt % when No. 6 fuel oil was used at 54 °C (Run A40, Table 6). The diesel fuel run resulted in an MF product ash of 2.1 wt %; the feed coal had an ash content of 3.7 wt % MF (not corrected for ash-SO₃).

Four agglomeration tests were made with Martin Lake Mine Texas lignite and No. 6 fuel oil. Because of unresolved difficulties with the ash analyses of the feed coal, products, and rejects, the results will be finalized and reported later.

Float/Sink Tests to Determine Feed Coal Cleanability

Float/sink test results at six gravities from 1.3 to 1.8 (1.7 was omitted) were obtained for -100 mesh samples of Burning Star 2 Mine coal, Martin Lake Mine Texas lignite, and Black Thunder Mine coal. The test method used is not strictly applicable to coal this fine, or to low-rank coal, so the results must be viewed with some caution. Overall, the results indicate that agglomeration performed substantially better than the washability curve predicts for Burning Star 2 Mine coal, Figure 2, and Martin Lake Mine Texas lignite, Figure 3. The performance of agglomeration for Black Thunder Mine coal seemed to match that predicted by the washability curve, Figure 4. In Figures 2 through 4, the agglomeration results were plotted using a "typical" MAF coal recovery value of 99%. Detailed results are presented in Table 7. Note that ash recovery was good for tests of Burning Star 2 Mine coal (feed ash of 11.64%, accumulated product ash of 11.71%), and Black Thunder Mine coal (feed ash of 6.69%, accumulated product ash of 6.12%), and for Martin Lake Mine Texas lignite (feed ash of 13.20%, accumulated product ash of 13.32%). We also plan to conduct float/sink tests on the ashy resid and ash concentrate samples, but will have to use another procedure, since the organic specific gravity liquids dissolve a portion of the resid present in these samples.

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)

No work was performed on this task.

Task 3.2 - Economic Evaluation (CONSOL)

Summary

We calculated the maximum possible yield of net product (gasoline containing 13.5% H) and the required hydrogen consumption for Black Thunder coal. Two cases were examined. In Case I, all oxygen is removed from the coal as CO_2 . In Case II, all oxygen is removed as H_2O . The results, detailed in Table 8, show the maximum gasoline yield increases from 77.9% to 86.1% MAF in going from Case I

to Case II. Hydrogen consumption simultaneously increases from 5.8% to 9.3% MAF. The hydrogen efficiencies are 13.4 and 9.3, respectively.

Analysis of a V-107 ash concentrate sample from Period J of Wilsonville Run 263 was obtained and reported. The ash elemental composition supports the validity of the ash-SO₃ correction for the baseline economic assessment made by LDP Associates. The ash concentrate analysis also is discussed in relation to options for use of the liquefaction bottoms, such as deashing and/or recycling.

Discussion

We calculated the maximum possible yield of net product (gasoline containing 13.5% H) and the required hydrogen consumption for Black Thunder coal. Two cases were examined. In Case I, all oxygen is removed from the coal as CO₂. In Case II, all oxygen is removed as H₂O. The calculations assume: 1) the Black Thunder coal analysis reported by CONSOL earlier in the project, 2) the gasoline product is a pure hydrocarbon with 13.5% H, and 3) all N reports as NH₃ and all S reports as H₂S. Any S that reports to the ash would slightly lower the H₂S yield and hydrogen consumption and would slightly increase the ash yield. The calculation results, detailed in Table 8, show the maximum gasoline yield increases from 77.9% to 86.1% MAF in going from Case I to Case II. Hydrogen consumption simultaneously increases from 5.8% to 9.3% MAF. The hydrogen efficiencies (lb product/lb H consumed) are 13.4 and 9.3, respectively. These theoretical yields, which represent upper limits of process yields, are a substantial improvement over those obtained in practice. It appears that in practice, the production of hydrocarbon gases and the rejection of some carbon with the ash is unavoidable; these are the two major causes of actual yields being less than the theoretical yields shown in Table 8.

Analysis of a V-107 ash concentrate sample (dated 1/31/92) from Period J of Wilsonville Run 263 is reported in Tables 9 and 10. This sample is of interest for two reasons. First, this sample is from the Wilsonville run period used by LDP Associates to define the baseline economic case. The sample analysis provides a checkpoint regarding the ash-SO₃ corrections and other aspects of the baseline economic case. Second, examination of this material allows us to better evaluate process options with regard to use of this stream in the liquefaction process.

The V-107 ultimate analysis and its ash elemental analysis are compared with those of the Black Thunder feed coal and V-1082 ashy resid from Run 262E in Table 9. The THF-solubility and properties of the soluble portion of the V-107 ash concentrate are compared with those of the V-1082 ashy resid from Run 262E in Table 10.

Relative to the feed coal (Table 9), the ash concentrate has high ash and sulfur contents, and low carbon, hydrogen, nitrogen, and oxygen contents. The ash elemental analysis indicates that the iron content of the V-107 ash is much higher than that of the coal ash; a consequence of the iron oxide catalyst fed with the coal in period 263J. The iron oxide addition rate was only 1 wt % MF coal in 263J, whereas it was 2 wt % MF during Run 262E when the V-1082 ashy resid was produced. As a result, the ash iron content of the Run 262E ashy resid is higher than that of the Run 263J ash concentrate. Nitrogen and oxygen contents are lower in the ash concentrate than in the feed coal. Sulfur concentrates in the ash. Therefore, the sulfur content of the Run 263J ash concentrate is greater than that of the Run 262E ashy resid.

The Run 263J ash concentrate contains more ash and IOM and less THF-solubles than the Run 262E ashy resid, Table 10. The soluble portion of the ash concentrate contains more condensed aromatic and cyclic alpha protons, and less beta and gamma protons than the ashy resid soluble fraction. The THF-soluble material from the ash concentrate contains less phenolic -OH than the ashy resid. However, the phenolic -OH peak location (ν) is lower in the ash concentrate THF-solubles, indicating a heavier, more-condensed phenol ring structure. This is consistent with the proton distributions. The composition of ash concentrate based on LDP Associates' ash-SO₃-corrected flowrates³ for 263J is (in wt %): 1.72% retained deashing solvent, 31.20% resid (soluble), 35.88% IOM, and 31.20% ash (SO₃-free). Thus, our measured concentration of THF-soluble material is lower than LDP's projections of cresol solubles. Perhaps the difference arises from the different solvents used and the aging of the sample. However, the ash content of 31.20% from the LDP Associates flowrates agrees quite well with our analysis value of 32.03 % (both SO₃-free). This provides some validation of the assumptions made by LDP Associates and the revised baseline case flowrates resulting from the ash-SO₃ correction.³

Examination of the ash concentrate analysis in the context of the overall liquefaction scheme suggests that there may be certain advantages to recycling or re-using the ash concentrate in some way. The ash concentrate has a lower oxygen content and higher iron and sulfur contents than the feed coal. If the ash concentrate is sufficiently reactive toward subsequent liquefaction, there are some advantages to using it as a recycle material. Much of the oxygen has been removed relative to the feed coal, so consumption of hydrogen to remove oxygen from the feed should be much lower. This can be seen more clearly by taking the ratio of wt % MF oxygen by difference (SO_3 -free) to that of wt % MF carbon (Table 9). This ratio is 0.254 for the coal, 0.043 for the ashy resid, and 0.129 for the ash concentrate. On a carbon basis, the ash concentrate contains half as much oxygen as the feed coal, and the ashy resid contains even less. For any ashy resid or ash concentrate that may be recycled, no iron oxide or sulfiding agent needs to be added. The potential advantage of recycling ash concentrate over recycling ashy resid is that the ash/organics ratio is higher in the ash concentrate, perhaps benefitting catalytic coal or resid conversion. Another potential benefit of recycling or re-using the ash concentrate is recovery of deashing solvent normally sent to gasification. Makeup deashing solvent of about 0.5 wt % of the MF coal is required in the plant flow scheme.³ Most of it exits the plant with the ash concentrate. Some economic benefit would result from recovery of this material. The feed coal contains a considerable amount of moisture; the ashy resid contains none.

There are potential disadvantages to recycling ash concentrate. These may include use of higher processing temperatures and or lower space velocities to convert less-reactive bottoms material. Higher gas yields may result if processing temperatures must be increased. Throughput of the reactors may decrease. Of course, there may be incidental equipment requirements, and adjustment/resizing of other equipment is likely. Additional technical data and some economic guidance will be required to evaluate any such process options.

Agglomeration or some other means of cleaning the ash concentrate may be able to provide recovery of catalyst, recycle of organics, or some other benefits. The Texaco gasifier used for ash concentrate gasification in the conceptual plant design typically feeds a 65 wt % slurry of coal which is pulverized to about 70%

finer than 200 mesh. This size consist is equivalent to that of our other coal feedstocks. Laboratory effort is being directed to explore these possibilities.

Miscellaneous

A paper entitled "Pretreatment of Coal and Recycle Oil for Direct Liquefaction" was submitted to the 7th International Conference on Coal Science. The paper was authored by R. A. Winschel, M. S. Lancet, G. A. Robbins, F. P. Burke, R. J. Kottenstette, and H. P. Stephens. A copy of the paper is included as Appendix 2 of this report.

References

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TABLE 1
ANALYSES FOR EVALUATION OF Mo-FREE SOLVENTS FOR 1621-22

Sample and Analysis	Present Simulation		Cand. A	Cand. A (Surrogate)	Cand. B	Target
	262D V-131B	262E V-131B	260 EOR V-1067	260 F V-1067	258K V-131B	263J V-131B
<u>wt % of Whole Sample</u>						
850 °F- Dist	29.1	24.8		18.0	30.4	27.7
850 °F+ THF Sol	50.3	54.2		56.2	49.6	50.3
THF Insol	20.3	20.5	25.0	23.6	19.1	21.4
IOM	10.0	10.0	14.4	14.3	9.3	9.4
Ash (incl. SO ₂)	10.3	10.5	10.6	9.3	9.8	12.0
Plant Resid (Cresol-Soluble 1050 °F+)	36.2	38.3		38.7	40.6	40.5
Plant Cresol Insolubles	19.6	20.0		19.7	20.6	20.4
Plant 1050 °F Dist. (Diff.)	44.2	41.7		41.6	38.8	39.1
<u>Wt % of 850 °F+ THF Solubles</u>						
Oils	64.2	66.6		54.6	61.8	
Asphaltenes	23.5	24.0		24.2	22.8	
Preasphaltenes	12.3	9.5		21.2	15.4	
<u>% of Protons</u>						
Whole Aromaticity	19.9	22.4		23.5	29.1	27.2
Dist. Aromaticity	11.6	15.0		15.0	19.7	18.3
THF-Sol. Resid Aromaticity	23.2	28.0		28.8	38.5	31.1
Whole Paraffinicity	40.3	39.6		35.1	27.5	44.7
Dist. Paraffinicity	50.8	47.4		46.3	36.3	
THF-Sol. Resid Paraffinicity	33.4	28.2		29.3	17.7	
<u>meq -OH/g sample</u>						
Dist. Phenolic -OH	0.36	0.38		0.53	0.36	0.43
THF-Sol. Resid Phenolic -OH	0.90	0.85		0.94	0.72	0.72
<u>% MAF Coal Conversion in Mod-EQ Test</u>						
Dist. SQ	57.8	59.2		62.7	89.1	77.1
Whole SQ	60.7	27.7		60.5	76.9	

TABLE 2
ANALYSES OF TEXAS LIGNITE AND ILLINOIS No. 6 COALS

	Martin Lake, Texas Lignite (1621-22-9)	Burning Star 2, Illinois No.6 Coal (1621-22-8)
Moisture, wt % as determined	25.85	1.34
Proximate, wt % dry, SO ₃ -free ash basis		
Ash, SO ₃ - free	8.39	11.49
Volatile Matter	46.57	39.16
Fixed Carbon	45.04	49.35
Ultimate, wt % dry, SO ₃ -free ash basis		
Carbon	66.10	68.95
Hydrogen	4.89	4.63
Nitrogen	1.23	1.16
Sulfur	1.36	3.65
Chlorine	0.040	0.063
Oxygen (by diff)	17.99	10.06
Ash, SO ₃ - free	8.39	11.49
Sulfur Forms, wt % (dry)		
Pyritic	0.28	1.62
Sulfate	0.02	0.09
Organic (by diff)	1.06	1.94
Ash Elementals, wt % of ash		
SiO ₂	31.13	46.71
Al ₂ O ₃	12.02	18.84
TiO ₂	0.94	0.88
Fe ₂ O ₃	6.56	21.27
CaO	18.61	6.45
MgO	4.29	0.88
Na ₂ O	1.13	0.50
K ₂ O	0.31	1.89
P ₂ O ₅	<0.019	0.03
SO ₃	22.85	1.97
Total	97.86	99.42
HHV, Btu/lb (MF)	11,305	12,310
Particle Size by Laser Diffraction, Vol %		
D ₁₀	8.4 μm	7.2 μm
D ₅₀	43.6 μm	37.6 μm
D ₉₀	125.0 μm	105.7 μm

TABLE 3
Microautoclave tests, Second Quarter 1993.

Run No.	Temp. °F	Time Min ¹	Recycle/ MF Coal ²	COAL		RECYCLE					Conversion, %MAF		Comments	
				wt, g	Comp 1	wt, g	Comp 2	wt, g	Comp 3	wt, g	Coal ³	IOH ³		
29	824	5	1.51	BT	4.55	V-1067	5.45	none	none	none	87.0	54.4	Mo-free V-1067 solvent, Wilsonville Run 260	
14	824	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	87.5	74.6	WV Run 262E V-1074 in Wilsonville solvent blend
16	824	5	1.51	BT	4.55	DW V-1074	2.33	V-130	0.36	V-1082	2.76	89.0	76.0	-35 °C Dewaxed WV Run 262E V-1074 in Wilsonville solvent blend
30	824	5	1.51	BT	4.55	V-1074 dist	2.33	V-130	0.36	V-1082	2.76	86.8	74.5	Distillate from V-1074 in Wilsonville solvent blend
31	824	5	1.51	BT	4.55	V-1074 resid	2.33	V-130	0.36	V-1082	2.76	84.0	72.1	Resid from V-1074 in Wilsonville solvent blend
32	824	5	1.51	BT	4.55	DW-dist	2.33	V-130	0.36	V-1082	2.76	87.6	75.2	-35 °C dewaxed distillate from V-1074 in Wilsonville solvent blend
33	824	5	1.51	BT	4.55	DW-resid	2.33	V-130	0.36	V-1082	2.76	89.4	76.7	-35 °C dewaxed resid from V-1074 in Wilsonville solvent blend
14	824	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	87.5	74.6	Test of Effect of Temperature on Conversion of Black Thunder coal with V-1074 distillate in Wilsonville solvent blend
37	840	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	91.0	78.1	
41	860	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	94.9	81.4	
40	880	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	89.8	76.9	
43	880	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	96.0	82.4	
44	880	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	91.8	78.8	Test of Effect of Temperature on Conversion of Black Thunder coal with Sandia SC1 distillate in Wilsonville solvent blend
45	880	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	94.9	81.5	
18	824	5	1.51	BT	4.55	SC-1	2.33	V-130	0.36	V-1082	2.76	92.1	78.6	
36	840	5	1.51	BT	4.55	SC-1	2.33	V-130	0.36	V-1082	2.76	94.0	80.7	
38	860	5	1.51	BT	4.55	SC-1	2.33	V-130	0.36	V-1082	2.76	94.0	80.8	
35	880	5	1.51	BT	4.55	SC-1	2.33	V-130	0.36	V-1082	2.76	98.3	84.4	V-107 substituted for coal in Wilsonville solvent blend
42	880	5	1.51	BT	4.55	SC-1	2.33	V-130	0.36	V-1082	2.76	96.6	82.9	
34	824	5	2.3 ³	V-107 ³	3.06	V-1074	3.00	V-130	0.46	V-1082	3.56	47.0	33.0	V-107 substituted for coal in Wilsonville solvent blend
39	824	30	2.0 ³	V-107 ³	3.33	SC1	6.67	none	none	none	84.2	54.2	V-107 alone	

¹ Residence time includes ~2.5-minute heatup. All runs at 1500 psig (cold) H₂

² SO₃ - free ash basis

³ No coal charged, coal replaced by V-107

TABLE 4

DISTILLATION AND DEWAXING OF V-1074 FROM WILSONVILLE RUN 262E

Fraction	Yield, wt %
Original V-1074	100
Dewaxed ^A V-1074	82.4
833 °F ⁻ Fraction	46.1
Dewaxed ^A 833 °F ⁻ Fraction	39.0
833 °F ⁻ Wax	7.1
833 °F ⁺ Fraction	53.4
Dewaxed ^A 833 °F ⁺ Fraction	44.1
833 °F ⁺ Wax	9.3

A =dewaxed at -35 °C in 55/45 (vol %) Acetone/MEK mixture.

TABLE 5

PROTON DISTRIBUTIONS OF DISTILLED AND DEWAXED WILSONVILLE RUN 262E V-1074

Sample	Proton Distributions, %						
	Condensed Aromatics	Uncondensed Aromatics	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Original V-1074	11.3	3.6	14.7	7.6	15.8	34.6	12.3
Dewaxed ^A V-1074	14.5	5.4	16.9	9.0	17.1	23.5	13.5
V-1074 Wax	0.8	0.7	3.4	2.7	11.2	68.1	13.0
833 °F ⁻ Fraction	10.3	3.2	14.7	7.7	16.0	35.2	12.9
Dewaxed ^A 833 °F ⁻	12.4	3.9	17.7	8.7	18.4	24.6	14.3
833 °F ⁻ Wax	0.0	0.3	2.3	2.7	7.8	74.5	12.3
833 °F ⁺ Fraction	12.9	3.1	15.6	7.8	16.1	33.7	10.9
Dewaxed ^A 833 °F ⁺	16.7	4.3	19.4	9.3	17.8	20.6	11.9
833 °F ⁺ Wax	0.4	1.3	3.5	3.2	12.0	65.5	14.1

A = dewaxed at -35 °C in 55/45 (vol %) Acetone/MEK mixture.

TABLE 6

SECOND 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 %
B29	OMK	P1	20.1	6.5, None	50	8.3	99.3	30.1	22.0	91.9
B30	OMK	P1	21.8	6.5, None	50	7.5	98.8	37.2	25.2	88.0
A24	BS2	P1	13.4	7.0, None	50	8.5	99.2	29.1	23.7	94.6
A26	BS2	P1	15.6	6.5, None	50	7.7	99.5	36.5	19.4	82.9
A27	BS2	P1	24.7	6.0, None	50	9.1	98.8	24.5	21.7	97.3
A29	BS2	P1	24.4	6.2, None	50	7.0	98.7	42.6	35.7	93.1
A30	BS2	C6	34.5	8.5, NaOH	23	7.7	96.2	36.4	27.9	91.5
A31	BS2	P1	15.2	8.0, NaOH	65	7.8	99.1	36.0	33.2	97.3
A32	BS2	P1	26.0	8.0, NaOH	65	7.6	98.8	37.4	31.4	94.0
A33	BS2	P1	35.3	8.0, NaOH	65	7.4	99.0	39.2	33.0	93.7
A34	BS2	P1	33.4	7.4, None	65	7.6	98.8	38.0	32.7	94.7
A35	BS2	P1	34.9	10.0, NaOH	65	7.7	99.3	36.7	33.1	96.3
A37	BS2	P1	36.2	8.0, NaOH	54	7.9	99.2	34.6	31.3	96.6
A38	BS2	P1	34.5	8.0, NaOH	85	7.4	99.1	39.4	33.4	94.0
A39	KM	P1	29.6	5.5, None	54	3.3	99.9	11.2	9.3	98.1
A40	KM	P3	26.0	5.6, None	23	2.1	99.9	44.3	30.4	86.0

Coals: OMK = McKinley (old sample), BS2 = Burning Star 2 Mine (new sample), KM = Kemmerer (old sample).

Oils: P1 = No. 6 fuel oil, C6 = Lummus 3LCF7 Product Distillate Composite, P3 = No. 2 diesel fuel.

(a) Run numbers with prefix A were made in the large vessel, those with prefix B were made in the small vessel.

(b) Based on feed ash which was not recovered in the product.

(c) Based on feed ash which was recovered in the solid reject (filter cake).

(d) Ash balance does not include dissolved ash.

TABLE 7

FLOAT/SINK TEST RESULTS FOR SELECTED AGGLOMERATION FEED COALS

Float/ Sink Test	Wt in g, As-Recovered	% Moist. in Fraction	% Dry Ash in Fraction	Cumulative % MF Ash	Cumulative % MF Recovery	Cumulative % MAF Recovery
Burning Star 2 Mine Coal (Feed 0.76 wt % Moisture, 11.64 wt % MF Ash)						
Fl. 1.30	12.5	3.33	2.57	0.13	5.08	5.61
Fl. 1.40	23.9	4.30	3.59	0.48	14.70	16.11
Fl. 1.50	101.8	4.51	5.72	2.81	55.59	59.78
Fl. 1.60	87.1	3.57	13.58	7.61	90.92	94.36
Fl. 1.80	10.3	3.49	27.90	8.78	95.10	97.77
Sk. 1.80	11.8	1.36	59.82	11.71	100.00	100.00
Sum	247.4					
Martin Lake Mine Lignite (Feed 23.41 wt % Moisture, 13.20 wt % MF Ash) (a)						
Fl. 1.30	3.6	7.55	8.73	0.15	1.69	1.78
Fl. 1.40	102.5	9.42	8.28	4.05	48.77	51.59
Fl. 1.50	19.5	7.74	9.49	4.91	57.89	61.12
Fl. 1.60	69.0	9.08	14.31	9.46	89.70	92.57
Fl. 1.80	14.5	6.77	25.10	11.18	96.56	98.49
Sk. 1.80	7.0	3.03	61.96	13.32	100.00	100.00
Sum	216.1					
Black Thunder Subbituminous Coal (Feed 22.40 wt % Moisture, 6.69 wt % MF Ash)						
Fl. 1.30	1.2	7.03	10.42	0.06	0.56	0.53
Fl. 1.40	55.5	5.78	4.60	1.26	26.64	27.04
Fl. 1.50	105.6	5.84	4.84	3.66	76.24	77.31
Fl. 1.60	44.3	6.62	6.99	5.10	96.87	97.75
Fl. 1.80	2.5	6.64	13.34	5.26	98.04	98.83
Sk. 1.80	4.1	4.12	43.87	6.12	100.00	100.00
Sum	213.2					

Ash values were not corrected for SO₃.

(a) This sample had a higher ash content than the original sample analyzed and reported in Table 2.

TABLE 8
MAXIMUM THEORETICAL GASOLINE YIELDS
FROM BLACK THUNDER MINE COAL

Product	Net Product Yields, wt % MF coal (wt % MAF coal)	
	Case I All O Yields CO ₂	Case II All O Yields H ₂ O
NH ₃	1.3	1.3
H ₂ S	0.5	0.5
H ₂ O	-	20.1
CO ₂	24.6	-
Gasoline	73.5 (77.9)	81.3 (86.1)
SO ₃ -free ash	5.5	5.5
H ₂ consumption	-5.5 (-5.8)	-8.8 (-9.3)
Total	99.9	99.9
H efficiency (a)	13.4	9.3

a) 1b product/lb H consumed

Assumptions:

- 1) Coal anal., MF basis: 70.32 %C, 4.68 %H, 1.04 %N, 0.50 %S, 5.54 %SO₃-free ash, 17.89 %O.
- 2) Gasoline analysis: 86.5 %C, 13.5 %H, no heteroatoms.
- 3) All N reports as NH₃; all S reports as H₂S (the ash contains no S; if it did, H₂S yield and H consumption would be lower and ash yield higher, but no other change).
- 4) All O reports as CO₂ (Case I) or H₂O (Case II).

TABLE 9
COMPARISON OF ELEMENTAL ANALYSES OF ASH CONCENTRATE
WITH OTHER SAMPLES

Analysis, Dry Basis Except as Noted	Black Thunder Mine coal (a)	Run 262E V-1082 Ashy Resid (a)	Run 263J V-107 Ash Conc.
wt % As-Received Moisture	22.40		0.40
wt % Ash	6.69	20.28	37.99
wt % Carbon	70.32	72.59	54.18
wt % Hydrogen	4.68	5.40	3.15
wt % Nitrogen	1.04	0.88	0.86
wt % Total Sulfur	0.50	1.93	2.79
Analysis, SO₃-Free Dry Basis			
wt % Ash	5.54	16.04	32.03
wt % Oxygen (Diff.)	17.89	3.15	6.99
Analysis, Oxide wt % of Ash			
Na ₂ O	0.48	0.47	0.57
K ₂ O	0.49	0.29	0.32
CaO	21.34	16.13	18.51
MgO	4.30	3.49	3.84
Fe ₂ O ₃	5.48	23.19	17.62
TiO ₂	1.14	0.89	1.05
P ₂ O ₅	0.96	1.14	1.16
SiO ₂	31.48	22.82	26.04
Al ₂ O ₃	15.76	10.71	14.05
SO ₃	17.26	20.92	15.70
Total	98.69	100.05	98.86

Analyses were performed by CONSOL R&D.

(a) Previously reported under this contract, see Reference 1.

TABLE 10
COMPARISON OF MISCELLANEOUS ANALYSES OF
ASH CONCENTRATE WITH OTHER SAMPLES

Analysis	Run 262 V-1082 Ashy Resid (c)	Run 263J V-107 Ash Conc.
Component Analysis, wt % of Sample, As-Received Basis		
Tetrahydrofuran (THF) Solubles	62.9	9.5
THF Insolubles (IOM), based on SO ₃ -free ash	21.1	58.5
Ash (SO ₃ -free)	16.0	32.0
Proton Distribution, % of Protons (a)		
Condensed Aromatic	24.6	31.1
Uncondensed Aromatic	4.0	4.4
Cyclic Alpha	20.2	27.7
Alkyl Alpha	9.5	9.0
Cyclic Beta	14.9	12.5
Alkyl Beta	18.1	12.6
Gamma	8.7	6.7
Phenolic -OH In Tetrahydrofuran-Solubles (b)		
Concentration, meq/g	0.96	0.79
ν , cm ⁻¹	3296	3293

Analyses were performed by CONSOL R&D.

- (a) Proton distribution measured on pyridine solubles by ¹H-NMR in 99.96 % d₅-pyridine.
- (b) Phenolic -OH measurements by FTIR.
- (c) Previously reported under this contract, see Reference 1.

NOTE: Five-minute (including ~2.5 min heat-up) microautoclave tests with 1.5:1 solvent/coal ratio, simulated Wilsonville Run 262E solvent, 1500 psig H₂(cold), distillate portion of solvent indicated on graph (SC1 = Sandia Hydrogenated -5 °C acetone dewaxed WV V-1074 heavy distillate).

Figure 1. Effect of Temperature on Black Thunder Coal Conversion.

Figure 2. Burning Star 2 Coal Float/Sink Results.

Figure 3. Martin Lake Lignite Float/Sink Results.

Figure 4. Black Thunder Coal Float/Sink Results.

Appendix 1

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May 14, 1993

Mr. Mike Peluso
LDP Associates
603 Fairview Avenue
Piscataway, NJ 08854

Dear Mike:

Enclosed is information concerning Wilsonville's use of ash-SO₃ data in material balances for Run 263. The bottom line is this: Wilsonville did not apply ash-SO₃ corrections to material balances in any low-rank coal run since Run 246 (reference: G. A. Robbins phone conversation with P. Vimalchand, Southern Clean Fuels, March 30, 1993). The enclosed excerpt, apparently from Wilsonville's Run 246 report, provides a lucid explanation for the need for, and effect of, the ash-SO₃ correction. Briefly, in Run 246 the result of the correction was a 2-3% decrease in MAF coal conversion, with adjustments to the oxygen and ash balances, as well. Thus, the Run 263 results should be corrected for ash-SO₃. Although Wilsonville did not correct for ash-SO₃, balance errors were required to be 5 % or lower for acceptance, and they typically obtained errors of 2 to 3%.

Consideration of these matters led me to the following question: How much of the purported benefit to coal conversion from addition of iron oxide at Wilsonville actually resulted from an increase in ash concentrate ash-SO₃ due to sulfiding agents fed with the iron oxide? It is possible that the ash-SO₃ increase due to added sulfur would be misinterpreted as lower unconverted coal, and that any apparent increase in coal conversion would actually be an artifact of the sulfur addition.

Give me a call if you have any comments or questions.

Sincerely,

G. A. Robbins
Sr. Research Chemist

/ls

enc.

cc: F. P. Burke
R. A. Winschel
M. S. Lancet

E. B. Klunder - PETC
F. J. Derbyshire - UK/CAER
R. Kottenstette - Sandia

10.3 SO₃-Free Ash Correction to Run 246 Yields

Elementally balanced yields reported for special product workup periods (A-H) have been calculated on an SO₃-free ash basis. This SO₃ correction has been found to be necessary at wilsonville and at other coal liquefaction research facilities whenever high-calcium coals are processed (Ref. 9, 10). This correction is needed for the following reason. When ASTM ash analyses are conducted in the laboratory, sulfur is oxidized and reacts with calcium in the ash to form CaSO₄ (which is stable at ashing temperatures and remains in the ash) (Ref. 25). The measurement of percent ash is therefore erroneously high because most of the sulfur (determined from LECO sulfur analysis) is also measured as coal ash. "SO₃-free ash" refers to the elemental difference between CaSO₄ and CaO.

To calculate the SO₃-free ash correction, the sample is ashed and an ash element analysis (including % SO₃) is conducted on the ash. The % ash is then reduced by the amount of SO₃. For example, if the ash analysis were 10%, and 20% of the ash were SO₃, the SO₃-free ash content would be 8%. Oxygen (by difference) would increase by 2%.

All ash-containing streams must be on an SO₃-free ash basis. For Run 246, these streams are coal, CSD feed, and ash concentrate. The percent SO₃ in the ash of these three streams for each of the eight product workup periods is shown below:

<u>Run Number</u>	<u>% SO₃ in coal ash</u>	<u>% SO₃ in CSD feed ash</u>	<u>% SO₃ in ash conc ash</u>
<u>DITSL:</u>			
246A	20.5	21.6	21.2
246B	20.5	20.3	21.0
246C	19.4	21.7	22.6
246D	19.9	21.3	20.7
246E	16.7	20.0	22.0
<u>ITSL:</u>			
246F	16.6	17.0	19.6
246G	15.3	19.4	20.0
246H	14.0	17.8	17.7

It may be observed that the percentages of SO₃ in CSD feed ash and ash concentrate ash are higher than in the coal ash. Therefore, if the ash values were not corrected for SO₃, it would appear that the quantity of ash leaving in the ash concentrate exceeded that entering with the coal. This is precisely what the as-is material balance data indicate: poor ash balance closure for the processing of Wyoming (high-calcium) coal. Technically, these corrections are needed for all coals to correct for the ash quantities determined from standard ASTM procedures. The effect is negligible, however, for lower-calcium (bituminous) coals, and the high cost of routine ash element analyses (for SO₃ correction) may be saved without significantly affecting material balances.

Elementally balanced yields were calculated with and without the SO₃ corrections to quantify the effect on yields. The results of this comparison are shown in Table 16 for the eight product workup periods. The means of all eight periods are shown below to illustrate the magnitude of the correction.

<u>Basis</u>	<u>As-Is</u>	<u>SO₃-Free</u>
Yield(a) (% MAF Coal):		
H ₂	-5.2	-5.0
H ₂ O	13.1	11.9
C ₁ -C ₃	7.9	7.7
C ₄ +Distillate	52.5	51.7
Resid	0.1	0.3
Organics Rejection	22.3	24.4
Energy Rejection (Before Elem. Bal.)	25.2	25.7
H ₂ Efficiency (C ₄ +Dist/H ₂)	10.1	10.4
Distillate Efficiency (C ₁ -C ₃ /C ₄ +Dist)	0.15	0.15
Coal Conversion (% MAF) Before Elem. Bal.	91.7	88.7
After Elem. Bal.	90.0	87.6
TLU Closure Error(b) (% MAF)		
Before Elem. Bal.		
Ash Balance	1.5	0.5
Oxygen Balance	-3.3	-2.2

Notes:

(a) Elementally Balanced Yields.

(b) Closure error (% MAF) = (lb/hr Out - lb/hr In)/(MAF Coal lb/hr) x 100.

To summarize the above table, key differences in yields, are are noted as follows:

- TL unit ash and oxygen balance closure errors are improved.

- Coal conversion is decreased by 2-3%, and hence the organic rejection (a material yield) is increased by the same margin.
- Water yield is reduced by 1.0-1.5% MAF.
- Hydrogen consumption and distillate yield are marginally decreased.

It is important to note that SO₃-free ash corrections have been made only for the eight product workup periods. The daily estimated yield structures (Tables 1, 4) are not elementally balanced and have not been likewise corrected.

10.4 Transfer-line Solids Buildup

In the liquefaction processing of subbituminous coal, many pilot plants have previously reported more operational problems associated with reactor solids buildup, line pluggage, etc., as compared with bituminous coal processing. Solids buildup was an operational concern at the start of Run 246. The anomalous dissolver temperature profile (Section 11.0), discovered early in the run, gave reason to suspect solids buildup in the reactor. A plant outage was taken on 23 April; inspection of the dissolver revealed only a negligible amount of solids buildup around the distributor plate. This has also been observed for bituminous coal processing. As the run progressed, however, the pressure drop between the dissolver draw-off and the high pressure separator increased. This increase was fairly rapid, rising from about 50 psig on May 01 to approximately 300 psig on June 01. Thereafter, the pressure drop increased at an even a higher rate, reaching 700 psig on June 25. Feed to the TL unit was stopped on July 01 to inspect and clear the transfer line.

Inspection of the transfer line (2" Sch. 160, SS pipe) revealed a uniform buildup of solids, decreasing the effective diameter to less than 1/4 inch. The solid material had a soft, clay-like texture. The transfer line was cut in several sections (Figure 25), and samples were analyzed for their chemical content. In addition, solid samples obtained from the dissolver were also analyzed. The results of these tests are shown below.

Description	Drawing Label	As received		Ash analysis wt % dry ash							K ₂ O, Na ₂ O, P ₂ O ₅ , TiO ₂		Undetermined (%)
		Ash (%)	CO ₂ (%)	CaO (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	SO ₃ (%)	MgO (%)	(%)			
Coal, MF	-	8.22	0.15	24.46	31.20	6.08	14.87	15.08	4.13	3.53	0.45		
1st Small Piece Below 3rd Deck	5A	65.51	2.32	18.36	30.79	12.67	14.78	7.48	3.32	10.03	2.36		
3rd Elbow Below 4th Deck	N	59.48	9.31	21.14	24.88	12.57	14.10	9.08	3.48	13.65	4.10		
8101 Wall Scale	3B	70.57	22.01	24.78	9.10	18.27	9.33	16.31	2.27	4.72	9.22		
Bottom Head (below distributor)	E	71.10	3.57	1.63	9.32	82.45	3.32	9.88	0.16	0.91	0.23		
8101 Solids withdrawal (June 20, 1961)	-	14.61	3.00	25.77	30.74	16.17	8.20	15.00	1.47	2.03	0.52		
8101 Blowdown Solids (July 01, 1961)	-	1.88	0.37	11.40	22.03	41.43	4.74	15.27	1.15	1.82	0.16		

Appendix 2

**PRETREATMENT OF COAL AND RECYCLE OIL
FOR DIRECT LIQUEFACTION**

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PRETREATMENT OF COAL AND RECYCLE OIL FOR DIRECT LIQUEFACTION

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INTRODUCTION

Although significant technical advances have been made in direct coal liquefaction technology in the last 15 years, further improvements are required to make coal-derived liquid fuels cost competitive with petroleum. A research and development program⁽¹⁾ is being conducted by the University of Kentucky/Center for Applied Energy Research, Sandia National Laboratories, LDP Associates and CONSOL Inc. to improve current coal liquefaction technology by physical and chemical pretreatments of the coal and recycle oil. These pretreatment steps include: 1) agglomeration of the coal with ash-containing recycle oil to simultaneously reject coal ash and recycle-oil ash, 2) fluid coking of the distillation bottoms (ash-purge) stream and recycle of the coker overhead, 3) dewaxing of the distillate portion of the recycle oil, and 4) low-severity hydrotreatment of the coker overhead and dewaxed oil using hydrogen from an in-situ water-gas shift reaction. These pretreatment steps will remove the ash and unconverted coal, reducing the ash load in the system and simultaneously recovering the maximum amount of organics. Dewaxing and hydrotreatment will yield a high-quality recycle oil distillate. These pretreatment steps are being evaluated technically and economically to develop an improved conceptual liquefaction process. The baseline process to which the improved process will be compared is the Two-Stage Liquefaction Process as it was practiced at the Wilsonville, AL, USA Advanced Coal Liquefaction Test Facility. The baseline coal is Black Thunder Mine subbituminous coal from the Powder River Basin of Wyoming, USA. The baseline for process performance is Wilsonville Run 263J, which was made with Black Thunder coal in the hybrid mode of operation ⁽²⁾ (i.e., supported catalyst in the second stage and dispersed Mo catalyst added with coal). The flow scheme of the conceptual, improved process is shown in Figure 1. This paper focuses on those elements of the concept that improve the quality of the recycle oil: dewaxing and hydrotreatment. Included are results concerning dewaxing experiments, hydrotreating experiments, and experiments designed to show potential process improvements from the ensuing changes in recycle solvent composition.

EXPERIMENTAL

The Wilsonville plant used a three-component recycle solvent: distillate (V-1074), ashy resid (V-1082), and deashed resid (V-130). All work described here employed these components sampled during Wilsonville Run 262E (Black Thunder coal,

hybrid operating mode).⁽³⁾ Experimental details not supplied here can be found in the technical reports of this project.⁽⁴⁾

DISCUSSION

Dewaxing. The distillate portion of the recycle oil produced from subbituminous coal contains a substantial concentration of paraffins, specifically n-paraffins. The paraffins are poor physical solvents for coal liquids and they reduce the hydrogen donor capacity of the oil by dilution. The fact that they concentrate in the recycle stream indicates that n-paraffins are relatively unreactive toward cracking at process conditions. Removal of the paraffins (wax) can substantially improve solvent quality⁽⁵⁾ and may produce a recycle stream that is more easily cracked to product. The by-product wax could be sold or fed to a catalytic cracking unit to produce gasoline. Table 1 shows yields and characteristics of the dewaxing products. The ketone dewaxing procedure was used for these experiments. We estimate that the steady-state wax yield from Black Thunder coal is about 4% MAF.

Hydrogenation. The dewaxed distillate is substantially more aromatic than the original recycle distillate. Low-severity hydrogenation can improve its hydrogen donation capacity while simultaneously reducing its heteroatom content. Conceptually, this hydrogenation step could also be applied to the coker overhead oil (Figure 1). Table 1 shows characteristics of the hydrogenation products. Hydrogenation was conducted in a trickle-bed reactor charged with presulfided Shell 324M (Ni/Mo/Al) catalyst under 7 MPa of 1:1:1 (molar) CO:H₂:steam mixture.

Process Performance Improvements. It is important to have a measure of the potential absolute improvement in process performance that can be achieved by the various solvent pretreatment steps in the integrated process. Microautoclave tests were made using simulated Wilsonville Run 262E recycle solvent to define conditions for solvent testing. In these tests, the recycle material was a composite of the three recycle components in the same proportion as used in Run 262E. In some cases, the original distillate component was replaced in the recycle mix with dewaxed or hydrogenated/dewaxed distillate. All conversions were measured by the THF solubility of the reaction products, corrected for the ash-SO₂ contents of the coal and recycle materials. The conversions are expressed both on an MAF-coal-fed basis and on a total-IOM-(insoluble organic matter)-fed basis (i.e., including the IOM in the ashy resid). Expressing the conversion on an MAF coal basis gives an indication of the steady-state conversion one might expect in a recycle system. Expressing the conversion on an IOM-fed basis gives a better indication of the per-pass conversion activity. The results of these experiments are given in Table 2. The variables included residence time, recycle distillate component, and recycle/coal ratio. The earliest tests were made at residence time of 15-30 min, approximating the residence times in the Wilsonville reactors. However, conversions at these conditions were well over 100 wt % MAF coal, compared to approximately 90% observed at the Wilsonville plant with subbituminous coals. Because the Wilsonville

reactors are highly back-mixed, less residence time is required for the batch microautoclave reactor to achieve a comparable conversion. Assuming that the intrinsic kinetics are first-order and the same for each system, a four-fold greater residence time is required in the continuous system than in the batch system, at 90% conversion. Therefore, subsequent microautoclave tests were made with a five-minute residence time. The results of the five-minute runs are given in Table 2. Conversions in the 90% range were obtained at recycle-to-coal ratios of 1.5 and above. Therefore, it appears that microautoclave tests at these conditions (i.e., 440°C, 5 min, 1.5 recycle-to-coal) provide a reasonable simulation of Wilsonville coal conversion results. Furthermore, at these conditions, there was a clear improvement in conversion when the dewaxed V-1074 and the hydrogenated-dewaxed V-1074 were substituted for the original V-1074 distillate in the recycle mixture. The overall improvement is in the range of 4-5 wt % MAF coal. The conversions greater than 100%, at 15 and 30 min residence time, demonstrate that the recycle IOM is moderately reactive toward additional conversion. This suggests the possibility that improvements in solvent quality can be beneficial in increasing both coal and recycle IOM conversion. For example, at 5 min, 2.3 recycle-to-coal, the conversion on an MAF coal basis is 93.6%, but the conversion on a total IOM basis (coal + recycle IOM) is only 74.1%. Improving the per-pass coal conversion or the total IOM conversion could improve yields directly or through process modifications.

CONCLUSIONS

Dewaxing and hydrotreating substantially improve the effectiveness of the distillate component of the recycle oil for converting coal and recycled IOM at simulated process conditions. This should result in improved product yields because of less rejection of organics during the deashing step.

ACKNOWLEDGMENT

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TABLE 1. DEWAXING AND HYDROTREATING CONDITIONS AND RESULTS

Code	Description	Acetone Dewaxing		Hydrogenation Conditions		H Content, wt %	Proton Types, %			Phenolic -OH Conc, mg/g	SQI(b)
		T, °C	Wax Yield, wt %	WHSV, h ⁻¹	T, °C		Arom- atic	Hydro- aromatic	Para- finic		
A	Feed Oil	-	-	-	-	9.9	14.9	30.5	48.9	0.44	63.8
B	A, Dewaxed	-5	25	-	-	8.5	21.6	35.9	33.4	0.56	82.1
C	A, Dewaxed	-35	35	-	-	8.0	23.5	37.1	29.1	0.61	85.3
D	B, Hydrogenated	-	-	0.32	300	8.9	18.0	38.1	35.9	0.29	80.8
E(a)	B, Hydrogenated	-	-	NA	NA	8.9	18.8	38.1	37.3	0.28	80.0
F	C, Hydrogenated	-	-	0.51	300	8.8	18.7	38.4	32.0	0.36	80.3

a) Composite of several tests with several conditions and catalysts; b) Solvent quality index from standard microautoclave test.

TABLE 2. MIROAUTOCLAVE TESTS AT SIMULATED WILSONVILLE RUN 262, PERIOD E CONDITIONS

Time Min (a)	Recycle/ MF Coal (b)	Distillate Component of Solvent (c)	Conversion, % MAF		Comments
			Coal (b)	IOM (b)	
5	1.04	A	71.8	64.1	Five-minute runs using original V-1074 as distillate portion of recycle. Recycle/coal ratio variable. 440 °C. Concentrations as in original Wilsonville composite solvent.
5	1.51	A	87.5	74.6	
5	2.3	A	88.8	70.3	
5	1.04	C	76.6	68.4	Same as above, but with dewaxed V-1074.
5	1.51	C	89.0	78.0	
5	2.3	C	89.7	71.1	
5	1.04	E	79.7	71.2	Same as above, but with hydrogenated, dewaxed V-1074.
5	1.51	E	92.1	78.6	
5	2.3	E	93.6	74.1	
15	2.3	A	106.4	84.2	Fifteen-minute run with V-1074.
30	1.51	A	103.5	88.3	Thirty-minute runs with V-1074 in Wilsonville composite solvent. Recycle/coal ratio variable.
30	2.3	A	109.5	86.7	
30	2.3	A	109.0	86.3	
30	1.51	C	104.4	89.1	Thirty-minute runs with dewaxed V-1074. Recycle ratio variable.
30	2.3	C	108.8	86.2	

a) Includes 2-min heat up. All tests with Black Thunder coal, 440 °C, 1500 psig (cold) H₂; b) SO₂-free ash basis; c) Code from Table 1.

Fig. 1 New Integrated Process Scheme. Coal and recycle oil pretreatments enclosed in dotted boxes.

SECTION THREE

SANDIA NATIONAL LABORATORIES

**ADVANCED DIRECT LIQUEFACTION CONCEPTS for PETC GENERIC UNITS
QUARTERLY PROGRESS REPORT FOR APRIL 1993 THROUGH JUNE 1993
SANDIA NATIONAL LABORATORIES**

Subtask 1.3 Laboratory Support

Economic assessments of proposed improvements in coal conversion and oil yield from the Advanced Concepts Program rely on quantitative measurements of coal conversion and oil formation. Coal conversion has been reliably measured by solubility in THF, however oil yield is more difficult to measure from microautoclave tests. In addition, resid components of the Wilsonville Recycle Oil are reactive and resid conversion (to distillate) calculations are essential to economic evaluation of improved concepts for liquefaction. To this end, CONSOL, CAER and Sandia have been evaluating and modifying a thermogravimetric (TGA) method which has been in use at HRI to evaluate resid content in liquefaction materials. The method involves heating the sample in the TGA and measuring weight loss to get a reproducible measurement of resid content and thus resid conversion. The temperature program and experimental procedure are as follows:

HRI TGA Method

Start nitrogen flow (40 cc/min)
Initial Temp 40°C
Ramp from 40°C to 110°C at 80°C/min.
Hold at 110°C for 5 min.
Ramp from 110°C to 375°C at 200°C/min.
Hold at 375°C for 5 min.
Switch to oxygen flow (40cc/min)
Ramp from 375°C to 732°C at 200°C/min.
Hold 3 min.

The temperature isotherm at 110°C is used to measure the THF remaining in a sample and the 375°C isotherm is used to measure the "-975°F distillate". Oxygen is introduced at 375°C to burn the residual (975°F+) material leaving ash to be determined at the final 732°C isotherm. The difference between the ash value and the value at the 375°C plateau is designated as "resid". This method produced a thermogram similar to Figure 1.

Figure 1 TGA of Ashy Resid (HRI method)

Figure 2 TGA of Heavy Distillate (HRI method)

Figure 3 TGA of 3:1 Ashy Resid:Heavy Distillate (HRI method)

Figure 4 TGA of 2:1 Ashy Resid:Heavy Distillate (HRI method)

Heavy Distillate/ Ashy Resid mixtures (slurried in THF)

In order to test the TGA method on samples with varying amounts of resid and distillate, mixtures of V1082 (ashy resid) and V1074 (heavy distillate) were prepared by slurrying the components in freshly distilled THF and then evaporating the THF. As described above, weight loss due to distillate was assigned to the second plateau (375°C) in the TGA plot. The remaining material corresponds roughly to the resid and ash contents of the sample and these numbers are reported in Table 1. Results for measured ash content and calculated resid and ash numbers are also shown in Table 1. The expected values are calculated using known weights of the two components in the mixture. All values in Table 1 were derived from the TGA method as prescribed by HRI. No attempt to reconcile these numbers with actual distillation data has yet been made. Figure 1 is the thermogram for the V1082 ashy resid and Figure 2 is the thermogram from the V1074 heavy distillate. Figures 3 and 4 show thermograms for two samples which were prepared by slurrying in THF and then drying (as described previously).

Table 1: Resid Determination Using TGA Method (THF Mixed)

Sample	Nominal wt Ratio	Expected 975°F+	Measured 975°F+	Expected Ash	Measured Ash
V1082*	NA	61	61	21	21
V1082: V1074	3:1	47	47	16	25
V1082: V1074	2:1	43	37	14	14
V1082: V1074	1:1	34	28	11	9
V1074*	NA	6	6	0	0

* For unmixed samples, values for expected quantities were assigned the experimentally determined value.

It was found that the plateau areas of the thermogram could be made more distinct if the ramp rate was slowed to 50°C/min from 200°C/min. In fact, previous studies in the literature ^{1,2} used ramp rates on the order of 20°C/min. These studies showed that slower ramp rates improve the correlation of the TGA determination with boiling point curves. The following temperature program with the slower ramp rate is the modified program now used at Sandia. The 50°C/min ramp was chosen to facilitate accuracy while maintaining a reasonable analysis time. An example thermogram is shown in Figure 5.

Figure 5 TGA of Mixture with 61% Heavy Distillate (modified method)

Figure 6 TGA of Mixture with 80% Heavy Distillate (modified method)

Modified TGA Method

Start nitrogen flow

Initial Temp 30°C

Ramp from 30°C to 110°C at 30°C/min.

Hold at 110°C for 5 min.

Ramp from 110°C to 375°C at 50°C/min.

Hold at 375°C for 4.5 min.

Switch to oxygen flow.

Ramp from 375°C to 732°C at 50°C/min.

Hold for 8 min.

Heavy Distillate / Ashy Resid mixtures

Results from the TGA experiments with mixtures prepared by mixing V1074 heavy distillate and V1082 ashy resid "neat" are shown in Table 2. The mixtures homogenized by heating and stirring the two components together, then rapidly cooling them. The ash measurement was taken after the organic material was completely burned off at the end of a run. The resid measurement is taken as the difference between the ash value and the weight value noted during the 375°C isothermal section of the TGA plot. Figures 5 and 6 are thermograms using the modified TGA method on the two samples shown in Table 2.

TABLE 2: Resid approximations with TGA

SAMPLE	V1074 %	V1082 %	Expected Ash %	Measured Ash %	Expected Resid %	Measured Resid %
1	60.6	39.4	7.9	6.0	24	18
2	79.7	20.3	4.0	4.0	12	12

In addition two TGA runs were made with the THF soluble portion of products from coal liquefaction with Black Thunder coal. Two experiments were performed at 440°C, 1400 psig H₂, with the Wilsonville Recycle Oil (see section 2.1.3) at 5 minutes and 30 minutes reaction time. Using this technique, the sample for the 5 minute run showed 34% resid and the sample from the 30 minute run showed 25% resid.

Subtask 2.1.3 Solvent Pretreatment

Coker Tar Hydrogenation

Substitution of a fluid coker into the liquefaction process has two potential advantages. The coker could reject ash, replacing the currently practiced ash separation technique, and it could generate an overhead tar stream which could be effectively hydrogenated for use as a donor solvent. A portion of this subtask is to hydrotreat the tar produced in a laboratory scale fluid coker which is operated at CAER. A 75g fluid coker tar sample was received from CAER during March 1993. The sample was a composite of four runs which was dissolved in methylene chloride, filtered, and rotoevaporated to remove the methylene chloride. The average weighted run data for this sample is as follows:

Table 3: Coker Tar Sample Description

SAMPLE NUMBER	Steam/Resid Ratio (lb./lb.)	Coking Temperature, °C	Tar Yield, % (AF Basis)
9302-9305	6.9	500	29

The aim of hydrotreating the coker tars is to increase the solvent quality of the tars by increasing their hydroaromatic nature. Batch microautoclave tests were performed to hydrogenate the coker tars. The coker tars were hydrogenated at two different temperatures, 350°C and 400°C for one hour with 1500 psig hydrogen (cold charge). Freshly sulfided Shell 324M catalyst was used (20 wt% catalyst to tar basis).

Product description - Although the coker tar had only 0.4% THF insoluble material before reaction it had 13.5% and 11.6% after reaction at 350°C and 400°C respectively (samples A and B). The increase in the THF insolubles indicates polymerization under these conditions. The reactors also showed some evidence of corrosion and the post reaction gas analysis showed about 6.5 vol. % methane in the products. Much of the methane and evidence of corrosion due to chloride were the result of the breakdown of residual methylene chloride in the sample. A set of repeat experiments (after heating the sample under vacuum to remove the methylene chloride) gave approximately 3% methane at 350°C and 4% methane at 400°C. The amount of hydrogen uptake by these samples (samples C and D) was nearly the same as the previous samples and the THF insolubles were 7.8% and 10.9% respectively. Solvent quality results from the hydrogenation experiments are reported in Table 4.

Table 4: Coker Tar Hydrogen Content and Distribution

Sample	TEMP °C	%H	Cond Arom	Uncond Arom	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
Coker Tar	NA	7.9	19.3	4.3	23.1	7.1	20.2	19.4	6.5
Coker Tar A*	350	10.2	11.3	5.2	26.6	8.9	20.7	19.2	8.1
Coker Tar B*	400	9.7	18.9	1.6	22.1	8.2	16.5	23.2	9.5
Coker Tar C*	350	ND	17.2	4.2	24.7	9.2	18.2	19.4	7.1
Coker Tar D*	400	ND	18.0	4.2	23.3	9.0	17.8	20.3	7.1

* Proton NMR results on these samples may be approximate since not all of the sample dissolved in the chloroform-d solvent.

The 350°C hydrogenated coker tar appeared to be more efficiently hydrogenated than the 400°C coker tar since the hydroaromatic hydrogen content was enriched in this sample and the aromatic content was significantly reduced. The higher temperature is thermodynamically less favorable for hydrogenation and may also enhance a small amount of solvent cracking. Coker tar samples A and B were shipped to CAER for solvent evaluation in coal liquefaction experiments. Samples C and D will be shipped to CONSOL in July for solvent evaluation.

Coal Liquefaction Testing-Black Thunder Coal

Previous coal liquefaction tests performed on this project at Sandia used Wyodak Subbituminous Coal (sample I.D. 202) from the Argonne Premium coal sample bank. CONSOL repackaged a one pound Black Thunder coal sample into several small samples so that Sandia's coal liquefaction experiments would be with the same coal that was used by CONSOL and CAER. Preliminary work with the Wilsonville Recycle Oil (WRO) and the Black Thunder Coal using Sandia's microautoclave reactors was begun this quarter. Table 5 shows the results from experiments performed at various hydrogen pressures using Black Thunder and Argonne Wyodak Coals. Preliminary results were calculated using an SO₃ free ash as the basis. The ash values for the Black Thunder Coal, and V1082 Ashy Resid were 5.5% and 16.0% respectively. The V1082 THF insoluble matter was 37.1% which gives an IOM content of 21.1% in the original V1082 (37.1-16.0).

TABLE 5: Coal Conversion Using WRO and Black Thunder Coal

Time	Coal ^a	wt	RECYCLE						Conversion %MAF		Press
			Comp1	wt	Comp 2	wt	Comp 3	wt	Coal	IOM	
5	BT	2.59	V-1074	1.30	V-130	.20	V-1082	1.53	62	53	1200
5	BT	2.58	V-1074	1.29	V-130	.20	V-1082	1.53	61	52	1200
30	BT	2.60	V-1074	1.30	V-130	.20	V-1082	1.53	62	53	1200
30	BT	2.57	V-1074	1.33	V-130	.20	V-1082	1.52	69	59	1200
30	BT	2.57	V-1074	1.29	V-130	.20	V-1082	1.52	76 ^b	65 ^b	1200
30	BT	2.55	V-1074	1.30	V-130	.20	V-1082	1.53	80	68	1400
5	WY	2.74	V-1074	1.32	V-130	.20	V-1082	1.52	66	56	1100
30	WY	2.70	V-1074	1.33	V-130	.20	V-1082	1.52	43	36	1100

a) WY= Argonne Wyodak, BT=Black Thunder. b) Different THF filtration technique.

Experiments using 1200 psig of hydrogen (cold charge) gave low coal conversions (62% and 65%) at 5 minutes and 30 minutes. Comparable experimental conditions at CONSOL gave coal conversions of 87.5% and 103.5% (CONSOL uses 1500 psig H₂ cold). The reason for Sandia's low conversions is not yet clear. These are the first sets of experiments with the rather pasty Wilsonville Composite Solvent and may reveal mass transfer limitations not previously noted when heavy distillate was used as the only solvent (as was the case with previous liquefaction experiments). An indication that mass transfer limitations may be present is the increased conversion noted for the experiment conducted at 1400 psig H₂. In addition, the 30 minute experiments at lower pressures show equivalent or reduced conversions, indicating that hydrogen availability during thermolysis may be insufficient, leading to polymerization reactions and solids formation. Experiments with lower viscosity solvents such as V1074 Heavy Distillate have not evidenced mass transfer limitations in the past.

Increased Solvent to Coal Ratio Since possible gas-liquid mass transfer difficulties are evidenced at the low (1.5:1) solvent to coal ratios used in the tests shown in Table 5, another set of experiments was performed at a 2.3:1 solvent to coal ratio. Table 6 shows the results from experiments performed at 1400 psig H₂ (cold charge) and 440°C for five and thirty minutes at temperature. Results were calculated using an SO₃ free ash as the basis.

TABLE 6: Coal Conversion Using WRO and Black Thunder Coal

	COAL	RECYCLE						Conversion % MAF	
Time	wt	Comp1	wt	Comp 2	wt	Comp 3	wt	Coal	IOM
5	2.49	V-1074	1.92	V-130	.30	V-1082	2.29	82	64
5 ^a	3.84	V-1074	3.00	V-130	.46	V-1082	3.56	89	70
5	2.52	Hyd/Dew ^b	1.93	V-130	.30	V-1082	2.28	88	69
30	2.49	V-1074	1.92	V-130	.30	V-1082	2.28	91	72
30 ^a	3.84	V-1074	3.00	V-130	.46	V-1082	3.56	109	86
30	2.50	Hyd/Dew ^b	1.96	V-130	.30	V-1082	2.28	96	75

a) Results from experiments performed at CONSOL b) Hyd/Dew is a hydrogenated dewaxed sample V-1074

Table 6 includes two experimental results from CONSOL which were performed at comparable conditions (CONSOL pressurizes to 1500 psig cold). These results are included to show, in a comparative sense, the relationship our experiments have to the other labs. Experiments performed at the lower solvent to coal ratios (Table 4) gave coal conversions which were significantly lower than the other laboratories. At this time it is postulated that the lower conversions may be caused in part by gas-liquid mass transfer problems which are exacerbated at low solvent to coal ratios in Sandia's microautoclave design. The higher solvent to coal ratios used this month have lessened the discrepancy between Sandia's conversions and CONSOL's. For comparison purposes, a hydrogenated dewaxed V-1074 distillate was added to the WRO. Results from these experiments showed increased conversion from 82% to 88% on an MAF coal basis for a five minute residence time and from 91% to 96 % on an MAF coal basis for the thirty minute residence time experiment.

Coal Liquefaction Results from CAER

Three heavy distillate samples were sent to CAER for incorporation into their coal liquefaction testing. Sample descriptions are shown in Table 7.

TABLE 7: Products Shipped to CAER

SAMPLE	Comment	Hydrogen Pressure	% H ₂	% Aromatic Hydrogen
Dewaxed H.D.	V1074 Dewaxed at -5°C (baseline)	NA	8.5	22.0
20502	Hydrogenated at 325°C (Hyd. only)	1000 psig	8.9	16.7
20405	Hydrogenated at 325°C (in situ WGS)	~670 psig	9.1	18.5

The heavy distillate samples were dewaxed at -5°C by CONSOL and then hydrogenated at Sandia using the microflow reactor with the in situ water-gas shift reaction (sample 20405) and hydrogen-only (sample 20502) as the gas phase. CAER incorporated the hydrotreated dewaxed distillate as well as hydrotreated V1074 which had not been dewaxed into the tests. Table 8 gives the results of solvent separation measurements which were made to establish the baseline solvent composition for microautoclave coal liquefaction experiments. These distributions are used in calculating net yield from coal, since the solvent is assumed to be inert for these experiments.

Table 8: Solvent Separation of the Unreacted V-1074 Heavy Distillate^a (CAER)

Distillate Label	E	F	G	H
Type of V-1074 Heavy Distillate	Run 262 1050°F	300°C Hydrotreated	Baseline -5°C dewaxed	Hydrotreated dewaxed (20502)
Hydrogen Content, %	9.9	10.5	8.5	8.9
Product ,wt% AR solvent				
Oils	95.9	95.0	89.4	93.6
PA+A	0.7	0.1	5.3	0.8
IOM + Ash	3.4	4.9	5.3	5.6
THF soluble total	96.6	95.1	94.7	94.4

a) Samples were extracted with THF as-received, with the ash included in the IOM fraction (0.3% in the Run 262 heavy distillate)

CAER has evaluated a number of iron catalysts in liquefaction experiments with the WRO solvent at 415°C. For this reason, liquefaction tests were designed to test the effect of adding dewaxed and hydrotreated heavy distillate samples to the WRO at 415°C. Table 9 shows the results from liquefaction experiments performed at 415°C and 30 minutes residence time. Heavy distillate and modified heavy distillate solvents were substituted into the WRO and tested thermally as well as with a Superfine Iron Oxide (SFIO) catalyst. No SFIO test was performed with sample G (baseline dewaxed heavy distillate).

Table 9: Liquefaction of Black Thunder Coal in Modified WRO 30 Minute Reactions at 415°C^a (CAER)

Modified Heavy Distillate ^b	E	E	F	F	G	H	H
Catalyst added	none	SFIO	none	SFIO	none	none	SFIO
Added Fe, wt% Coal ^c	0	1.0	0	1.0	0	0	1.0
Added S, wt% Coal	0	1.5	0	1.6	0	0	1.5
S Added Fe, m/m	N/A	2.6	N/A	2.9	N/A	N/A	2.7
Products, wt% maf Coal							
HC gases	1.1	1.7	1.2	1.7	1.2	1.3	1.6
CO+CO ₂	5.0	4.9	5.2	5.3	4.9	5.2	4.7
Oils	36.4	45.1	55.7	47.9	45.8	53.5	49.7
PA+A	56.2	52.6	43	56.5	52.9	46.6	49.5
IOM	1.3	-4.3	-5.1	-11.4	-4.8	-6.6	-5.5
THF Conv	98.7	104.3	105.1	111.4	104.8	106.6	105.5
mg H ₂ /g maf Coal	43.2	N/A ^d	43.9	46.2	42.6	45.0	48.9
Run number	2-167-2	3-074-1	3-159-1	3-168-1	3-161-3	3-159-3	3-160-4

a) 30 minute reaction time, 3 g Black Thunder coal, 5.4g WRO, 1000 psig H₂ cold.

b) E= Run 262 heavy distillate; F= hydrotreated heavy distillate; G= baseline dewaxed distillate
H= hydrotreated dewaxed heavy distillate #20502.

c) Based on 63% Fe in SFIO

d) Not available, hydrogen added to gas sample.

The highest conversion is with the SFIO added at 1% iron on coal in the hydrogenated heavy distillate, while the highest oil yield is from the run with the hydrotreated distillate without the SFIO. Added SFIO seems to improve oil yield for the original heavy distillate and the hydrogenated heavy distillate (samples E and F). The hydrotreated dewaxed distillate (sample H) also has a high coal conversion and high oil yield. Also note that with SFIO the hydrocarbon gas yield is slightly higher than that from thermal experiments.

Table 10 presents liquefaction results at 415°C, for 60 minutes of reaction time to test the effect of solvent modification on liquefaction conversions for the more refractory residual material which is present in the WRO. Each treated distillate produced significantly more oil and much higher coal conversions than the original heavy distillate (solvent E). The oil yield increased from 51% for solvent E to 66% for the hydrogenated dewaxed distillate (solvent H).

Table 10: Liquefaction of Black Thunder Coal in Modified WRO 60 minute reactions at 415°C^a (CAER)

Modified Heavy Distillate^b	E	E	F	G	H
Catalyst added	none	SFIO	none	none	none
Added Fe, wt% Coal^c	0	1.0	0	0	0
Added S, wt% Coal	0	1.6	0	0	0
S Added Fe, m/m	N/A	2.7	N/A	N/A	N/A
Products, wt% maf Coal					
HC gases	1.9	1.2	1.8	2.0	2.2
CO+CO₂	5.0	5.0	5.7	5.6	5.8
Oils	51.3	56.7	65.2	62	66
PA+A	48.4	45.0	38.5	44.8	37.6
IOM	-6.6	-7.9	-11.2	-14.4	-11.6
THF Conv	106.6	107.9	111.2	114.4	111.6
mg H₂/g maf Coal	57.0	54.8	52.1	49.5	48.8
Run number	2-139-1 2-167-1 2-337-1	2-272-1	3-158-3	3-165-1	3-159-2

a) 60 minute reaction time, 3 g Black Thunder coal, 5.4g WRO, 1000 psig H₂ cold.

b) E= Run 262 heavy distillate; F= hydrotreated heavy distillate; G= baseline dewaxed distillate
H= hydrotreated dewaxed heavy distillate #20502.

c) Based on 63% Fe in SFIO

Future Work

The results from CAER show significantly improved coal conversions and oil formation in the microautoclave experiments with dewaxing and hydrotreating the heavy distillate portion of the WRO. Future experiments will be performed to optimize these solvent improvements and efforts will also include resid hydrogenation (hydrotreating a "light SRC" portion of the recycle stream) to test the effect of boiling point on the efficacy of solvent dewaxing and hydrotreating.

Miscellaneous

A quarterly program review meeting was held in Library PA on June 29 and 30, 1993. Discussion centered around resid conversion measurements and base case coal conversion. Consultation and discussion with CONSOL and CAER concerning microautoclave design and operation was very helpful in examining the possible mass transfer limitations in the microautoclave reactors. Additionally, Sandia's Black Thunder coal sample was repackaged by CONSOL and shipped back to Sandia in April.

References

1. F. Mondragon and K. Ouchi, FUEL, January 1984, Vol 63,61-65.
2. H. E. Schwartz, R. G. Brownlee, M. M. Boduszynski, and F. Su, Anal. Chem. 1987, 59, 1393-1401.

SECTION FOUR

LDP ASSOCIATES

:

LDP ASSOCIATES

**Michael Peluso, Proprietor
908-752-5581**

**603 Fairview Ave.
Piscataway, N.J. 08854**

August 10, 1993

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

Dear Ed:

Subject: QUARTERLY PROGRESS REPORT FOR APRIL THRU JUNE 1993

During the quarter ending June 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

A revision of the baseline economic assessment (W'ville Run #263J) to account for the change to an SO₃-Free Ash basis, was completed. The baseline study (See Attachment #1) serves as the reference against which the results of this program will be compared.

The revision of the Base Case to an SO₃-Free Ash basis was made because it was revealed that none of the material and elemental balances for Wilsonville sub-bituminous coal runs #249, #251, #258, #260, #262 & #263 were done on an SO₃-Free Ash basis (1). Ironically, Catalytic Inc. had stated in their Wilsonville Run #246 report (2) that: "This SO₃ correction has been found to be necessary at Wilsonville and other coal liquefaction facilities whenever high-calcium coals are processed." In accordance with item #2 of the "Specific Points" of the March '93 Quarterly Meeting Conference Record (3), it was necessary to revise the Base Case Assessment which had been previously completed. Since a redo of the Base Case was necessary, it was decided to use CONSOL's analysis of the Black Thunder coal (see Attach. #1, Tables 1 & 1A) as the basis for the Revised Base Case (RBC) because all the experimental work done in this program uses this same coal.

One important reason for revising the base case is the overstatement of MAF coal conversion based when using the as-is ash basis. The RBC MAF coal conversion is 92.0% as compared to the 93.6% MAF coal conversion rate reported on the ash as-is basis (4). Likewise, individual reactor resid + IOM conversions are higher on the ash as-is basis (22.4% vs 23.2% for the first stage reactor and 17.1% vs 17.6% for the second stage) (4).

Once the parameters for Wilsonville Run #263J had been determined on an SO₃-Free Ash basis, the RBC was developed using: (a) the Consol coal analysis, (b) a 92.0% MAF coal conversion and (c) 6.7% lower reactor space velocities in order to achieve the desired all-distillate product slate. The RBC Resid, IOM and SO₃-Free Ash balances per 100 lb. of MF coal are shown in Attach. #1, Figure 1A.

REFERENCES

- (1) G.A. Robbins (CONSOL) to M. Peluso, May 14, 1993.
- (2) Catalytic, Inc., Wilsonville Advanced Coal Liquefaction R & D Facility, Technical Progress Report, "Run 246 with Wyodak Coal", DE86-000566, August 1985, p.52.
- (3) F. Derbyshire to Meeting Participants, April 28, 1993.
- (4) Southern Electric International, Inc., Advanced Coal Liquefaction R & D Facility, Wilsonville, Alabama, "Technical Progress Report Run 263 with Black Thunder Mine Subbituminous Coal and Dispersed Molybdenum Catalysts", Document No. DOE/PC/90033-23, December 1992, p.53.

ASSESSMENT OF IMPROVED COAL CONVERSION CASE

This was the first alternate case selected for comparison with the above Base Case. The technical and economic parts of the Revised Improved Coal Conversion Case (RICC), incorporating the SO₃-Free Ash basis, were also completed (See Attachment #2). A key basis for the RICC is an increase in MAF coal conversion to 96.0% from 92.0% in the RBC. The economic assessment indicates that the RICC has a \$93.4 million capital cost advantage and a \$10.1 million/year operating cost advantage over the RBC.

UPGRADING OF DEWAXED OIL & SLACK WAX

No activity.

FLUID COKING

A meeting was held with Syamal Poddar of Bechtel in an attempt to reconcile their significantly lower total plant investment (\$196.7 million) when replacing the ROSE unit with a Fluid Coker in their DOE sponsored study with Illinois Coal feed. Poddar stated that the ROSE case was superior to the Fluid Coker case due to the significantly higher liquid product rate in the ROSE case. Bechtel's overall material balances for these two cases confirm this statement. However, Bechtel's material balance around the Fluid Coker results in a much lower than anticipated liquid product yield. Further investigation and clarification of this issue is required.

DOE CONTRACTORS CONFERENCE

At the request of S. Lee of PETC, an abstract of a paper entitled, "Economic Assessment of Solvent Dewaxing of the Distillate Recycle Solvent in the Liquefaction of Sub-Bituminous Coal", was prepared and submitted. This paper is part of the "Focused Research for Improved Economics" workshop session, which is scheduled to precede the regular DOE Contractors Conference.

If you have any questions or comments on the above, please contact me.

Very truly yours,

A handwritten signature in black ink that reads "Michael Peluso". The signature is fluid and cursive, with a long horizontal stroke at the end.

Michael Peluso
LDP Associates

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

ATTACHMENT #1

BLACK THUNDER LIQUEFACTION STUDY
REVISION OF BASE CASE TO
SO₃ - FREE ASH BASIS

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

TABLE 1
BLACK THUNDER COAL PROPERTIES (REVISED)

ELEMENTALS, WT% MF

• CARBON	70.32
• HYDROGEN	4.68
• OXYGEN	17.92
• NITROGEN	1.04
• SULFUR	0.50
• SO ₃ Free ASH	<u>5.54</u>
Total	100.00

MOISTURE, AS-RECEIVED 30%

HEATING VALUE, Btu/lb.

•LHV, As-Rec'd	7,939
•HHV, MF	11,760

TABLE 1A
BLACK THUNDER COAL LIQUEFACTION STUDY
HYBRID CONFIGURATION - W'VILLE RUN# 263J
DIFFERENCES IN COAL & ASH CONCENTRATE COMPOSITION
BETWEEN ORIGINAL & REVISED BASE CASES

<u>MF COAL (Wt. %)</u>	<u>ORIGINAL BASE CASE</u>	<u>REVISED BASE CASE</u>
• Carbon	68.50	70.32
• Hydrogen	4.80	4.68
• Oxygen (By Diff.)	18.90	16.77 [17.92]
• Nitrogen	1.00	1.04
• Sulfur	0.50	0.50
• Ash	<u>6.30</u>	<u>6.69</u> [5.54]
Total	100.00	100.00
• HHV, (Btu/lb.)	11,495	11,850 [11,760]

[] = After Correction to SO₃ - Free Ash Basis

<u>ASH CONCENTRATE (Wt. %)</u>		
• Carbon	53.94	55.05
• Hydrogen	3.29	3.36
• Oxygen	2.00	6.70
• Nitrogen	0.83	0.84
• Sulfur	2.80	2.85
• Ash	<u>37.14</u>	<u>31.20</u>
Total	100.00	100.00

<u>MAF COAL CONVERSION</u>	93.6	92.0
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TABLE 1C

REVISED BASE CASE (263J with Ash on SO₃-Free Basis) : RESID + MAF COAL + IOM CONVERSION BALANCE

30% MF Coal Conc in Slurry.

FIRST STAGE					
SV _{new} / SV _{base}	1st Stg Conv.(base)	[(1-C) / C] base	[(1-C) / C] new	1st Stg Conv.(new)	1 - C ₁
0.932830	0.22418	3.460701	3.228246	0.236505	0.7634953
SECOND STAGE					
SV _{new} / SV _{base}	2nd Stg Conv.(base)	[(1-C) / C] base	[(1-C) / C] new	2nd Stg Conv.(new)	1 - C ₂
0.932830	0.170854	4.852950	4.526978	0.180931	0.8190693
	(1-C ₁)x(1-C ₂)	(1-C ₁)x(1-C ₂)			
	Required	Calculated	Difference		
	0.625356	0.625356	0.000000		
		IN	OUT	CONVERTED	% CONVERTED
	lb / 100 lb MF Coal	214.422	134.090	80.332	37.464
	MAF Coal	94.460			
	Recycle Resid	94.499	94.499		
	Recycle IOM	25.463	25.463		
	Resid in Ash Conc.		6.571		
	IOM in Ash Conc.		7.557		
	Total =	214.422	134.090		

MF 5/21/93

uf
5/24/94

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

INPUTS:

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

OUTPUTS:

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

TABLE 3
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED C4+ DISTILLATE PRODUCT PROPERTIES

• YIELD, Wt% on MF COAL	59.545
• PRODUCTION RATE, BPSD	50,000
• DENSITY, Degrees API	26.5
• HIGHER HEATING VALUE, Btu/lb.	19,424
• ELEMENTALS, Wt. %:	
- CARBON	86.08
- HYDROGEN	11.37
- OXYGEN	1.93
- NITROGEN	0.58
- SULFUR	<u>0.04</u>
	Total = 100.00
• CUTS, Wt. % :	
- IBP to 350 F	20.5
- 350 to 450 F	13.1
- 450 to 650 F	38.0
- 650 to EP (800F)	<u>28.4</u>
	Total = 100.0

TABLE 4
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED FIRST STAGE REACTOR PARAMETERS (Revised)

- Six Once-Thru Reactors in Parallel,
9.55 Feet ID. (12" Wall Thk.) x 75 Feet Height
- 647 Tons Each, 3,882 Tons Total
- MF Coal Concentration in Slurry = 30%
- Process Solvent Composition :
 - Distillate 39.10%
 - Resid 40.50%
 - UC 10.91%
 - Ash 9.49%
- Liquefaction Additives :
 - Dispersed Moly (Molyvan L) @ 100 ppm on MF Coal
 - Iron Oxide + H₂S @ 0.7% Fe on MF Coal
- Temperatures :
 - Preheater Outlet = 757° F
 - Reactor Inlet / Outlet = 762° F / 873° F
 - Reactor Effective = 840° F
 - Reactor Design = 898° F
- Operating/ Design Pressure = 2,910 / 3,200 psig
- Average Hydrogen Partial Pressure = 2,185 psig
- Inlet / Outlet Hydrogen Purity = 89.0 / 61.4 Vol. %
- H₂ Consumed / Available = 146.3 / 378.4 MMSCFD
- Actual / Nominal Slurry Residence Time = 17.6 / 34.1 Min.
- MAF Coal Conversion = 88.4%
- Resid + IOM Conversion = 23.65%

TABLE 5
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMAT'D SECOND STAGE REACTOR PARAMETERS (Revised)

- Six Ebullated Reactors in Parallel,
11.78 Feet ID. (11.4" Wall Thk.) x 37 Feet Height
- 401 Tons Each, 2,406 Tons Total
- Criterion (Shell) 324 Ni-Moly Catalyst
- Slurry Feedrate = 38,585 T/D
- MAF Coal Conversion In / Out = 88.4 / 92.0 %
- Resid + UC Conversion = 18.09%
- Space Velocity = 312.9 lb. Feed / Hr.- ft³ Catalyst
- Temperatures:
 - Slurry @ Reactor Inlet = 685°F
 - Gas @ Reactor Inlet = 800°F
 - Reactor Inlet = 795°F
 - Reactor Outlet = 825°F
 - Reactor Effective = 810°F
 - Reactor Design = 850°F
- Operating / Design Pressure = 2,760 / 3,035 psig
- Average Hydrogen Partial Pressure = 2,220 psig
- Inlet / Outlet Hydrogen Purity = 89.5 / 71.6 Vol. %
- H₂ Consumed / Available = 146.3 / 420.3 MMSCFD
- Total Catalyst Inventory = 554,900 lbs.
- Catalyst Replace't Rate = 19.7 T/D, (3 lb./ton MF)

TABLE 6
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED DEASHING UNIT PARAMETERS (Revised)

- MAF Coal Conversion = 92.0%
- Flowrates, T/SD :
 - Vacuum Bottoms Feed = 5,066
 - Makeup DAS = 64
 - Clean Resid Product = 2,358
 - Ash Concentrate = 2,772
- Organic Rejection = 14.5% of MF Coal
- Energy Rejection = 17.3% of Coal HHV

TABLE 7
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
OVERALL UPGRADING YIELDS (Revised)

INPUTS (Wt.% on C₄+ Distillate):

• C ₄ + DISTILLATE	100.00
• HYDROGEN	<u>2.22</u>

Total = 102.22

OUTPUTS:

• WATER	2.17
• HYDROGEN SULFIDE	0.04
• AMMONIA	0.71
• C ₁ to C ₃ GASES	3.78
• C ₄ 's	11.79
• LIGHT NAPHTHA	9.06
• REFORMATE	<u>74.67</u>

Total = 102.22

FIGURE 4
 BLACK THUNDER LIQUEFACTION STUDY
 UPGRADING UNITS SIMPLIFIED BLOCK FLOW DIAGRAM
 REVISED BASE CASE (SO₃ Free Ash & W'ville Run # 263J)

FIGURE 5
BLACK THUNDER LIQUEFACTION STUDY - HYBRID MODE
SIMPLIFIED BLOCK FLOW DIAGRAM - CONCEPTUAL COMMERCIAL PLANT
REVISED BASE CASE (SO₃-Free Ash, Wilsonville Run # 263J)

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

HYDROGEN BALANCE (MMSCFD):

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

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

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

**TABLE 9A
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
ELECTRICAL POWER REQUIREMENTS**

<u>UNIT</u>	<u>MEGAWATTS</u>
COAL GRINDING	15.7
COAL SLURRY PREPARATION & DRYING	2.0
FIRST STAGE REACTION SYSTEM	15.5
SECOND STAGE REACTION, LETDOWN & VACUUM FRACTIONATION SYSTEMS	2.9
ROSE UNIT	1.7
RECYCLE HYDROGEN RECOVERY & COMPRESS'N	16.1
GASIFICATION SYSTEMS	19.8
OXYGEN PLANT	91.0
STEAM REFORMER	1.6
MAKEUP HYDROGEN COMPRESSION	45.0
UPGRADING UNITS	12.0
STEAM GENERATION	1.9
OFFSITES & UTILITIES	28.7
DISTRIBUTION LOSSES	7.6
IN-PLANT PRODUCTION	<u>- 13.7</u>
TOTAL = 247.8	

TABLE 9B
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
THERMAL EFFICIENCY (Revised)

• INPUTS (Billions of Btu/D):

- MF COAL, 16,545 T/D	389.1
- MAKEUP DAS	2.4
- SULFIDING AGENTS	0.8
- ELECTRICAL POWER*, 248 MW	<u>59.5</u>

Total = 451.8

* Thermal Equivalent @ 10,000 btu/ kw-hr

• OUTPUT (Billions of Btu/D):

- GASOLINE, 50,000 BPSD	281.9
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OVERALL THERMAL EFFICIENCY = 62.4 %

LIQUEFACTION UNIT ONLY = 70.7%

TABLE 10
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
PROCESS UNIT INVESTMENT (Revised)

<u>UNIT</u>	<u>INVESTMENT</u> (Millions of Mid '92 \$: Wyoming Location)
COAL GRINDING	34
COAL SLURRY PREPARATION & DRYING	76
FIRST STAGE REACTION SYSTEM	290
SECOND STAGE REACTION SYSTEM	123
LETDOWN SYSTEM	38
VACUUM FRACTIONATION	142
ROSE UNIT	46
RECYCLE HYDROGEN RECOVERY & COMPRESS'N	114
ASH CONCENTRATE GASIFICATION SYSTEM	166
COAL GASIFICATION SYSTEM	317
OXYGEN PLANT	169
STEAM REFORMER	85
MAKEUP HYDROGEN COMPRESSION	112
UPGRADING UNITS	<u>480</u>

TOTAL PUI = 2,192

TABLE 11
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
OFFSITE UNITS INVESTMENT (Revised)

<u>UNIT</u>	<u>INVESTMENT</u> <u>(Millions of Mid '92 \$:Wyoming Location)</u>
LIQUID TANKAGE	194
ELECTRICAL DISTRIBUTION	187
SEWERS AND WASTEWATER TR'TMENT	178
SITE DEVELOPMENT	134
COAL RECEIVING & STORAGE	118
INTERCONNECTING PIPING	105
WATER SYSTEMS	103
BUILDINGS	61
FIRE SYSTEMS	41
STEAM GENERATION & BFW PREP'N	36
SULFUR PLANT	28
FLARE SYSTEM	24
RAILROAD & TRUCK FACILITIES	24
SOUR WATER TREATING	19
OTHER UNITS (6)	<u>53</u>

TOTAL OFFSITES = 1,305

TABLE 12
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
TOTAL PLANT COST (Revised)

	<u>INVESTMENT (\$ Millions)</u>
PROCESS UNITS	2,192
OFFSITE UNITS	1,305
ESTIMATING ALLOWANCE @ 15%	<u>524</u>
TOTAL PLANT COST (Mid '92\$, Wyoming) =	4,021

TABLE 13
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
TOTAL CAPITAL REQUIREMENT (Revised)

	<u>INVESTMENT (\$ Millions)</u>
TOTAL PLANT COST	4,021
INVENTORY CAPITAL	121
PRE-PRODUCTION COSTS	167
INITIAL CATALYSTS & CHEMICALS	<u>64</u>

TCR (Mid '92\$, Wyoming) = 4,373

\$/BPSD of Gasoline = 87,460

TABLE 14
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
ANNUAL OPERATING COSTS (Revised)

	<u>COST (\$ Millions/Yr.)</u>
MF COAL: 17,004T/D @ \$10/T	52.94
PURCHASED ELECTRICAL POWER, 248 MW @ 4¢/ Kw-hr.	76.12
LIQUEFACTION SYSTEM ADDITIVES :	
- Iron + Sulfiding Agents @ \$0.072/lb.	8.67
- Dispersed @ \$3.20/ lb.	32.34
- Supported @ \$3/lb.	37.90
UPGRADING UNITS CATALYSTS & CHEM.	12.00
OTHER CATALYSTS & CHEMICALS	21.36
OPERATING LABOR	16.27
MAINTENANCE @ 2% of TPC + ICC	81.71
INSURANCE & LOCAL TAXES @ 1.5% of TPC + ICC	61.29
ADMINISTRATION & OPERATIONS SUPPORT	<u>12.22</u>
	AOC = 412.82

OPERATING COST = \$ 25.80/ Bbl. of Gasoline

ATTACHMENT #2

**BLACK THUNDER LIQUEFACTION STUDY
REVISION OF IMPROVED COAL CONVERSION CASE
TO AN SO₃ - FREE ASH BASIS**

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

**BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION
BASIS FOR IMPROVED COAL CONVERSION CASE**

- **Reduce IOM in Ash Concentrate by 50%
(96.0% MAF coal conversion vs 92.0% in base case)**
- **Keep Distillate, Resid & Ash in Recycle Process Solvent Constant. IOM in Recycle Solvent Decreases by 50%.**
- **Assume Solids Concentration in Ash Concentrate Remains the Same as in Base Case (67.08%). As a Result, the Amount of Resid in the Ash Concentrate Decreases. The same Assumption reduces the Deashing Solvent in the Ash Concentrate, thereby lowering the Makeup Deashing Solvent Rate.**
- **Convert Additonal IOM & Resid to Distillate & Lighter Products by Lowering Reactor Space Velocities to Compensate for Higher Conversion Requirements.**
- **Assume First Order Kinetics Adequately Describes the Resid + IOM Conversion vs Space Velocity Relationship.**

TABLE 1
BLACK THUNDER COAL PROPERTIES (REVISED)

ELEMENTALS, WT% MF

• CARBON	70.32
• HYDROGEN	4.68
• OXYGEN	17.92
• NITROGEN	1.04
• SULFUR	0.50
• SO ₃ Free ASH	<u>5.54</u>
Total	100.00

MOISTURE, AS-RECEIVED 30%

HEATING VALUE, Btu/lb.

•LHV, As-Rec'd	7,939
•HHV, MF	11,760

REVISED IMPROVED COAL CONVERSION CASE (263J with Ash on SO₃-Free Basis) : RESID + MAF COAL + IOM CONVERSION BALANCE .
 50% Reduction of IOM in Ash Conc (96.0 vs 92.06 MAF Coal Conv.).

FIRST STAGE					
SV _{new} / SV _{base}	1st Stg Conv.(base)	[(1-C) / C] base	[(1-C) / C] new	1st Stg Conv.(new)	1 - C ₁
0.771740	0.22418	3.460701	2.670762	0.272423	0.727577
Vs 0.932830 in Revised Base Case (a 17.27% Reduction in SV vs RBC)					
SECOND STAGE					
SV _{new} / SV _{base}	2nd Stg Conv.(base)	[(1-C) / C] base	[(1-C) / C] new	2nd Stg Conv.(new)	1 - C ₂
0.771740	0.170854	4.852950	3.745216	0.210739	0.7892614
	(1-C ₁)x(1-C ₂)	(1-C ₁)x(1-C ₂)			
	Required	Calculated	Difference		
	0.574248	0.574248	0.000000		
		IN	OUT	CONVERTED	% CONVERTED
	lb / 100 lb MF Coal	201.688	115.819	85.869	42.575
	MAF Coal	94.460		80.372	
	Recycle Resid	94.499	94.499		
	Recycle IOM	12.729	12.729		
	Resid in Ash Conc.		4.813		
	IOM in Ash Conc.		3.778		
	Total =	201.688	115.819		

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FIGURE 1B SIMPLIFIED RESID, IOM & ASH BALANCE

REVISED IMPROVED COAL CONVERS'N CASE (SO₃- Free ash basis, WR#263J)

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FIGURE 5
 BLACK THUNDER LIQUEFACTION STUDY - HYBRID MODE
 SIMPLIFIED BLOCK FLOW DIAGRAM - CONCEPTUAL COMMERCIAL PLANT
 REVISED BASE CASE (SO₃-Free Ash, Wilsonville Run # 263J)

↑
 IMPROVED COAL CONV.

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FIGURE 5
BLACK THUNDER LIQUEFACTION STUDY - HYBRID MODE
SIMPLIFIED BLOCK FLOW DIAGRAM - CONCEPTUAL COMMERCIAL PLANT
REVISED IMPROVED COAL CONV. CASE (SO₃-Free Ash, W'ville Run #263J)

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

INPUTS:

• MF COAL	100.000	
• DISPERSED MOLY CATALYST	0.120	(Molyvan L)
• IRON OXIDE	1.000	
• SULFIDING AGENT (H ₂ S)	0.430	
• MAKEUP DAS	0.489	[0.401]
• HYDROGEN	<u>5.906</u>	[6.365]
Total = 107.945		[108.316]

OUTPUTS:

• WATER	12.450	[12.840]
• HYDROGEN SULFIDE	0.310	[0.310]
• AMMONIA	0.630	[0.690]
• CARBON MONOXIDE	0.970	[1.040]
• CARBON DIOXIDE	5.150	[5.540]
• C1 to C3 GASES	7.830	[8.430]
• C4+ DISTILLATE	59.545	[64.050]
• ASH CONCENTRATE	<u>21.060</u>	[15.426]
Total = 107.945		[108.316]

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TABLE 3
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED C4+ DISTILLATE PRODUCT PROPERTIES

• YIELD, Wt% on MF COAL	59.545	[64.050]
• PRODUCTION RATE, BPSD	50,000	
• DENSITY, Degrees API	26.5	
• HIGHER HEATING VALUE, Btu/lb.	19,424	
• ELEMENTALS, Wt.%:		
- CARBON	86.08	
- HYDROGEN	11.37	
- OXYGEN	1.93	
- NITROGEN	0.58	
- SULFUR	0.04	
	Total =	100.00
• CUTS, Wt.% :		
- IBP to 350 F	20.5	
- 350 to 450 F	13.1	
- 450 to 650 F	38.0	
- 650 to EP (800F)	28.4	
	Total =	100.0

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TABLE 4
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED FIRST STAGE REACTOR PARAMETERS (Revised)

- Six Once-Thru Reactors in Parallel,
9.55 [9.33] Feet ID. (12" Wall Thk.) x 75 [85] Feet Height
- 647 [711] Tons Each, 3,882 [4,266] Tons Total
- MF Coal Concentration in Slurry = 30% [31.2]
- Process Solvent Composition :
 - Distillate 39.10% [Same ratio to coal]
 - Resid 40.50% [Same ratio to coal]
 - UC 10.91% [1/2 ratio to coal]
 - Ash 9.49% [Same ratio to coal]
- Liquefaction Additives :
 - Dispersed Moly (Molyvan L) @ 100 ppm on MF Coal
 - Iron Oxide + H₂S @ 0.7% Fe on MF Coal
- Temperatures :
 - Preheater Outlet = 757° F [748]
 - Reactor Inlet / Outlet = 762° F / 873° F [754/876]
 - Reactor Effective = 840° F
 - Reactor Design = 898° F [901]
- Operating/ Design Pressure = 2,910 / 3,200 psig
- Average Hydrogen Partial Pressure = 2,185 psig
- Inlet / Outlet Hydrogen Purity = 89.0 / 61.4 Vol. %
- H₂ Consumed / Available = 146.3 / 378.4 MMSCFD
[146.6 / 372.6]
- Actual / Nominal Slurry Residence Time = 17.6 / 34.1 Min.
[21.1/ 41.5]
- MAF Coal Conversion = 88.4% [91.4]
- Resid + IOM Conversion = 23.65% [27.24]

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TABLE 5
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMAT'D SECOND STAGE REACTOR PARAMETERS (Revised)

- Six Ebullated Reactors in Parallel,
11.78 Feet ID. (11.4" Wall Thk.) x 37 Feet Height [39]
 - 401 [421] Tons Each, 2,406 [2,526] Tons Total
 - Criterion (Shell) 324 Ni-Moly Catalyst
 - Slurry Feedrate = 38,585 T/D [34,002]
 - MAF Coal Conversion In / Out = 88.4 / 92.0 % [91.4/ 96.0]
 - Resid + UC Conversion = 18.09% [21.07]
 - Space Velocity = 312.9 lb. Feed / Hr.- ft³ Catalyst [258.8]
 - Temperatures:
 - Slurry @ Reactor Inlet = 685°F [666]
 - Gas @ Reactor Inlet = 800°F
 - Reactor Inlet = 795°F
 - Reactor Outlet = 825°F
 - Reactor Effective = 810°F
 - Reactor Design = 850°F
 - Operating / Design Pressure = 2,760 / 3,035 psig
 - Average Hydrogen Partial Pressure = 2,220 psig
 - Inlet / Outlet Hydrogen Purity = 89.5 / 71.6 Vol. %
 - H₂ Cons'd / Available = 146.3 / 420.3 MMSCFD [146.6/ 420.0]
 - Total Catalyst Inventory = 554,900 lbs. [591,300]
 - Catalyst Replace't Rate = 19.7 T/D, [18.4] (3 lb./ton MF)
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TABLE 6
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED DEASHING UNIT PARAMETERS (Revised)

- MAF Coal Conversion = 92.0% [96.0]

- Flowrates, T/SD :
 - Vacuum Bottoms Feed = 5,066 [4,181]
 - Makeup DAS = 64 [49]
 - Clean Resid Product = 2,358 [2,342]
 - Ash Concentrate = 2,772 [1,888]

- Organic Rejection = 14.5% of MF Coal [8.86]

- Energy Rejection = 17.3% of Coal HHV [10.9]

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TABLE 7
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
OVERALL UPGRADING YIELDS (Revised)

INPUTS (Wt.% on C₄+ Distillate):

• C ₄ + DISTILLATE	100.00
• HYDROGEN	<u>2.22</u>

Total = 102.22

OUTPUTS:

• WATER	2.17
• HYDROGEN SULFIDE	0.04
• AMMONIA	0.71
• C ₁ to C ₃ GASES	3.78
• C ₄ 's	11.79
• LIGHT NAPHTHA	9.06
• REFORMATE	<u>74.67</u>

Total = 102.22

FIGURE 4
 BLACK THUNDER LIQUEFACTION STUDY
 UPGRADING UNITS SIMPLIFIED BLOCK FLOW DIAGRAM
 REVISED IMPROVED COAL CNVERSION CASE BASED ON
 WILSONVILLE RUN # 263J

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

HYDROGEN BALANCE (MMSCFD):

• CONSUMPTION		
- LIQUEFACTION UNIT	308.8	[309.4]
- UPGRADING	<u>144.2</u>	
Total =	453.0	[453.6]
• PRODUCTION		
- GASIFICATION OF ASH CONC.	108.0	[58.8]
- GASIFICATION OF COAL	196.7	[239.7]
- PRODUCED IN CAT. REFORMING	71.1	
- STEAM REFORMING OF HC GASES	<u>77.2</u>	[84.0]
Total =	453.0	[453.6]

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

• CONSUMPTION		
- SLURRY PREHEATER	971	[844]
- STEAM REFORMER	611	[665]
- CAT. REFORMER	661	
- DISTILLATE HYDROPROCESSING	217	
- VACUUM UNIT	149	[141]
- GASIFICATION COAL, DRYING	148	[181]
- ROSE UNIT	97	[80]
- SULFUR RECOVERY UNIT & MISC.	<u>20</u>	
Total =	2,874	[2,809]
• PRODUCTION		
- LIQUEFACTION OFF GAS	2,010	
- DISTILLATE HYDRO. OFF GAS	1,553	
- CAT. REFORMING OFF GAS	<u>57</u>	
Sub-Total =	3,620	
- STEAM REFORMING FEED	<u>- 746</u>	[- 811]
Total =	2,874	[2,809]

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TABLE 9A
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
ELECTRICAL POWER REQUIREMENTS

<u>UNIT</u>	<u>MEGAWATTS</u>	
COAL GRINDING	15.7	[- 1.1]
COAL SLURRY PREPARATION & DRYING	2.0	[- 0.2]
FIRST STAGE REACTION SYSTEM	15.5	[- 1.7]
SECOND STAGE REACTION, LETDOWN & VACUUM FRACTIONATION SYSTEMS	2.9	[- 0.3]
ROSE UNIT	1.7	[- 0.3]
RECYCLE HYDROGEN RECOVERY & COMPRESS'N	16.1	[- 0.6]
GASIFICATION SYSTEMS	19.8	[- 0.3]
OXYGEN PLANT	91.0	[- 6.1]
STEAM REFORMER	1.6	[+ 0.1]
MAKEUP HYDROGEN COMPRESSION	45.0	[+ 3.9]
UPGRADING UNITS	12.0	
STEAM GENERATION	1.9	[- 0.6]
OFFSITES & UTILITIES	28.7	
DISTRIBUTION LOSSES	7.6	[- 0.2]
IN-PLANT PRODUCTION	<u>- 13.7</u>	[+ 13.7]
TOTAL = 247.8		[+ 6.3]

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TABLE 9B
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
THERMAL EFFICIENCY (Revised)

• INPUTS (Billions of Btu/D):

- MF COAL, 16,545 T/D [16,359]	389.1	[384.7]
- MAKEUP DAS	2.4	[1.8]
- SULFIDING AGENTS	0.8	
- ELECTRICAL POWER*, 248 MW [254]	<u>59.5</u>	[61.0]
	Total = 451.8	[448.3]

* Thermal Equivalent @ 10,000 btu/ kw-hr

• OUTPUT (Billions of Btu/D):

- GASOLINE, 50,000 BPSD	281.9
-------------------------	-------

OVERALL THERMAL EFFICIENCY = 62.4 % [62.9]

LIQUEFACTION UNIT ONLY = 70.7% [71.3]

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TABLE 10
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
PROCESS UNIT INVESTMENT (Revised)

<u>UNIT</u>	<u>INVESTMENT</u> (Millions of Mid '92 \$:Wyoming Location)	
COAL GRINDING	34	[- 1.7]
COAL SLURRY PREPARATION & DRYING	76	[- 4.0]
FIRST STAGE REACTION SYSTEM	290	[- 11.6]
SECOND STAGE REACTION SYSTEM	123	[- 0.2]
LETDOWN SYSTEM	38	[- 2.0]
VACUUM FRACTIONATION	142	[- 6.9]
ROSE UNIT	46	[- 5.7]
RECYCLE HYDROGEN RECOVERY & COMPRESS'N	114	[- 5.3]
ASH CONCENTRATE GASIFICATION SYSTEM	166	[- 11.3]
COAL GASIFICATION SYSTEM	317	
OXYGEN PLANT	169	
STEAM REFORMER	85	
MAKEUP HYDROGEN COMPRESSION	112	
UPGRADING UNITS	<u>480</u>	
TOTAL PUI = 2,192		[- 48.7]

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TABLE 11
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
OFFSITE UNITS INVESTMENT (Revised)

<u>UNIT</u>	<u>INVESTMENT</u>	
	<u>(Millions of Mid '92 \$:Wyoming Location)</u>	
LIQUID TANKAGE	194	[- 5.5]
ELECTRICAL DISTRIBUTION	187	[- 3.9]
SEWERS AND WASTEWATER TREATMENT	178	[- 0.6]
SITE DEVELOPMENT	134	[- 1.0]
COAL RECEIVING & STORAGE	118	[- 1.1]
INTERCONNECTING PIPING	105	[- 4.1]
WATER SYSTEMS	103	[- 1.5]
BUILDINGS	61	
FIRE SYSTEMS	41	[- 0.2]
STEAM GENERATION & BFW PREP'N	36	[- 4.4]
SULFUR PLANT	28	[- 1.1]
FLARE SYSTEM	24	[- 1.1]
RAILROAD & TRUCK FACILITIES	24	
SOUR WATER TREATING	19	[- 0.7]
OTHER UNITS (6)	<u>53</u>	[- 1.3]
TOTAL OFFSITES = 1,305 [- 26.5]		

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TABLE 12
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
TOTAL PLANT COST (Revised)

	<u>INVESTMENT (\$ Millions)</u>	
PROCESS UNITS	2,192	[- 48.7]
OFFSITE UNITS	1,305	[- 26.5]
ESTIMATING ALLOWANCE @ 15%	<u>524</u>	[- 11.3]
TOTAL PLANT COST (Mid '92\$, Wyoming) =	4,021	[- 86.5]

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TABLE 13
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
TOTAL CAPITAL REQUIREMENT (Revised)

	<u>INVESTMENT (\$ Millions)</u>	
TOTAL PLANT COST	4,021	[- 86.5]
INVENTORY CAPITAL	121	[- 0.8]
PRE-PRODUCTION COSTS	167	[- 2.6]
INITIAL CATALYSTS & CHEMICALS	<u>64</u>	[- 3.5]
TCR (Mid '92\$, Wyoming) = 4,373		
		[- 93.4]
	\$/BPSD of Gasoline = 87,460	[- 1,870]

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TABLE 14
BLACK THUNDER LIQUEFACTION STUDY
HYBRID CONFIGURATION - RUN# 263J
ANNUAL OPERATING COSTS (Revised)

	<u>COST (\$ Millions/Yr.)</u>	
MF COAL: 17,004T/D @ \$10/T	52.94	[- 0.59]
PURCHASED ELECTRICAL POWER, 248 MW @ 4¢/ Kw-hr.	76.12	[+ 1.94]
LIQUEFACTION SYSTEM ADDITIVES :		
- Iron + Sulfiding Agents @ \$0.072/lb.	8.67	[- 0.61]
- Dispersed @ \$3.20/ lb.	32.34	[- 2.27]
- Supported @ \$3/lb.	37.90	[- 2.66]
UPGRADING UNITS CATALYSTS & CHEM.	12.00	
OTHER CATALYSTS & CHEMICALS	21.36	[- 2.71]
OPERATING LABOR	16.27	
MAINTENANCE @ 2% of TPC + ICC	81.71	[- 1.80]
INSURANCE & LOCAL TAXES @ 1.5% of TPC + ICC	61.29	[- 1.35]
ADMINISTRATION & OPERATIONS SUPPORT	<u>12.22</u>	
	AOC = 412.82	[- 10.05]

OPERATING COST = \$ 25.80/ Bbl. of Gasoline [- 0.63]

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