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ADVANCED DIRECT LIQUEFACTION CONCEPTS for PETC GENERIC UNITS

Quarterly Technical Progress Report for Period October 1992 through December 1992

by

University of Kentucky
Center for Applied Energy Research

Sandia National Laboratories

CONSOL Inc.

LDP Associates

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INDEX

SUMMARY

TASK 1.1 LABORATORY SUPPORT (UK/CAER)

The reactivity of the THF insoluble fraction of the ashy resid component of Wilsonville recycle oil (WRO) during liquefaction of Black Thunder coal in tetralin was determined at 415°C and 60 minutes. The liquefaction runs were made by combining this material with Black Thunder coal at the same ratio used in the WRO coal runs. THF conversion and product distribution from liquefaction in tetralin in the presence of the THF insoluble fraction of the ashy resid were similar to results from liquefaction in WRO. THF conversion was greater than 100% with an oil yield that was somewhat higher than in WRO. Differences in HC gas yield and H_2 consumption were slight, while conversion and product distribution from liquefaction of Black Thunder coal in tetralin or in the WRO distillate were quite different. In both these solvents the 85-86% THF conversions were less than for runs in which the THF insoluble fraction of the ashy resid was present. This establishes that the THF insoluble fraction of the ashy resid is the reactive fraction of the WRO.

A sample of molybdenum free V-1067 from Wilsonville Run 260 was used to check the effect of liquefaction of Black Thunder coal in a molybdenum-free WRO. THF conversion in this solvent was essentially the same as for the Mo-containing Run 262 WRO. However, oil yield and hydrogen consumption of the Mo containing WRO was higher than in the Mo-free solvent which suggests a catalytic influence of Mo in the Run 262 WRO. Therefore, catalytic effects that have been observed in these studies have to be superimposed upon the background catalytic effect due to the presence of the molybdenum in the ashy resid.

TASK 1.2 LABORATORY SUPPORT (CONSOL)

Nine hydrogenated oil samples were received from Sandia. Proton distributions, phenolic -OH concentrations and solvent qualities were determined on each of these samples. Hydrogenation consistently improved the measured solvent quality of both the feed distillate and the dewaxed oils. Overall, the combination of dewaxing and hydrogenation increased the V-1074 distillate solvent quality from 64% to 90%.

An error in the moisture determination of the Indiana V coal used in the CONSOL solvent quality measurement resulted in errors of 0.6 to 1.4%. The corrected solvent quality results for all previously reported work are included in this report.

TASK 1.3 LABORATORY SUPPORT (SANDIA)
Characterization of both dewaxed and hydrogenated dewaxed solvent using capillary gas chromatography showed an increase in hydrogenated product peaks and a decrease in parent aromatic peaks. Samples were screened for nitrogen and sulfur removal during hydrotreating. Catalyst coking and deactivation using elemental analysis and hydrogenation activity testing were performed; the latter using a batch microautoclave test to evaluate catalyst hydrogenation activity. Reaction products from these tests were measured by high resolution gas chromatography.

TASK 2.1.1 CO PRETREATMENT (UK/CAER)
A parametric study of the CO pretreatment reaction using Black Thunder coal was conducted at CO pressures from 300-800 psig, NaOH concentrations from 0.02-0.33 M and temperatures from 250-300°C. Each variable was examined at both high and low levels for yield of water insoluble product, THF conversion, PA+A yield, water-gas-shift (WGS) conversion, and H_2 consumption. Temperature has a significant impact on the reaction increasing conversion to both THF and water-soluble products. This sensitivity to temperature is far greater for coal solubilization than sensitivity to CO partial pressure and NaOH concentration. At 800 psig CO, THF conversion using either 0.02 or 0.33 M NaOH is 32%. This shows that the concentration of NaOH can be reduced from 4.5% to 0.25% (maf coal basis) without compromising the

effect of pretreatment. Consistent with our earlier findings with Clovis Point Wyodak coal, greater than 90% of the converted products of the Black Thunder coal reports to the PA+A fraction.

The amount of H_2 consumption, that is, the amount of H_2 that was not accounted for in the gas analysis, is much higher at 800 psig CO than at the lower CO pressures. It also appears that CO conversion plateaus at approximately 50%. In a separate two hour coal pretreatment run, CO conversion increased by only 5% during the second hour. THF conversions observed at 250°C were low. Optical microscopic analysis of these samples confirmed that no significant structural changes occurred during the pretreatment.

A number of scale-up reactions of the pretreatment process with Black Thunder coal were carried out in a one-liter stirred autoclave equipped with a hot-charge tank to inject the coal slurry into the reactor at reaction temperature. The yields of water insoluble products from the NaOH and Na_2CO_3 experiments were on the order of 85 ± 1 wt% maf coal which corresponds to greater than 90% carbon recovery while hydrogen recovery was 98 and 90%, respectively. The atomic H/C ratios of the NaOH and Na_2CO_3 generated H_2O-insoluble products were 0.90 and 0.84, respectively, compared to 0.85 for the raw coal.

TASK 2.1.2.1 PRETREATMENT / DEWAXING - (CONSOL)

Use of methyl ethyl ketone (MEK) and mixtures of MEK with toluene and acetone to dewax Wilsonville V-1074 distillate leads to the production of high yields of dewaxed oil with significantly improved solvent qualities. The waxes obtained from these dewaxings were relatively hard and clean and were easy to purify. Dewaxing the Wilsonville V-1074 distillate in a 45/55 (vol %) MEK/acetone mixture at -35°C produced an 84 wt% yield of dewaxed oil with a solvent quality of 83%. Maximum solvent quality for this oil is attained at about 15 wt% wax removal. Further wax reduction has little effect on the solvent quality of the dewaxed oil.

Densities of the waxes separated from the V-1074 distillate at -5°C and -35°C were measured and their chemical compositions were determined. These measurements were made so that LDP Associates can estimate yields from a catalytic cracker that operates on wax.

The trends obtained in solvent quality testing of the dewaxed oil with Black Thunder coal were similar to those obtained using our standard Indiana V coal. The dewaxed oils are better donor solvents than the feed distillate for the conversion of Black Thunder coal.

TASK 2.1.2.2 - PRETREATMENT / AGGLOMERATION - (CONSOL)

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

Black Thunder coal was agglomerated with coal distillate verifying the performance observed using No. 6 fuel oil. Except for low-pH runs, the overall agglomeration performance of Black Thunder coal has been poor. Adaptation of the benchtop stirred autoclave for agglomeration at elevated pressure and temperatures was completed, and the autoclave was successfully used for agglomeration tests. Tests with Wilsonville distillate and No. 6 fuel oil gave results similar to those obtained in the larger agglomeration vessel with Black Thunder coal. Seven agglomeration runs were made at elevated pressure (150 to 250°C, 50 to 650 psig) with Black Thunder feed coal and a distillate/ashy resid blend as the agglomerating oil. Results ranged from no agglomeration to production of small agglomerates, but no significant resid deashing took place.

A new basis for ash rejection results is being used to reduce uncertainties in physically-cleaned vs. water-solubilized ash rejection and problems with the use of SO_3-containing ash for calculations.

Viscosity - temperature measurements were made on No. 6 fuel oil, Wilsonville V-130 deashed resid, V-1082 ashy resid, and three distillate/ashy resid blends to assist in establishing conditions for agglomeration tests.

TASK 2.1.3 SOLVENT PRETREATMENT (SANDIA)

Heavy distillate V-1074 and V1074 dewaxed at -5°C and -35°C was hydrogenated by the low severity water-gas shift reaction over Shell 324M, Pt HTO (5.4%Pt), and coated NiMo HTO (8.1% Mo, 2.7% Ni) catalysts. Baseline testing with Shell 324M catalyst showed that distillate hydrogen content increased from 9.9% to 10.7% for V-1074, from 8.5% to 9.3% for the -5°C dewaxed solvent, and from 8.0% to 8.9.% for the -35°C dewaxed solvent. Some catalyst deactivation was noticed during the first several hours on-line. These increases in hydrogen content should make notable improvement in coal liquefaction runs. Analysis of the water-gas shift reaction showed that CO conversions were very high at 300°C (> 95%). When the platinum catalyst was used to hydrogenate the -5°C dewaxed distillate only moderate hydrogenation was measured. The relatively mild hydrogenation with the water-gas shift reaction using platinum was probably due to the formation of methane (14 vol% in the product gas at 325°C). The platinum catalyst was very effective at hydrogenating the dewaxed distillate when only hydrogen was used in the gas phase. The distillate was deeply hydrogenated (+1.1% hydrogen) at 325°C using 1000 psig of hydrogen pressure. The platinum catalyst exhibited good activity after two days on-line with the rather "dirty" dewaxed heavy distillate feed.

TASK 2.2.3 MODIFIED REACTOR CONCEPTS (SANDIA)

Several coal liquefaction tests were run using autogenic reaction conditions at 100 psig nitrogen. These tests were used to evaluate the solvent quality of hydrotreated distillates produced with the trickle bed reactor.

Results for two types of solvents were obtained: 1) baseline and hydrogenated V-1074 heavy distillate and 2) baseline and hydrogenated dewaxed V-1074, which was dewaxed at -5°C. Coal conversion and oil yield increased with hydrogenated V-1074. It is anticipated that Wyodak coal conversions at 425°C-450°C using these solvents will reflect the improved solvent quality in the coal conversion measurement. Solvent upgrading using synthesis gas mixtures and the in situ water-gas shift reaction was indicated by the nitrogen and sulfur removal; as much as half of the initial nitrogen can be removed at temperatures as low as 300°C.

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS (UK/CAER)

Liquefaction runs were made with Black Thunder coal with up to 3.2 wt% added Fe as SFIO. The added Fe was superimposed on the 4 wt% iron concentration in the WRO-coal slurry. Mossbauer analysis of several of the residues from the liquefaction runs was used to characterize the form of the iron present in the product. The iron in the residue from the thermal run, to which no iron was added, was mostly $Fe_{1-x}S$ with 1-3% of the Fe as magnetite. Analysis of the coal showed that of the Fe, 80% was present as pyrite with the remaining as jarosite, $(Na,K)Fe_3(SO_4)(OH)_6$, and as clay/ferrous sulfate. The iron in the mineral content of the coal converts quite readily to pyrrhotite. Addition of only 0.19 wt% iron (1900 ppm) as SFIO resulted in an increase in oils, which includes water, of 8.1%. The oils from all of the seven SFIO runs fall in the range from 57-61 wt% with an average of 59.2 wt%. However, the THF conversion in the presence of added SFIO went from 107 wt% up to 108-110% at the highest iron concentration. These increases provide evidence for catalysis by the added SFIO.

Mossbauer analysis showed that 90-95% of the iron present in the WRO was present as pyrrhotite. The observed increase in oil yield due to addition of SFIO is puzzling since pyrrhotite has always been assumed to be the major catalytic component in these reactions. If indeed pyrrhotite is the active component, then adding pyrrhotite to the liquefaction run at the same level as addition of SFIO should give a result comparable to the SFIO. A sample of nanometer size pyrrhotite prepared by a laser pyrolysis method was added at a level of 0.7 and 1.4 wt% Fe to coal slurry. Oil yield increased from 51.3 to 55.8 wt% at the highest pyrrhotite addition level while THF conversion remained steady at 107%. Further studies will be necessary to better define the effect.

Impregnating coal by the incipient wetness (IW) technique is being evaluated as one catalyst alternative. The high dispersion of the metal on and within the coal particle should provide greater contact of the metal with the coal during the liquefaction process. A discussion of the individual steps in the preparation of these materials is presented along with data that have been obtained thus far in this program. The incipient wetness point and its effect on metal carrier and metal dispersion are being evaluated along with the iron oxide formation step and coal drying. Samples made under comparative conditions are being tested to determine the best method of preparation. Among the metal carrier salts that have been evaluated are ferric nitrate and ferric sulfate. Other iron salts plus various molybdenum materials are also being studied. Liquefaction results show that activities of the IW Fe coals give product yields very similar to SFIO. XPS measurements have shown that a major portion of the Fe is present on the surface as FeOOH. Mossbauer analysis of the residue from a 15 minute liquefaction run of IW Fe impregnated coal indicates that the 60-70% of the Fe was present as super-paramagnetic oxide/oxyhydroxide and 30-40% pyrrhotite. The size of the residual oxide/oxyhydroxide suggests that the iron is dispersed as very small particles on the surface of the coal. The dominant factor thus far appears to be the concentration of Fe on the coal. Coal conversion increases with the addition of up to about 0.77 wt% added Fe, where it levels out. Additional Fe up to 1.26 wt% appears not to give any added advantage. Oil yields show the same trend with the molybdenum catalyst, giving a sizable increase over the Fe. Other variations in preparation do not seem to, as yet, provide clear benefit. These results are still incomplete. !

Sulfated iron oxides were prepared by the aqueous precipitation of ammonium ferric sulfate in urea in the presence of sulfate ion. Urea caused the gradual precipitation of the iron within 2 hrs. The filter cake was dried and calcined in air at 500°C for ~1 hr. Various concentrations of molybdenum were added, in the form of ammonium molybdate, to produce a sulfated hematite doped with molybdenum. The average particle sizes were shown to be in the 5 - 30 nm range, with most particles ranging from 15-20 nm. SEM analysis revealed that the particles exist as an agglomeration of very small particles below the resolution of the instrument. Testing is in progress.

Task 2.3.2 - CATALYST STUDIES (CONSOL)

We received a sample of Nanocat superfine iron oxide catalyst from UK/CAER for use in agglomeration tests. The iron oxide we received is untreated, but it is likely that the version eventually used will be modified by some additional treatment. No experimental work was performed on this task.

TASK 2.3.3 CATALYST STUDIES (SANDIA)

Two catalysts were prepared and tested in the solvent pretreatment reactor. A large batch of Hydrous Titanium Oxide (HTO) catalyst was prepared with 5.4 wt% platinum. A molybdenum (8.1 wt%) and nickel (2.7 wt%) on alumina supported HTO catalyst was synthesized by coating the titanate onto Amocat 1C alumina. Molybdenum was ion exchanged onto the coating and nickel was added from solution. Pyrene hydrogenation tests on used catalysts shows the residual activity of platinum HTO is slightly better than that of coated NiMo HTO. High levels of carbon deposition on the commercial alumina supported catalyst indicate that residual hydrogenation activity of this catalyst may be very low.

TASK 2.4.2 SOLIDS SEPARATION BY OIL AGGLOMERATION (CONSOL)

Two approaches were taken to deashing liquefaction bottoms (resid) by agglomeration. These were: 1) to use the resid as the agglomerating oil, and 2) to use the resid as the hydrophobic solid (instead of or along with coal). The first approach is described under Task 2.1.2.2. The second strategy for rejecting ash from ashy resid is to grind it (it is solid at room temperature) and treat it as the agglomeration feed. An oil is used which allows agglomeration at low temperature, so that no melting of the resid occurs. Four runs were made with ball-milled ashy resid as the feed. There was agglomeration, but no substantial deashing in the four runs.

TASK 2.6.1 FLUIDIZED COKING (UK/CAER)

Seven shakedown runs were completed using the CAER 3-inch fluid bed reactor system to test the mechanical system of the modified fluid bed reactor, to develop a tar sample preparation procedure, and produce small "scouting" samples for subsequent analysis by CONSOL. The original 3-inch reactor system was modified for continuous flow operation by adding a screw feeder system. A 3:1 alumina/resid mixture had a high angle of repose and tended to "rat-hole" in the feed hopper and the feeder transport line eventually became blocked. The alumina/resid mixture was increased to a 10:1 ratio and the seals in the screw feeder system, which were leaking, were upgraded. The flow properties of this mixture ratio were greatly improved. However, after about 30 minutes, the feed nozzle injector became occluded, which was caused by the resid material sticking to the hot sections of the nozzle tube near the entrance of the reactor. A water-cooled injector replacement nozzle was designed, fabricated and placed in the lowest bed port of the 3-inch reactor. This nozzle appears to have solved the sticking problem.

In these experiments a thick aerosol formed in the condenser section of the sample recovery stream and fouled the steam condenser units. Analysis of the aerosol revealed that it was a condensed hydrocarbon. Since the capacity of the current sample recovery train is not sufficient to handle the steam and tars, a separate recovery section that can be cleaned on-line will be added in parallel to the existing one.

TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT (LDP ASSOCIATES)

Preparation of the baseline economic assessment, based on Wilsonville Run #263J, has continued. This baseline study will serve as the reference against which the results of this program will be compared. Detailed heat and material balances were calculated for both the coal and ash concentrate gasification units. The hydrogen, fuel gas and steam balances were recalculated. The economic portion of the baseline assessment was begun with investment cost for the oxygen plant, which serves both gasification units, determined on a mid-1991, Wyoming plant location basis. Dewaxing the distillate portion of the process solvent and upgrading the slack wax (paraffinic reject from dewaxing) to a premium-value, fully refined paraffin wax is being evaluated. Since wax supply will exceed demand in a multi-plant scenario, alternate upgrading routes are being evaluated. An arrangement is being pursued to have small scale cracking tests on the highly paraffinic slack wax material conducted.

WORK PERFORMED

TASK 1.1 LABORATORY SUPPORT (UK/CAER)

Reactivity of WRO During Liquefaction

Coal conversions consistently higher than theoretical in the presence of WRO suggest that the IOM fraction of the ashy resid is converting during the reaction resulting in a higher apparent coal conversion than is actually being realized. It was pointed out in previous reports that a similar effect has been observed with ash concentrate taken from the Wilsonville ROSE-SR unit.[1] In order to better define this unusual behavior of the WRO, additional data have been obtained both on the reactivity of distillate without resid and the THF insoluble residual fraction of the WRO in liquefaction of BT coal. A sample of the ash plus IOM from Wilsonville Run 262 ashy resid, which is one component in the WRO, was isolated by extraction with THF. Liquefaction runs were then made in which this material was combined with Black Thunder coal at the same ratio as used in the WRO coal runs. However, rather than using WRO distillate, tetralin was used as solvent. Coal conversion and product distribution in the presence of these THF insolubles in tetralin are shown in Table 1.

THF conversion and product distribution from liquefaction of BT coal in tetralin in the presence of the THF insoluble fraction of the ashy resid were very similar to results from liquefaction in WRO. THF conversion was greater than 100% with an oil yield that was somewhat higher than in WRO. Differences in HC gases yield and H_2 consumption were slight. By contrast, conversion and product distribution from liquefaction of Black Thunder coal in tetralin or in the WRO distillate were quite different. In both of these solvents the 85-86% THF conversions were lower than for runs in which the THF insoluble fraction of the ashy resid was present. This establishes that the THF insoluble fraction of the ashy resid is the reactive fraction of the WRO. These data also

Table 1. Effect of WRO THF Insolubles on Liquefaction of Black Thunder Coal[a]

	THF Insols in Tetralin	WRO	Tetralin	WRO Distillate
Solvent/As Received coal (w/w ratio)				
WRO Distillate	-	0.77	-	1.8
WRO Residual	0.34[b]	1.04	-	0
Tetralin	1.47	-	1.8	-
Fresh Fe_2O_3 Added (wt% mf coal)	none	none	none	none
Yields, wt% maf coal				
HC Gases	1.2	1.9	1.0	2.0
CO + CO_2	5.1	5.0	5.0	5.3
Oils	56.4	51.3	43.4	24.9
PA + A	44.3	48.4	35.8	54.5
IOM	-7.0	-6.6	14.9	13.3
THF Conv wt%	107.0	106.6	85.1	86.6
H_2 Consumption				
mg/g maf coal	46.4	57.0	36.2	35.3
mg/g maf feed	14.5			10.2
wt% H_2 feed Consumed	35.7	34.8	27.7	27.0
Run Numbers	195-1	139-1/ 167-1/ 337-1	160-2	281-1

a. Conditions: 415° C, 1000 psig H_2 cold, 60 minutes.
b. THF insoluble fraction of ashy resid from Wilsonville Run 262.

show that the oils produced when tetralin was used as solvent tended to be greater than when WRO distillate was used, regardless of whether THF insolubles are present. Although Mo was present when THF insolubles were present, it is impossible from these data to determine if the Mo had any effect on the oil yield.

Reactivity of WRO Molybdenum During Liquefaction

A sample of V-1067 product from Wilsonville Run 260 was supplied by CONSOL to check the effect of liquefaction of Black Thunder coal in a molybdenum-free WRO. In Wilsonville Run 262, the run from which the WRO that has been used in this program was taken, molybdenum was added as a catalyst to the first stage reactor. In order to use this material in our liquefaction studies which are based upon solvent fractionation, the V-1067 material that was received from CONSOL was separated into its component solvent fractions. These data are shown in Table 2 and are compared with similar data' on WRO from Run 262. The quantity of the oil fractions of these two materials differ, however, the higher level of pentane solubles in the Run 262 sample probably does not reflect a larger amount of distillate in this materials since we found earlier that the residual fractions from Run 262 contain a large amount of pentane solubles. This difference should not

Table 2. Solubility Fractions in As-Received Run 262 WRO and RUN 260 V-1067 Liquids

	Run 262 WRO[a]	RUN 260 V-1067
Solvent Fraction, wt%		
Oils	60.3	50.1
PA+A	18.6	23.6
IOM + Ash	21.1	26.3
Total THF Solubles	78.9	73.7
Reference Number	Ashy Resid 126-3 Deashed Resid 127-1 Distillate 127-2	17-4 / 17-5

[a] See Quarterly Technical Progress Report, Advanced Direst Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-17, April-June 1992, Table 5, p 8.

interfere with determining an effect of Mo catalysis influence on runs in Run 262 WRO.

Results from liquefaction of Black Thunder coal in V-1067 are shown in Table 3. The level of conversion in these two solvents is essentially the same while the oil yield and hydrogen consumption of the Mo-containing WRO was higher than in the Mo-free solvent. The higher oil yield and hydrogen consumption certainly suggest a catalytic influence of Mo in the Run 262 WRO. Therefore, any catalysis observed in our studies has to be superimposed upon the catalytic effect due to the presence of the molybdenum in the ashy resid. Additional runs will be necessary

Table 3. Black Thunder Liquefaction[a]

	Run 262 WRO	Run 260 V-1067
Solvent/As Rec coal (w/w ratio)	1.8	1.8
Yields, wt% maf coal		
HC Gases	1.9	2.2
$CO + CO_2$	5.0	5.9
Oils	51.3	44.5
PA + A	48.4	54.7
IOM	-6.6	-7.3
THF Conv wt%	106.6	107.3
H_2 Consumption		
mg/g maf coal	57.0	49.2
Run Numbers	139-1/ 167-1/ 337-1	17-1

[a] Conditions: 415° C, 1000 psig H_2 cold, 60 minutes.

to definitely establish the reproducibility of this data. Likewise, as data become available on the composition of the Run 260 V-1067 material, the concentrations of ash and iron in this sample can be established.

TASK 1.2 LABORATORY SUPPORT (CONSOL)

Summary

Nine hydrogenated oil samples were received from Sandia. Proton distributions, phenolic -OH concentrations and solvent qualities were determined on each of these samples. Hydrogenation consistently improved the measured solvent quality of both the feed distillate and the dewaxed oils. Overall, the combination of dewaxing and hydrogenation increased the V-1074 distillate solvent quality from 64% to 90%.

An error in the moisture determination of the Indiana V coal used in the CONSOL solvent quality measurement resulted in errors of 0.6 to 1.4%. The corrected solvent quality results for all previously reported work are included.

Discussion

Proton distributions, phenolic -OH concentrations and solvent qualities were determined on each of the nine hydrogenated oil samples that were received from Sandia. The conditions Sandia used to hydrotreat the samples are listed in Table 4. Nearly all of the samples contained a significant amount of water, which can interfere in our phenolic -OH determination. The following modification of our standard method was used to dry the samples. Each oil sample was weighed and diluted with dry HPLC grade tetrahydrofuran in a 2 mL volumetric flask. The solution was mixed well, about 50 mg of molecular sieve (Davison grade 516, 14-30 mesh granules,4 Å effective pore size) were added, and the solution was left in contact with the molecular sieve for several hours (or overnight). A liquid sample then was withdrawn and run in the normal manner. Since this drying treatment was experimental, phenolic -OH determinations with and without drying were compared. The phenolic -OH concentration determined in samples which originally contained water increased by 0.01 to 0.05 meq/g when the samples were dried. The phenolic -OH concentration determined in one sample which was already dry did not change when the sample was subjected to the drying treatment. Because the drying method worked well, it may have general applicability to coal liquid samples which are wet.

The proton distributions, phenolic -OH concentrations and solvent qualities, defined as the wt % conversion of Indiana V, Old Ben #1 Mine coal to THF solubles in a modified equilibrium test (750°F, 30 min, 1.5/1 solvent/coal ratio), of feed oils and hydrotreatment products are shown in Table 5. Hydrogenation improves the solvent quality of both the feed and dewaxed oils. The solvent quality of the V-1074 feed distillate was increased from ~64% to ~71%. In all but the low pressure (333 psig) hydrogen-only run, the solvent qualities of the dewaxed oils were increased to around 90%. The low pressure, H_2-only hydrogenation had no effect on solvent quality.

In general, hydrogenation lowered the aromatic proton concentration (particularly the condensed aromatics) while slightly increasing the cyclic and alkyl beta proton concentrations. Hydrogenation had little effect on the concentrations of the alpha and gamma protons.

The Indiana V coal used in the solvent quality determination, as defined above, is stored in sealed, nitrogen-purged bags which contain ~200 g each. Moisture and ash are determined on the coal each time a new bag is opened for use. A calculation error in the moisture content of the coal sample used in the dewaxing studies led to errors in the calculated solvent qualities. The corrected values are given in Table 6. These corrections

TABLE 4

CONDITIONS FOR SANDIA HYDROTREATMENT STUDIES

	Hydrotreatment Conditions			
SAMPLE No.	Feed	Temp., °C	WHSV (hr^{-1})	Pressure (psig)[A]
5-92804	V-1074 Distillate	300	0.44	1000
5-92906	V-1074 Distillate	325	0.83	1000
5C-102205	-5°C dewaxed Distillate	300	0.32	1000
5C-102305	-5°C dewaxed Distillate	325	0.77	1000
5A-110404	-35°C dewaxed Distillate	300	0.51	1000
5A-110505	-35°C dewaxed Distillate	325	0.8	1000
5A-110507	-35°C dewaxed Distillate	325	0.83	1000
5A-110602	-35°C dewaxed Distillate	325	0.72	1000[B]
5A-110607	-35°C dewaxed Distillate	325	0.68	333[B]

A = CO/steam, except as noted.
B = Hydrogen only, no carbon monoxide or steam.

TABLE 5

PROTON DISTRIBUTIONS, PHENOLIC -OH CONCENTRATIONS AND SOLVENT QUALITIES OF SANDIA HYDROGENATED DISTILLATES

	Proton Distributions, %							Phenolic -OH[D]		
Sample No.	Condensed Aromatics	Uncondensed Aromatics	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Concentration, meq/g	v, cm^{-1}	Solvent Quality, %[E]
				Runs with V-1074 Distillate						
5[A]	11.3	3.6	14.7	7.6	15.8	34.6	12.3	0.44	3306	63.8
5-92804	7.7	3.3	14.0	7.3	17.8	35.7	14.2	0.16	3316	70.9
5-92906	9.1	3.6	14.4	7.3	16.5	35.7	13.4	0.22	3314	70.7
				Runs with -35°C dewaxed V-1074 distillate						
5A[B]	17.3	6.2	20.0	10.3	17.1	17.9	11.2	0.61	3304	85.3
5A-110404	13.7	5.0	20.7	9.8	18.7	19.6	12.4	0.36	3309	90.3
5A-110505	15.2	5.1	21.0	10.0	18.7	18.7	11.4	0.37	3309	89.2
5A-110507	15.1	5.4	20.6	10.0	18.0	19.2	11.7	0.38	3308	89.1
5A-110602	13.7	5.2	20.8	10.2	19.0	19.4	11.7	0.35	3311	90.3
5A-110607	17.7	4.9	21.3	9.9	17.7	18.3	10.2	0.47	3307	85.7
				Runs with -5°C dewaxed V-1074 distillate						
5C[C]	16.5	5.1	18.4	9.2	17.4	21.3	12.1	0.56	3304	82.1
5C-102205	11.1	4.9	19.0	9.9	19.1	22.8	13.1	0.29	3312	90.8
5C-102305	13.5	4.8	19.3	9.8	19.0	21.8	11.9	0.32	3310	88.6

Notes:
A = Untreated V-1074 distillate.
B = Untreated -35°C dewaxed V-1074 Distillate
C = Untreated -5°C dewaxed V-1074 Distillate
D = Most of the samples treated with CO/steam contained some interfering H_2O. The H_2O was removed by the method described in the discussion.
E = Coal conversion to THF solubles in modified equilibrium test.

TABLE 6

CORRECTION OF PREVIOUSLY REPORTED SOLVENT QUALITIES FOR DEWAXING EXPERIMENTS

Sample Number	Run Date	Material	Dewaxing Solvent[A]	Dewaxing Temp. °C	Originally Reported[B] SQ, %	Corrected[B] SQ, %
5		V-1074 feed	N/A	N/A	62.4	63.8
5-1A	06/09/92	Dewaxed Distillate	100% A	-20	84.1	84.6
5-2A	06/15/92	Dewaxed Distillate	100% A	-10	82.9	83.6
5-3A	06/16/92	Dewaxed Distillate	100% A	0	71.2	72.3
5-4A	06/24/92	Dewaxed Distillate	100% A	-35	82.5	83.1
5-5A	06/30/92	Dewaxed Distillate	100% A	-5	81.8	82.5
5A	09/02/92	Dewaxed Distillate Composite	100% A	-35	84.7	85.3
5C	09/16/92	Dewaxed Distillate Composite	100% A	-5	81.4	82.1
5-25A	10/02/92	Dewaxed Distillate	45%M/55% T	-5	65.1	66.4
5-26A	10/06/92	Dewaxed Distillate	45%M/55% T	-35	72.0	73.0
5-28A	10/14/92	Dewaxed Distillate	100% M	-35	72.9	73.9

Notes:

A) Solvent symbols A = Acetone, M = methyl ethyl ketone (MEK), T = Toluene, ratios are volume%.

B) Difference in corrected and original solvent quality reflects error in moisture determination on coal sample.

increased the solvent quality values by 0.6 to 1.4% but have no impact on the conclusions of the dewaxing work.

Two gallons of the flashed second stage product (V-1067) from Wilsonville Run 260 was shipped to UK/CAER in early December. This material is the only resid-containing Wilsonville subbituminous coal-derived oil in CONSOL's inventory in which no Mo catalyst precursor was present. UK/CAER personnel will distill the sample for testing. A portion of the distillation products may be returned to CONSOL for characterization.

Arrangements were made with TUMCO mine personnel to obtain a 10 gallon sample of Martin Lake lignite, provided that it is approved by their main office.

TASK 1.3 LABORATORY SUPPORT (SANDIA)

Laboratory support activities at Sandia included solvent characterization using capillary gas chromatography and organic elemental analysis. Since receiving dewaxed samples from CONSOL, solvent hydrogenation tests have been performed using the dewaxed solvent. Gas chromatographic analysis of the hydrogenated product showed an increase in hydrogenated product peaks and a decrease in parent aromatic peaks. Figures 1 and 2 show high resolution gas chromatograms of feed and hydrogenated dewaxed distillate. Several of the peaks are annotated to show the increase in hydrogenated products. Figure 3 shows a hydrogenated sample which also shows an increase in the amount of compounds that elute at earlier retention times thus indicating extensive hydrogenation. Carbon and hydrogen were determined with a Perkin Elmer Model 2400 CHN analyzer and H/C ratios of the samples are shown on the gas chromatograms. Since many of the hydrogenated samples had some residual water from the water-gas shift reaction, it was necessary to dry them first to determine the organic elemental analysis. Results from these analyses are presented in subtask 2.1.3. An Antek Model 7000 nitrogen/sulfur analyzer was used to screen samples for nitrogen and sulfur removal during hydrotreating and results of these determinations are given in subtask 2.1.3.

Additionally, laboratory support activities were used to determine catalyst coking and deactivation using elemental analysis and hydrogenation activity testing. Batch microautoclave tests were performed using the "screening" conditions developed at Sandia[2] to evaluate catalyst hydrogenation activity. Reaction products from these tests were measured by high resolution gas chromatography. Results and discussion of catalyst studies are given in subtask 2.3.3

Figure 1 High resolution gas chromatogram of -5°C dewaxed heavy distillate V1074

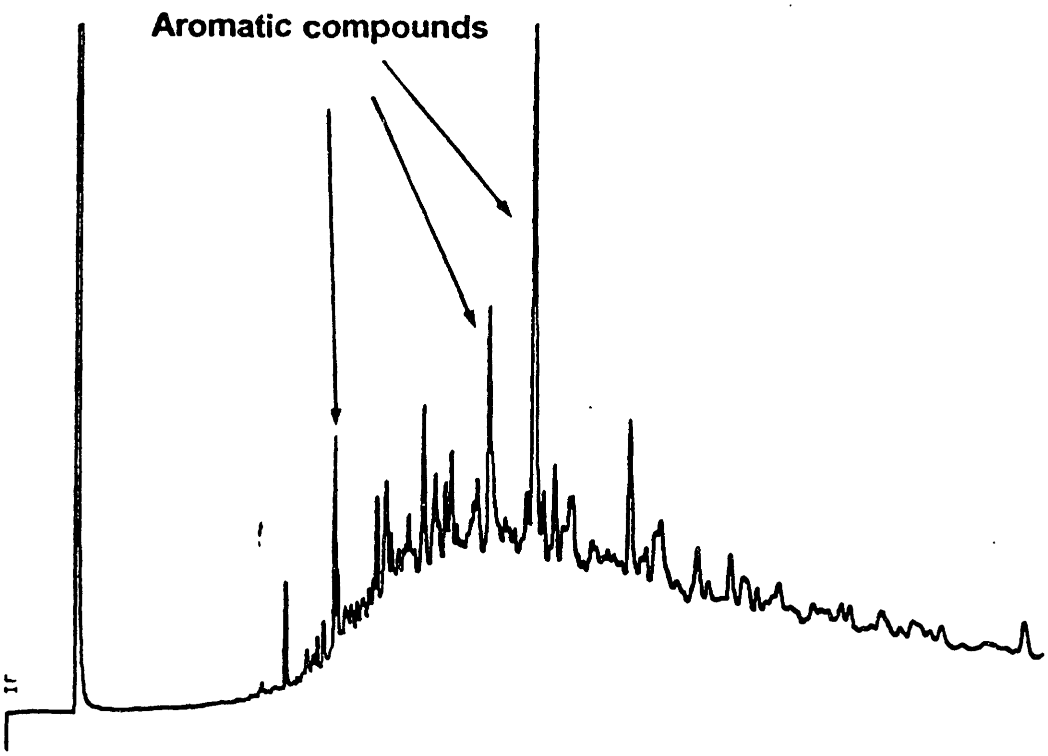


Figure 2 High resolution gas chromatogram of hydrogenated -5°C dewaxed heavy distillate V1074

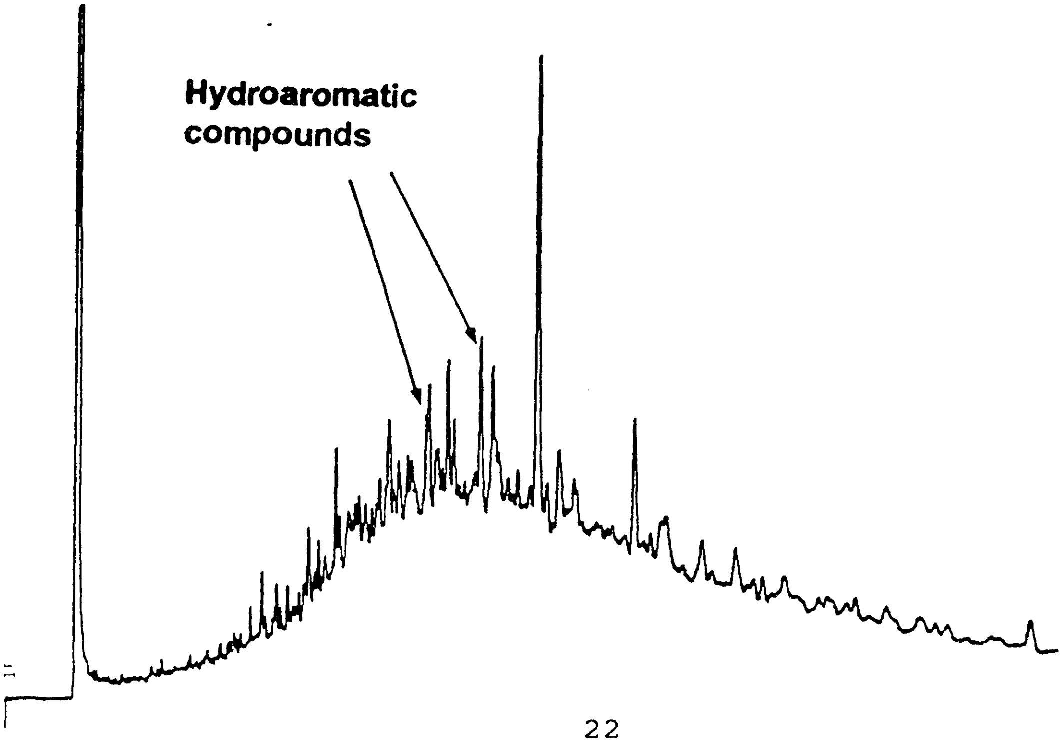
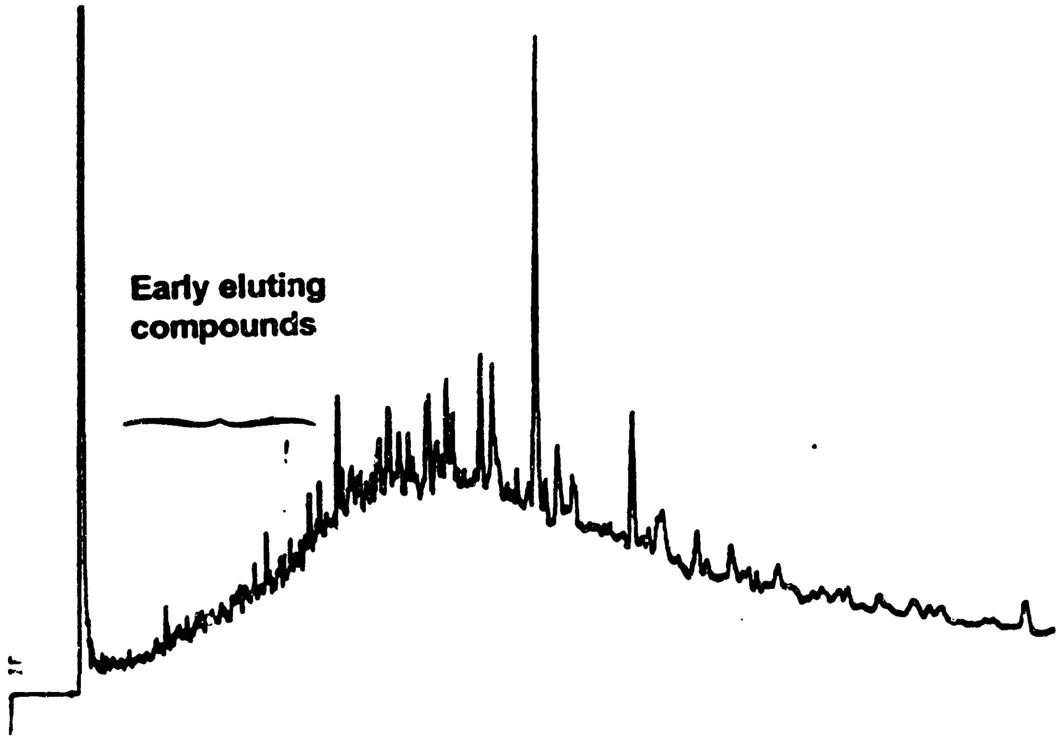


Figure 3 High resolution gas chromatogram of extensively hydrogenated -5°C dewaxed heavy distillate V1074



TASK 2.1.1 CO PRETREATMENT (UK/CAER)

A parametric study of the CO pretreatment process using Black Thunder coal has been carried out in 25 mL microautoclaves. The various parameters examined for the pretreatment reaction are CO pressure (300-800 psig), NaOH concentration (0.02-0.33 M solutions) and temperature (250-300°C). Each variable is examined at two levels, high and low, for the main effect and its interaction with the other reaction variables under investigation. A discussion of the results from these reactions is presented.

In addition to the microautoclave work, a number of scale-up reactions of the pretreatment process with Black Thunder coal was carried out in a 1 liter stirred autoclave. The reactor is equipped with a hot-charge facility to inject the coal slurry at reaction temperature. Yields of recovered material and the analysis of the samples will be discussed.

Parametric Study

Experimental Design - The 2^3 factorial experimental design for CO pretreatment of coal at three independent variables is summarized in Table 7. Two separate values for each of the independent factors were evaluated. Temperatures of 250 and 300°C were chosen primarily based upon our already observed experiments at 300°C plus a desire to determine the lowest temperature at which this solid phase transformation occurs. The CO pressures were largely chosen based upon the earlier experiments which were run at 200, 400 and 800 psig. The upper pressure was largely based upon perceived limitation of equipment at reaction temperature. The selection of 0.33 M NaOH concentrations was originally based upon prior work[3] and the earlier experiments in this program. Setting the lower level at 0.02 M NaOH was a need to establish reactivity at lower base concentrations to minimize chemical consumption in this process.

Table 7. 2^3 Factorial Design for CO Pretreatment of Black Thunder Coal in Alkaline Solution			
Run No.	Temp °C	CO (psig)	NaOH, moles/L
125	250 (low)	300 (low)	0.02 (low)
113	300 (high)	300 (low)	0.02 (low)
118	250 (low)	800 (high)	0.02 (low)
112	300 (high)	800 (high)	0.02 (low)
	250 (low)	300 (low)	0.33 (high)
111/134	300 (high)	300 (low)	0.33 (high)
126/139	250 (low)	800 (high)	0.33 (high)
110/132	300 (high)	800 (high)	0.33 (high)
	275 (CP)	550 (CP)	0.155 (CP)
CP= Center point for the set.			

The experimental design has a significant effect on the ratios of the reactant and catalyst components in the water gas shift reaction. These values are presented in Table 8. Since the temperatures at which these runs were made are subcritical, the water partial pressures are strictly a function of temperature with water vapor density varying between 0.020 and 0.046 g/cc and the corresponding vapor pressures varying between 600 and 1300 psi. This vapor density is quite low relative to the vapor density at the supercritical temperature (374°C) of 0.32 g/cc which occurs at the supercritical pressure of 3300 psi. At ambient temperature the slurry concentration on a dry coal basis is approximately 25 wt% while at the highest temperature, the slurry concentration would increase slightly to approximately 30 wt%. The quantity of liquid phase water present at reaction temperature does not differ by a large amount in this closed system.

The variation in CO pressure from 300 to 800 psig corresponds to a change in the CO to maf coal weight ratio from 0.33 to 0.86. This rather limited range is largely a result of the reactor system that is used in this study. Obviously, this will be one factor that will have to be addressed as scale up progresses. The corresponding NaOH to maf coal weight ratio varies over a much wider range from 0.27 up to 4.5. The lower value corresponds to a NaOH loading of 0.2 wt% on dried coal.

The variations in CO and NaOH result in a very wide range of CO/NaOH concentrations which may dramatically affect the water gas shift reaction. This ratio ranges from 10 to 446. If the turnover number for catalyzing the water gas shift is indeed a limiting factor this wide range should show such an effect.

The effects of the independent variables on the reaction for the 2^3 factorial designed study are shown in Table 9. At present one of the data sets remains incomplete. However, the data available on the remaining experiments provide considerable insight into this reaction. A series of box diagrams shown in Figure 4 are presented to facilitate easy interpretation of the data. The impact of the independent factors on THF conversion, preasphaltene and asphaltene yield (PA+A), hydrogen consumption and water gas shift is evaluated and discussed.

Effect of Temperature - The diagram in Figure 4a indicates that temperature has a significant impact on THF conversion. Increasing the pretreatment temperature from 250° to 300°C substantially increases the coal conversion to THF and aqueous soluble products and gases. Clearly the sensitivity to temperature is far greater on coal solubilization than CO partial pressure and NaOH concentration. At 250°C, all of the conversions are below 10 wt% irrespective of initial CO partial pressure and NaOH concentration.

The conversion reported mainly to the PA+A fraction (Figure 4b and Table 9) with no humic acid being recovered from the aqueous layer at this lower temperature even at the lower CO partial pressure (300 psig). Of course, the low temperature-low pressure run is not yet available. At this temperature, the balance of the converted material reported to the oil+gas+water fraction. Unlike at higher temperature, the solid product retained its finely divided texture and foams readily when the gas in the reactor is released. In these runs a trap had to be used to avoid losing material during collection of gaseous products. The small conversion obtained in these reactions is consistent with the optical microscopic examination of the water insoluble products which indicates no major disruption of the coal structure during the pretreatment process.

At 300 psig CO, conversion in 0.33 M NaOH solution appears to be higher than obtained with the 0.02 M solution. At 800 psig CO, THF conversion for both NaOH concentrations is 32%. Because of the significant structural changes and increased conversion that occurs upon raising the temperature from 250 to 300°C, thermolysis and hydrogenation of the coal apparently occurs during pretreatment.

The interactive effect of CO and NaOH concentration is clearer at 300°C where greater coal solubilization occurs during pretreatment. At high CO pressure (800 psig) THF conversion and product distribution in 0.33 and 0.02 M NaOH solution are the same (Figure 4a and b). Consistent with our earlier findings with Clovis Point Wyodak subbituminous coal, greater than 90% of the conversion of Black Thunder coal reports to the PA+A fraction. This is encouraging

Table 8. Features of 2^3 Factorial Design Experiments[a]

Run No.	Temp °C	CO (psig)	NaOH, moles/l	g CO/ g maf coal	g NaOH/ g maf coal $\times 10^2$	moles CO/ mole H_2O	moles CO/ mole NaOH
125	250 (low)	300 (low)	0.02 (low)	0.33	0.27-	0.066	172/1
113	300 (high)	300 (low)	0.02 (low)	0.33	0.27	0.066	172/1
118	250 (low)	800 (high)	0.02 (low)	0.86	0.27	0.17	446/1
112	300 (high)	800 (high)	0.02 (low)	0.86	0.27	0.17	446/1
	250 (low)	300 (low)	0.33 (high)	0.33	4.7	0.066	10/1
111/1 34	300 (high)	300 (low)	0.33 (high)	0.33	4.7	0.066	10/1
126/1 39	250 (low)	800 (high)	0.33 (high)	0.86	4.7	0.17	27/1
110/1 32	300 (high)	800 (high)	0.33 (high)	0.86	4.7	0.17	27/1

a. 25 ml reactor, 1 hour reaction time, 2 grams dry coal, 20-22 wt% moisture, 3.25 g water/g maf coal,

Table 9. Results from 2^3 Factorial Designed Experiments for CO Pretreatment of Black Thunder Coal[a]

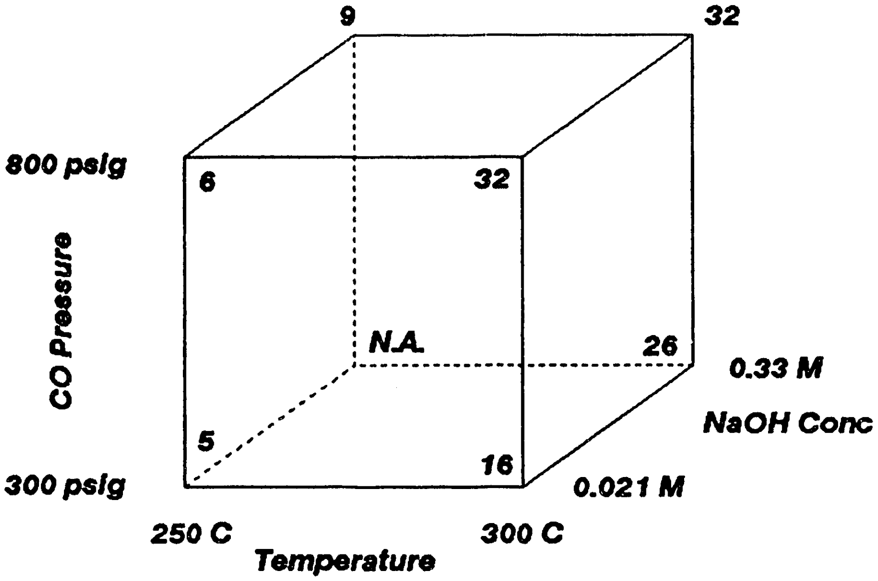
Run No.	Temp °C	CO (psig)	NaOH, moles/l	THF Conv	PA+A	Humic Acids	Oils + Gas + Water	WGS	H_2 Consump mg/g maf coal
125	250 (low)	300 (low)	0.02 (low)	5	3	-	2	58	10
113	300 (high)	300 (low)	0.02 (low)	16	8	1	7	56	9
118	250 (low)	800 (high)	0.02 (low)	6	2	-	4	36	18
112	300 (high)	800 (high)	0.02 (low)	32	27	-	5	41	20
	250 (low)	300 (low)	0.33 (high)						
111/ 134	300 (high)	300 (low)	0.33 (high)	26	18	4	4	88	6
126/ 139	250 (low)	800 (high)	0.33 (high)	9	9	-	-	45	20
110/ 132	300 (high)	800 (high)	0.33 (high)	32	29	-	3	45	20

CP= Center point for the set.

a. All conversions and yields based upon maf coal.

Figure 4. Results from Factorial Design Experiment

a. THF Conversion



b. PA + A

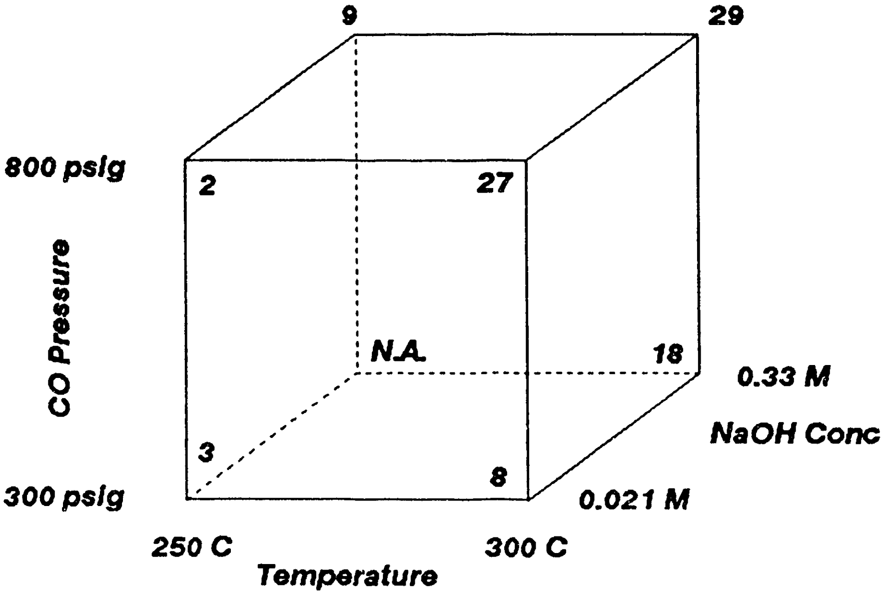
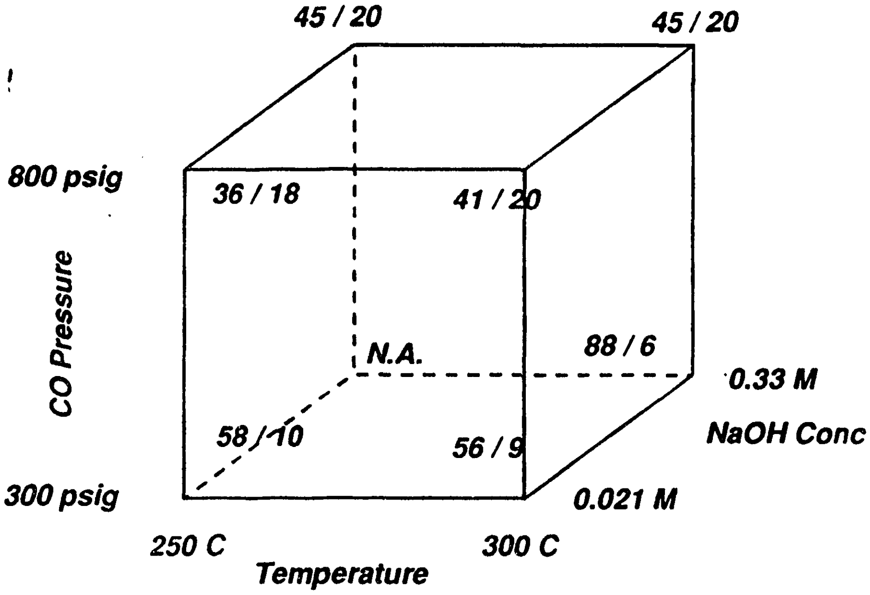


Figure 4. Results from Factorial Design Experiment

c. Water-Gas-Shift Reaction

(H2 Production / H2 Consumption)



*H2 Production (mg/g maf coal) = [CO (in) - CO (out)] * 2*

H2 Consumption (mg/gram maf coal) = [H2 (from WGS) - H2 (final)] because it shows that the concentration of NaOH can be reduced from 4.5% to 0.25% (maf coal basis) without compromising the effect of pretreatment.

However, at 300 psig CO pressure, a higher THF conversion was observed with the 0.33 M NaOH solution than with the 0.02 M solution, i.e., 26% vs 16%, respectively. In our earlier work with Clovis Point coal, we showed that at low CO partial pressure (200 psig), hydrogenation is not a significant part of the overall reaction. We also found that the total water-insoluble products are intractable with pyridine (9% yield, maf basis) and the majority of the THF solubles report to the oil+gas+water component instead of the PA+A fraction. Increasing the CO pressure should increase the hydrogenation. Accordingly, for Black Thunder coal, the yields and product distribution obtained from the reactions with 300 psig CO gave higher THF conversion and PA+A yield than the Clovis Point coal at 200 psig CO and the same NaOH concentration in the system, namely, 26% vs. 21% THF conversion and 18% vs. 2% PA+A yield, respectively. It appears that the chemistry of coal pretreatment in the presence of an adequate hydrogenation source is different than when hydrogen starvation occurs. This contention has been supported by chemical analysis of the products as reported in the August and November reports.

Water-Gas-Shift Reaction: Data Analysis - In our earlier work, the conversion of CO in the water-gas-shift reaction was calculated by Equation No. 1. Based upon the amount of hydrogen detected at the end of the reaction, we reported the amount of hydrogen consumed during the reaction by the coal as expressed by Equation No. 2:

$$\text{WGS \%} = 100 \times [CO_{in}-CO_{out}] \;/\; [CO_{in}] \qquad \text{EQ. 1}$$

$$H_2 \text{ consumed} = \{\text{mg } H_2 \text{ (from WGS)} - \text{mg } H_2 \text{ (final)}\}/\text{g maf coal} \qquad \text{EQ 2}$$

This value of H_2 consumption is, in fact, the amount of H_2 that was not accounted for in the gas analysis. On this basis, Figure 4c shows the extent of the WGS reaction and the amount of hydrogen consumed from the WGS reaction at the various reaction conditions. The uncertainty in these measurements are ± 3% and ± 5% for the WGS conversion and hydrogen consumption, respectively. In general, in our reactor system, temperature appears to have little impact on the extent of the WGS reaction. The maximum WGS conversion obtained in this series of runs is 88%, which is experimental confirmation that the reaction is not thermodynamically limited under these conditions. Taking into account results observed for reactions with Clovis Point coal and blank runs where no coal is present, CO conversion appears to plateau at approximately 50%. In a separate two hour run only a 5% increase in CO conversion was observed. Similar results have been reported in the reaction of CO with sodium hydroxide to make sodium formate.[4] An upper CO conversion plateau that was related to a rate limiting step necessitated venting from 30-40% of the CO feed.

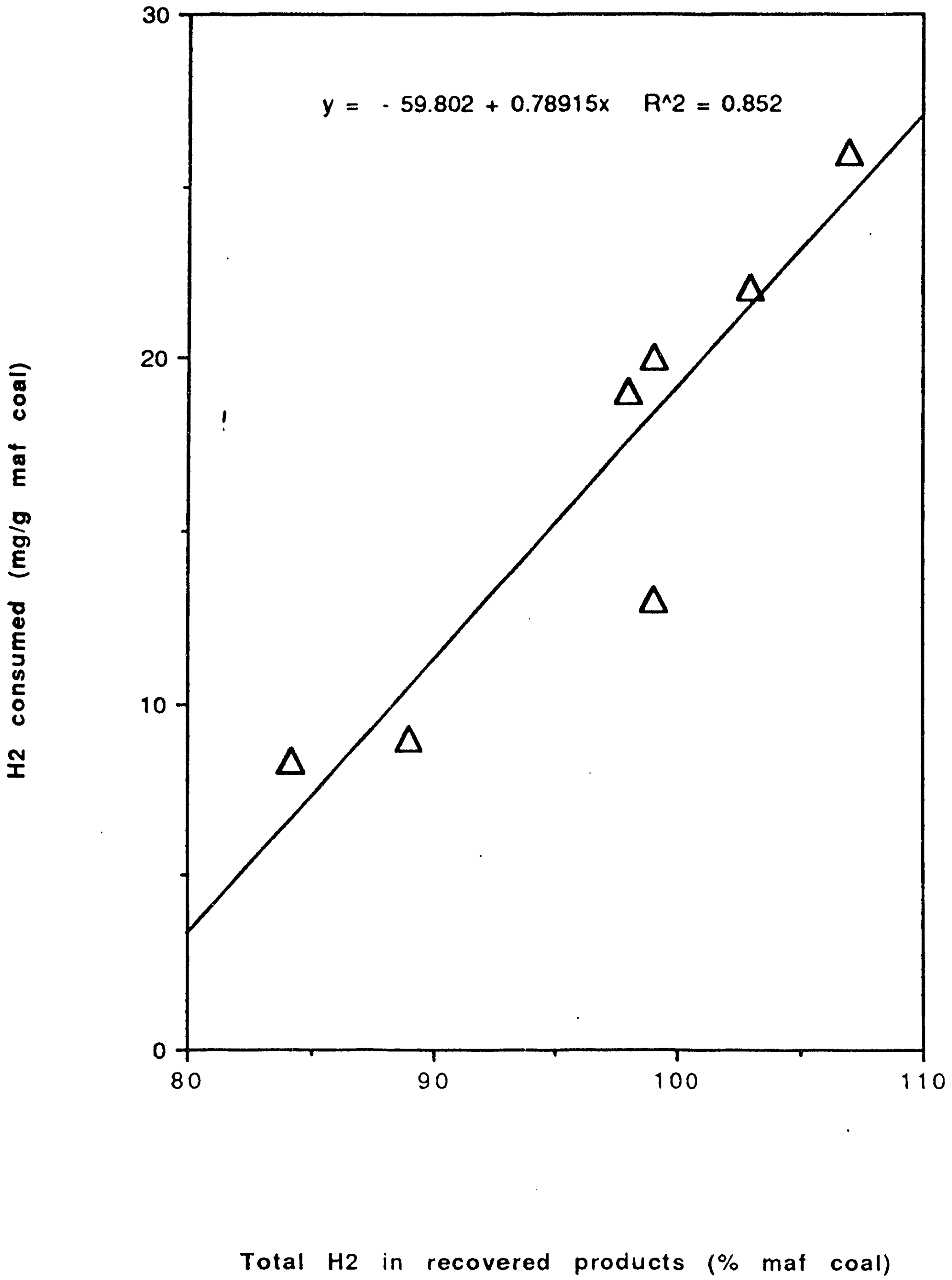
The hydrogen consumption value calculated from the WGS reaction shows an interesting trend. At 300 psig CO at either 250 or 300°C with 0.02 or 0.33 M NaOH solution, consumption is relatively low (~10 mg/g maf coal). In contrast, these values are much higher (18-20 mg/g maf coal) when 800 psig CO was used. Our earlier CO pretreatment work with Clovis Point subbituminous coal showed significant hydrogenation and major reconstruction of the structure at 300 °C, particularly when using 800 psig CO. Figure 5 shows the strong dependence between coal hydrogenation and the amount of H_2 consumed from the WGS reaction. The results observed in Figure 4c suggest that either: (1) significant coal hydrogenation is occurring at 250°C under high CO pressure or (2) the hydrogen produced from the WGS reaction is trapped elsewhere, possibly as soluble salts or organic species in the aqueous layer in the reaction system. The low THF conversion obtained for these reactions and recent optical microscopic analysis of the 250°C samples confirm that no significant structural changes occur during pretreatment. This negates the possibility of substantial coal hydrogenation.

Thus, it appears likely that hydrogen is being 'stored up' in some manner. Following are several possibilities consistent with known CO/base chemistry: sodium formate, sodium bicarbonate, formic acid and carbonic acid. All these species have been either found or proposed to be present as part of the WGS cycle of reaction.[5] To confirm that hydrogen from the WGS reaction is stored in addition to being utilized by the coal, experiments were performed in the absence of coal. In these experiments 800 psig CO was reacted with the same level of aqueous alkali, i.e., 6 ml of 0.33 M NaOH solution, at 250 and 300 °C for 1 hour. The WGS conversion and the amount of hydrogen remaining at the end of the reaction was determined. At both temperatures essentially the same amount of WGS conversion and yield of hydrogen was found, within experimental error, as when coal was present.

Although Elliott and Sealock[6] have shown that sodium formate, HCOONa, is the stable WGS intermediate up to 300°C with a CO over pressure, in our reaction system the amount of Na^+ ions available is not sufficient to account for the amount of H_2 that is consumed. It is interesting that the ratio of the amount of H_2 that is consumed and the amount of unaccounted CO_2 is ca. 0.5 in all these cases.

Figure 5

Data from "H2 Vs. WGS"



Royen and Ehrhard[7] proposed a scheme in which formate decomposes to formic acid and subsequently to CO_2 and H_2.

$$CO + KOH \rightarrow HCOOK$$
$$HCOOK + H_2O \rightarrow HCOOH + KOH$$
$$HCOOH \rightarrow CO_2 + H_2$$

Hartman and Hisatsune[8] reported the decomposition of sodium formate to sodium carbonate, CO and H_2 at temperatures less than 330°C. In addition, Elliott and Sealock[6] reported that the decomposition of the formate salt appears to be rate limiting.

In light of the current developments, it cannot be assumed that the hydrogen produced from the WGS reaction is exclusively consumed by the coal, even at 300°C. However, these results warrant further investigation as they suggest that the active WGS intermediates could be generated external to the coal treatment reactor at lower temperatures and pressures and subsequently combined with the coal at higher temperatures around 300-310°C where it would react. At the higher temperature, reconstruction of the coal structure has been shown to increase which could parallel the decomposition of the WGS intermediate. This scenario would allow reduction of the total pressure in the system. If the WGS intermediate is generated <u>in-situ</u> during pretreatment, the partial pressure of CO at 300°C constitutes nearly two thirds of the total pressure. If the CO partial pressure can be significantly reduced this would represent a significant cost saving.

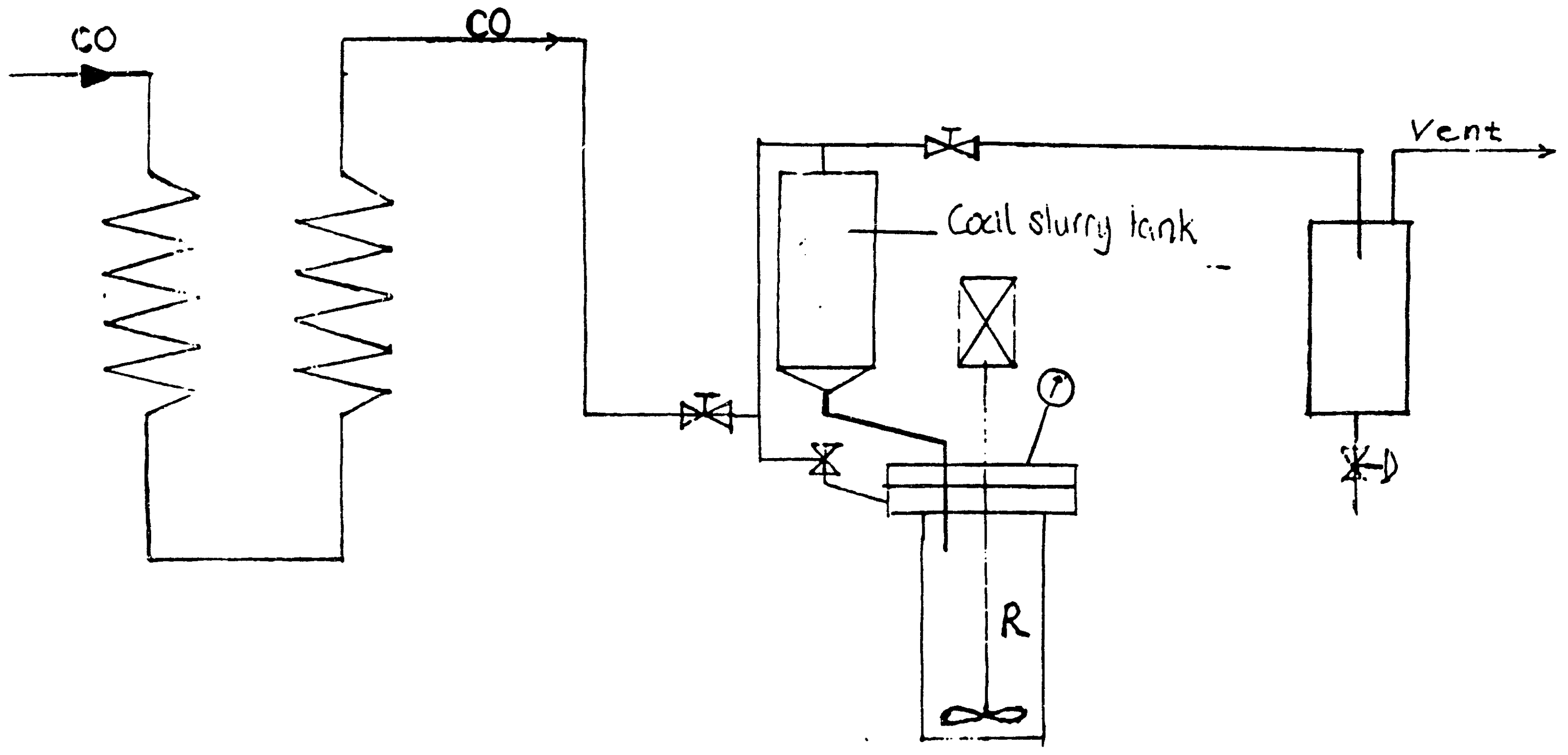
1-Liter Stirred Autoclave Experiments

A 1-liter stirred autoclave has been utilized to generate 80 gram samples (dry basis) of CO pretreated product. Oil agglomeration tests on these samples will be carried out at CONSOL. The schematic of the 1- liter autoclave is shown in Figure 6. In a typical run, 70 ml water and 800 psig of CO are charged into the leak-tight reactor after purging it three times with CO. The reaction mixture is heated to 300°C in approximately 150 minutes. The reported temperature was measured via an internal thermocouple in the reactor. At 300°C the total pressure generated by the gas and steam was ~2800 psig and the stirring speed was 400 rpm.

In the run 150 grams of as-received Black Thunder coal (23 wt.% moisture) was slurried with 200 ml of either 0.38 M NaOH solution or 0.19 M Na_2CO_3 in a beaker to give 2.7 wt% NaOH or 3.7 wt% Na_2CO_3, on maf coal. The coal slurry was transferred into the slurry holding tank 2-3 minutes prior to charging the contents into the reactor at reaction temperature. The coal slurry was forced into the reactor under CO pressure by N_2 pressure of 3200 psig. This 'hot-charging' avoided a long heat-up time which has been shown to have a detrimental impact on coal hydrogenation in the CO-H_2O system.[9] This avoids wasting the CO-WGS intermediate through failure to capture the intermediate which will form at lower temperatures than where the coal conversion/hydrogenation reaction will occur.

Thermal Recovery Upon charging the coal slurry into the reactor, the internal reactor temperature dropped from 300°C to 200°C within seconds and climbed back to 300°C within 8.5 minutes. The temperature of the runs reported in this discussion was 310 ± 5°C.

After the 1 h reaction time at temperature, the gases are vented off slowly to help the cooling process. External and limited internal cooling of the reactor is facilitated by cold compressed air and an internal cooling coil. It takes about 45 min to one hour to cool the reactor to @ 100°C after the reaction and a further 1-2 hours to cool to room temperature.



SCHEMATIC FOR 1-LITRE STIRRED AUTOCLAVE

Product and Elemental Recovery - The products are scraped from the reactor using distilled water. It was evident that some of the original water in the reaction had escaped through the vent together with the gaseous products. Despite the difficulty in recovery of the gases, water and water soluble organic products from this equipment, estimates on the conversion of the coal in these scaled-up experiments are reported based on solid products and coal recovered from the charging tank. Table 10 shows that the yields of water insoluble products recovered from the NaOH and Na_2CO_3 experiments are on the order of 85 ± 1 wt% maf coal. This corresponds to greater than 90% carbon recovery in both cases. The hydrogen recovery was 98 and 90%, respectively. The oxygen recovery for the NaOH generated product is higher than that of the Na_2CO_3 sample (59 vs 53%). The atomic H/C ratio of the NaOH and Na_2CO_3 generated H_2O-insoluble products was 0.9 and 0.84, respectively, compared to 0.85 for the raw coal. These numbers are very similar to those obtained from the microautoclave reactions.

Product Extraction with Pyridine and THF - The water-insoluble material generated from the reaction of Black Thunder subbituminous coal with NaOH and Na_2CO_3 was extracted with pyridine. The results are presented in Table 11 together with those obtained from microautoclave experiments.

It was noted that after extracting about 12 hours, both thimbles containing the NaOH and Na_2CO_3 generated material became blocked. However, none of the solid material was lost from the thimble. The material in the thimbles resembled a gel. Earlier tests of the NaOH generated material in 50 ml vials showed that the material swelled and completely dissolved in pyridine at room temperature. It is not clear, however, whether the resulting mixture was a true solution.

Table 10. Product Yields and Elemental Recovery

	NaOH	Na_2CO_3
Coal Charge, g	110.35	111.37
Unreacted Coal, g	16.34	15.10
Water Insoluble Product, g	80.9	81.0
Water Insoluble Products, wt%[a]	86.0	84.1
Elemental Recovery in Water Insoluble Product, wt% maf coal[b]		
Carbon	91.8	90.3
Hydrogen'	97.5	89.8
Nitrogen	84.7	83.2
Sulfur	61.6	70.0
Oxygen	58.9	53.3
H/C Ratio of WIP	0.90	0.84

a. 100 x water insoluble product/[coal charge - unreacted coal]
b. Conc of element in WIP (wt%) x WIP (wt%)/Element Conc in Coal (wt%)

The 1-liter reaction with NaOH generated a material of which 60 wt% was soluble in pyridine. This yield is identical to that obtained from the corresponding reaction with Clovis Point subbituminous coal in a 26 ml microautoclave. The pyridine extract yield for the microautoclave reaction was 30 wt% higher than the THF extract yield. Further analysis is being conducted to ascertain whether this THF extract yield has increased for the 1-liter reaction due to the relatively higher temperature and longer cool down time compared to the microautoclave. Chemical analysis of the pyridine and THF extracts is currently being carried out.

Table 11. THF and Pyridine Extraction of CO-Pretreated Products

	THF Solubles[a]	Pyridine Solubles[a]
Microautoclave Experiments		
NaOH (0.35 M)[b]	30	60
Na_2CO_3[d]	37	N.A.[c]
1-Liter Stirred Autoclave		
NaOH (0.35 M)[d]	N.A.	60
Na_2CO_3[d]	39	56

a. Wt% maf basis
b. Clovis Point Wyodak subbituminous coal.
c. N.A. Not available
d. Black Thunder Wyodak subbituminous coal.

The Na_2CO_3 generated sample gave a lower pyridine conversion than that obtained from the NaOH experiment (ca. 56 vs 60%). However, the difference between the pyridine extract and THF extract yield obtained for the 1-liter reaction with Na_2CO_3 is only approximately 16 wt%. The relative differences in pyridine and THF extract yields with NaOH and Na_2CO_3 is interesting and the significance of this observation in relation to the overall process is still under investigation.

Thermal Analysis - As-received Black Thunder coal and samples of the coal that had been treated with CO and NaOH or Na_2CO_3 solution at a maximum reactor temperature of 315°C were subjected to simultaneous thermogravimetry/differential thermal analysis (TG/DTA). TG, DTA, and DTG (differential thermogravimetry) analyses were performed simultaneously on a Seiko TG/DTA 320, connected to a disk station for programmable control of the furnace, acquisition of continuous weight measurements, sweep gas valve switching, data analysis, and export of data to other computers. The TG has a temperature range from room temperature to 1300°C. The TG conditions were: a heating rate of 10°C/min from room temperature to 120°C; a 15 min hold at 120°C to remove surface moisture; a heating rate of 10°C/min from 120°C to 600°C; He sweep gas, 200 ml/min; and constant sample volume weighing approximately 20 mg.

Weight loss profiles showed that both coal treatments lowered the temperature for the onset of decomposition and increased total conversion compared to as-received coal (Figures 7). Additional information on the conversion benefits of the treatments was obtained from the DTG curves which indicated a significant increase in the rate of decomposition and a decrease in the temperature at which maximum decomposition occurred (Figure 8). The temperature of the maximum conversion rate decreased from 442°C for the raw coal to 432°C and 429°C for the Na_2CO_3 and NaOH treated samples, respectively.

Decomposition occurred for both treated and raw coals as a broad endothermic depression of the DTA curve relative to the DTA baseline (Figure 9). DTA curves for the treated samples suggest that less heat was required for conversion for the NaOH treated coal since its DTA profile most closely approached the DTA baseline curve.

These TG/DTA results suggest that treatment with either base would improve the conversion of the coal relative to the parent coal with the NaOH treatment enhancing conversion potential more than the Na_2CO_3 treatment.

Optical Microscopy - CO pretreatment of the Black Thunder coal in the 1 L stirred reactor (800 psi CO, NaOH, 310°C) produced a material that was morphologically similar to that produced from Clovis Point Wyodak coal in the microautoclave; most of the vitrinite has been melted and agglomerated to form larger (relative to the feedstock), coherent masses, whereas the liptinite and, in particular, the inertinite macerals appear to have been less reactive to the process. The mean reflectance of the altered (melted) vitrinite was approximately 0.40%, a value similar to that reported for the Wyodak coal after similar pretreatment in the microautoclave. The treated material contained pores ranging from submicron to tens of microns in size, some of which were filled with solid, homogeneous, bitumen-type material.

Reaction of the subbituminous coal with CO and Na_2CO_3 (at 310°C) produced a material that was ostensibly similar in appearance to that produced using NaOH as the water-gas shift catalyst, although reaction in the presence of Na_2CO_3 caused a more extensive development of porosity within the agglomerates. The mean reflectance of the altered vitrinite was 0.43%. The solid bitumen pore fillings were also present in this sample, and were effectively removed from the melted vitrinite when the pretreated coal was extracted with pyridine.

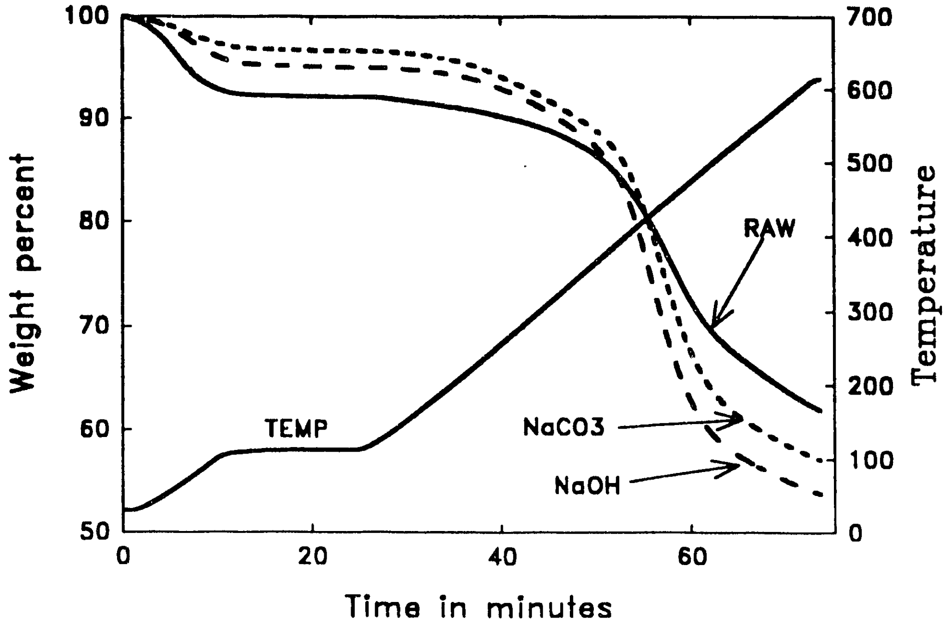


Figure 7 . Weight loss profiles for raw and treated Black Thunder coals.

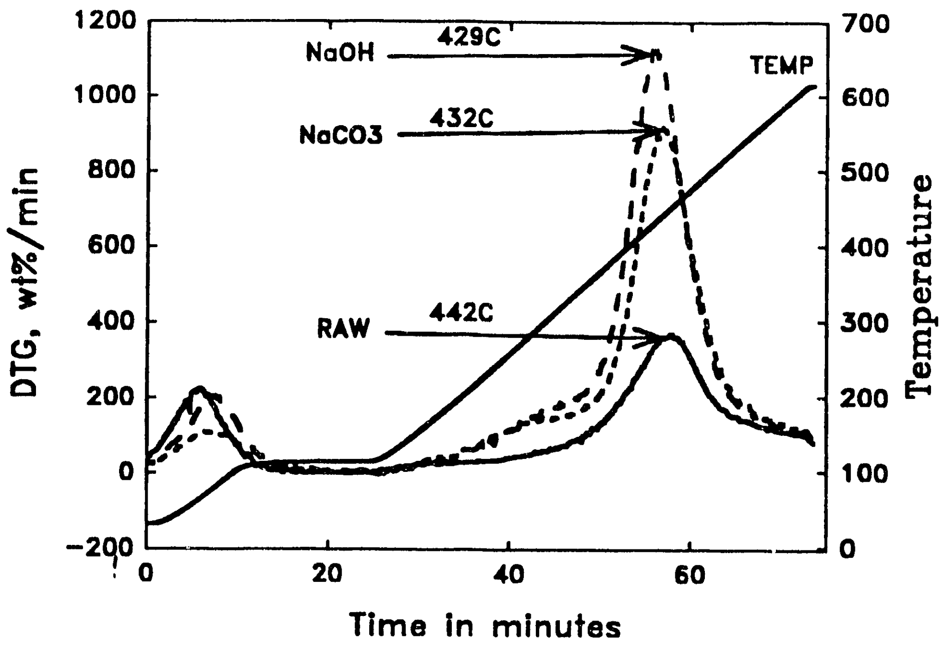


Figure 8 . DTG curves for raw and treated Black Thunder coals.

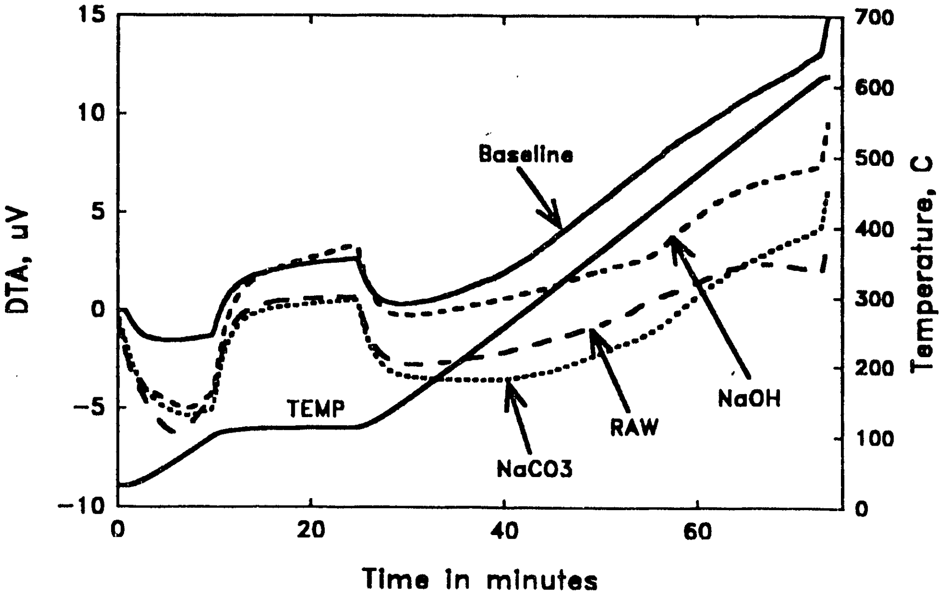


Figure 9 . DTA curves for Black Thunder raw and treated coals.

TASK 2.1.2.1 PRETREATMENT / DEWAXING - (CONSOL)

Summary

Use of methyl ethyl ketone (MEK) and mixtures of MEK with toluene and acetone to dewax Wilsonville V-1074 distillate leads to the production of high yields of dewaxed oil with significantly improved solvent qualities. The waxes obtained from these dewaxings were relatively hard and clean and were easy to purify. Dewaxing the Wilsonville V-1074 distillate in a 45/55 (vol %) MEK/acetone mixture at -35°C produced an 84 wt% yield of dewaxed oil with a solvent quality of 83%. Maximum solvent quality for this oil is attained at about 15 wt% wax removal. Further wax reduction has little effect on the solvent quality of the dewaxed oil.

Densities of the waxes separated from the V-1074 distillate at -5°C and -35°C were measured and their chemical compositions were determined. These measurements were made so that LDP Associates can estimate yields from a catalytic cracker that operates on wax.

The trends obtained in solvent quality testing of the dewaxed oil with Black Thunder coal were similar to those obtained using our standard Indiana V coal. The dewaxed oils are better donor solvents than the feed distillate toward Black Thunder coal.

Discussion

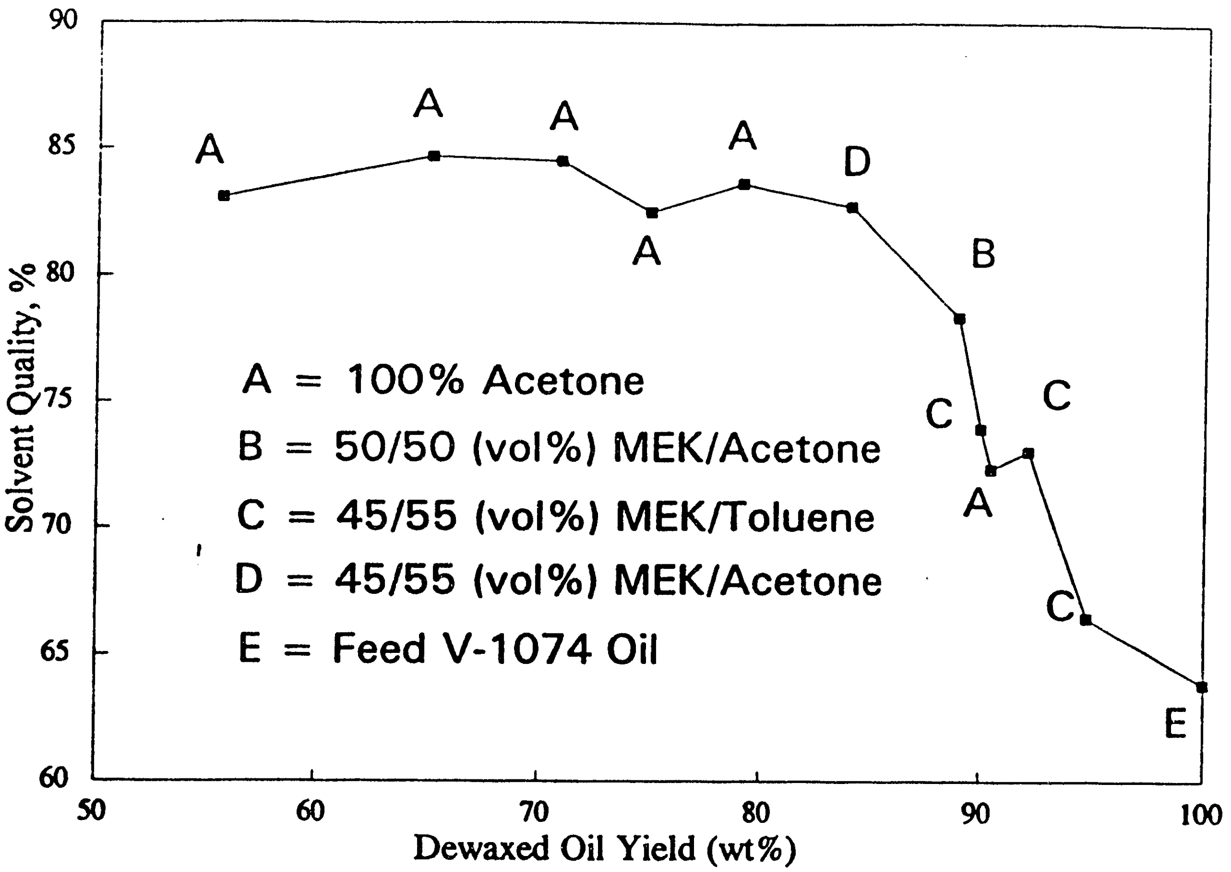
Last quarter, it was established that the wax obtained by dewaxing coal distillate could be refined into a colorless, odorless, aromatic-proton-free product by contacting with activated alumina. This quarter, commercially used dewaxing solvents were used to produce a high-solvent-quality dewaxed oil and a clean wax product. The most commonly used commercial dewaxing solvent is a mixture of methy ethyl ketone (MEK) and toluene. MEK, toluene and acetone were used alone and in combination with each other to dewax the Wilsonville Run 262 V-

1074 distillate.

The solvent quality of the oil produced by dewaxing the V-1074 distillate with 45/55 (vol %) MEK/toluene at -5°C and at -35°C were ~65% and 72% respectively, Table 12. For this discussion, "solvent quality" is defined as the wt % conversion of Indiana V, Old Ben #1 Mine coal to THF solubles in a modified equilibrium test (750°F, 30 min, 1.5/1 solvent/coal ratio) with the subject solvent. This is slightly higher than the quality of the starting distillate (64%), but considerably lower than that observed for the same distillate dewaxed at the same temperatures in 100% acetone. The dewaxed oil yields were considerably higher than those obtained at the same temperatures in 100% acetone (95 wt % and 92 wt % vs. 75 wt % and 65 wt %, respectively).

Samples of Wilsonville Run 262 V-1074 distillate were also dewaxed at -35°C in 100% MEK and in 50/50 (vol %), 45/55 (vol %) and 40/60 (vol %) MEK/acetone mixtures. The wax yields from the runs with MEK/acetone mixtures were 11 wt %, 16 wt % and 17 wt %, respectively vs. 10 wt % in 100% MEK and 35 wt % in 100% acetone, Table 12. The solvent quality of the oil dewaxed in the 50/50 MEK/acetone mixture was 78%, and the solvent quality of the oil dewaxed in the 45/55 MEK/acetone mixture was 83%. This is a substantial increase over the 73% solvent quality of the oil obtained by dewaxing with 100% MEK at the same temperature. The dewaxing data show a strong correlation of solvent quality with wax yield in which maximum solvent quality is attained at wax removals of ~15 wt % and above.

Figure 10 is a plot of wax removal vs. solvent quality for dewaxing the V-1074 distillate from Wilsonville Run 262. The data in this plot are from our preliminary dewaxing tests, the -5°C and -35°C production dewaxing runs and from the currently reported tests with solvents other than acetone. The solvent quality of the dewaxed oil is strongly dependent on the



Note: **Solvent quality defined as wt % MAF conversion of Indiana V, Old Ben #1 Mine coal to THF solubles in modified equilibrium test with subject solvent.**

Figure 10 Solvent Quality vs. Wax Removal for Wilsonville V-1074 Distillate quantity of wax removed in the dewaxing step, up to about 15 wt % wax removal (~85 wt % dewaxed oil yield). At wax removals above ~15 wt %, solvent quality remains at about 84%. These data suggest that the solvent quality of the dewaxed oil depends primarily on the degree of wax removal and not directly on the specific dewaxing solvent used or the dewaxing temperature. Production of high-solvent-quality dewaxed oil with minimal wax removal (thus, a more pure wax product) is desirable for production of byproduct wax. The higher the purity of the initial slack wax, the higher will be the yield of clean wax. Also, with a higher purity slack wax, there will be less wax to clean-up.

Analysis of the products from the MEK and MEK/toluene dewaxing tests showed the wax to be nearly free of aromatic protons, Table 13, and considerably harder than the waxes removed with acetone. In addition, a single deoiling of the wax with the dewaxing solvent removed all remaining aromatic protons from the wax, Table 13.

LDP Associates requested elemental analyses, specific gravities and distillation information on selected waxes produced by dewaxing the Wilsonville V-1074 distillate. The chemical analyses for these waxes are given in Table 14. API gravities also were requested. However, API gravities apply to only liquids at 60°F and at 60°F these waxes are solids. Therefore, the following method was developed to measure the densities of these waxes. The wax sample was melted at ~90°C and poured into a 5 mm id glass cylinder and allowed to cool. After solidification at room temperature, the glass mold was further cooled in dry ice. At dry ice temperature, the wax contracted

TABLE 12

SOLVENT DEWAXING OF V-1074 DISTILLATE FROM WILSONVILLE RUN 262

Dewaxing Solvent	Dewaxing Temp., °C	Dewaxed Oil Yield, wt%	Wax Yield, wt %(a)	Dewaxed Oil Solvent Quality,% (b)
100% Acetone	-5	75	25	81
100% Acetone	-35	65	35	85
45/55 (vol%) MEK/Toluene	-5	92	8 (6)	65
45/55 (vol%) MEK/Toluene	-35	91	9 (8)	72
100% MEK	-35	89	11 (10)	73
50/50 (vol%) MEK/Acetone	-35	89	11	78
55/45 (vol%) MEK/Acetone	-35	84	16	83
40/60 (vol%) MEK/Acetone	-35	83	17	ND

a = Values in parentheses are deoiled wax yields.

b = Solvent quality defined as wt% MAF conversion of Indiana V, Old Ben #1 mine coal to THF solubles in modified equilibrium test with subject solvent (750°F, 30 min, 1.5/1 solvent/coal ratio).

ND = Not Determined.

TABLE 13

PROTON DISTRIBUTIONS IN V-1074 DISTILLATE DEWAXED WITH MEK, TOLUENE AND ACETONE MIXTURES

			Proton Distributions, %						
Dewaxing Solvent[A]	Dewaxing Temp., °C	Fraction	Condensed Aromatics	Uncondensed Aromatics	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
45% M/55% T	-5	Oil	12.7	3.8	15.1	8.1	17.1	29.2	14.0
45% M/55% T	-5	Wax[B]	0.0	0.0	0.0	1.8	2.2	83.7	12.3
45% M/55% T	-35	Oil	13.3	3.9	14.8	7.9	16.4	28.0	15.6
45% M/55% T	-35	Wax[B]	0.0	0.0	0.0	1.8	3.2	78.7	16.3
100% M	-35	Oil	13.6	3.9	14.4	8.3	16.8	26.6	16.3
100% M	-35	Wax[B]	0.0	0.0	1.8	1.6	7.0	79.2	10.3
50% M/50% A	-35	Oil	14.2	4.1	16.6	8.8	17.8	25.3	13.2
50% M/50% A	-35	Wax	0.0	0.7	1.5	0.9	10.6	74.6	11.6
45% M/55% A	-35	Oil	15.4	4.8	17.3	9.3	17.7	22.6	13.0
45% M/55% A	-35	Wax	0.0	0.7	2.2	2.2	11.2	69.9	13.8
40% M/60% A	-35	Oil	14.3	4.8	16.1	8.6	17.2	24.6	14.4
40% M/60% A	-35	Wax	0.0	0.7	2.7	2.6	9.7	69.7	14.0

Notes:
A) Solvent symbols M = Methyl ethyl ketone (MEK), T = Toluene, A = Acetone.
B) Deoiled by second solvent dewaxing step.

TABLE 14

CHEMICAL COMPOSITIONS AND SPECIFIC GRAVITIES OF SELECTED WAXES

	Chemical Composition, wt %						
Material	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen (by diff.)	Specific Gravity, 70°F	Estimated API Gravity^D
35°C composite wax^A	87.2	12.4	0.1	<0.03	0.3	0.96 ± 0.02	12 ± 4
-5°C composite wax^A	86.6	13.4	0.1	0.03	-0.1	0.88 ± 0.02	29 ± 4
-5°C composite wax^A, cleaned^B	85.8	14.2	0.1	<0.03	-0.1	0.88 ± 0.02	29 ± 3
-35 °C wax^C	85.5	14.0	0.0	<0.03	0.5	0.91 ± 0.02	24 ± 4
Paraseal*	85.0	14.8	0.1	<0.03	0.1	0.92 ± 0.03	21 ± 5

Notes:
A = dewaxed in 100% acetone.
B = cleaned by contacting with alumina.
C = dewaxed in 55 vol % acetone/45 vol % MEK.
D = c.f. text for description.

and was easily removed from the mold. The wax pellet was then re-warmed to room temperature and trimmed with a scalpel to a length of about 1.5 cm. The pellet was weighed and its density was determined by methanol displacement at 70°F. The results of these density measurements are shown in Table 14. The uncertainties reported in the table are the standard deviations of the means of five determinations. The measured densities were converted to a pseudo-API gravity value by the following equation.

$$API\ Gravity = \{\frac{141.5}{specific\ gravity} - 131.5\}$$

Note, however, that these values differ from the API gravity in that the samples are solids and the temperature of determination was about 70°F. The waxes from the deeper dewaxing experiments (i.e., those that are less pure and that are produced at greater wax yields) were more dense than those obtained at lower wax yields. Undoubtedly, this is due to the dilution of the less dense wax with higher density non-waxy oil.

Tests were made to compare the results of our baseline modified equilibrium solvent quality tests, which were made with Indiana V coal (Old Ben #1 Mine), with those obtained with Black Thunder coal under the same conditions. It is important to establish that dewaxing the recycle distillate enhances the conversion of the base case Black Thunder coal. Conversion of the Black Thunder coal with Wilsonville Run 262 V-1074 distillate was higher than that of the Old Ben coal (~67% vs. ~64%). Conversions of the Black Thunder coal and V-1074 distillate dewaxed at -5°C and -35°C were lower than those of our standard Indiana V coal (79% and 81% vs. 82% and 85% respectively). Importantly, the improvement in solvent quality was substantial when measured with Black Thunder coal and the overall trends were the same with both coals.

TASK 2.1.2.2 PRETREATMENT / AGGLOMERATION - (CONSOL)

Summary

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

Black Thunder coal agglomerated with coal distillate verified the performance observed using No. 6 fuel oil. Except for low-pH runs, overall performance of agglomeration with Black Thunder coal has been poor. Adaptation of the benchtop stirred autoclave for agglomeration at elevated pressure and temperatures was completed, and the autoclave was successfully used for agglomeration tests. Tests with Wilsonville distillate and No. 6 fuel oil gave results similar to those obtained in the larger agglomeration vessel with Black Thunder coal. Seven agglomeration runs were made at elevated pressure (150 to 250°C, 50 to 650 psig) with Black Thunder feed coal and a distillate/ashy resid blend as the agglomerating oil. Results ranged from no agglomeration to production of small agglomerates, but no significant resid deashing took place.

A new basis for ash rejection results is being used to reduce uncertainties in physically-cleaned vs. water-solubilized ash rejection and problems with the use of SO_3-containing ash for calculations.

Viscosity - temperature measurements were made on No. 6 fuel oil, Wilsonville V-130 deashed resid, V-1082 ashy resid, and three distillate/ashy resid blends to assist in establishing conditions for agglomeration tests.

Discussion

Agglomeration at Ambient Pressure

Two objectives met this quarter were: 1) to demonstrate that coal distillate performed similarly to No. 6 fuel oil in agglomerating Black Thunder coal, and 2) to demonstrate that the new, smaller autoclave vessel for agglomeration performed similarly to the standard vessel used up to this point. Physical ash rejection in all the conventional (ambient pressure) agglomeration runs (Table 15) has been poor, ranging from 1 to 8%. Extensive dissolution of minerals occurred at low pH, as previously reported.[10,11] The first objective was met by agglomerating Black Thunder coal with a heavy distillate (V-1074) from Wilsonville in the standard vessel. This gave results similar to those obtained with No. 6 fuel oil (Table 15, compare Run A16 with Runs A1 and A2). A baseline test (Run A17) made at agglomeration conditions, but without any oil, showed that much of the apparent deashing in previous Black Thunder tests at the natural slurry pH (5.3 to 5.6) was probably an artifact of the high SO_3 content in the feed coal ash (see discussion below). The second objective was met in three agglomeration runs (Runs B1 through B3) which were made with Black Thunder coal at atmospheric pressure in the 300 mL Parr autoclave (described below). One run used No. 6 fuel oil, and two used the Wilsonville V-1074 as the agglomerant. Results (Table 15) were similar to those achieved in the larger unit: organic recoveries $\geq$99.8%, 1-4% ash rejection, and 87-91% ash balances. Thus, the new vessel, which is capable of high pressure operation, gave the same performance as the older, larger vessel.

Pressure Agglomeration at High Temperature

We met one objective of successfully agglomerating Black Thunder coal at high temperature and elevated pressure. However, coal deashing was poor, and successful deashing of the ashy resid remains an unmet objective. High temperature and dilution of the ashy resid with distillate were used to lower the viscosity to facilitate physical agglomeration and resid deashing. Adaptation of a 300 mL (nominal) capacity Parr benchtop autoclave to perform agglomeration experiments at temperatures up to 300°C and at

TABLE 15

AGGLOMERATION RESULTS

Run[A]	Feed	Oil[B]	Oil Dose, wt % MF	Temp., °C	pH[C]	pH Agent	Organic Recovery, wt %	Ash Rejection wt % (Ash Reccvered in Reject Solids)
A1	BT Coal	P1	25.6	54	5.6		99.9	7.6
A2	BT Coal	P1	13.1	54	5.6		99.9	2.7
A16	BT Coal	C1	14.7	50	5.6		99.9	1.4
A17	BT Coal	None	0.0	50	5.6		100.0	0.0
B1	BT Coal	P1	26.0	54	5.6		99.8	4.2
B2	BT Coal	C1	16.0	50	5.6		99.9	1.2
B3	BT Coal	C1	33.7	50	5.6		99.9	1.1
B5H	BT Coal	P1	28.0	150	5.6		99.8	3.1
B6H	BT Coal	C2	32.8	200	5.6		92.5	6.2
B7H	BT Coal	C2	51.4	200	5.6		99.1	0.6
B8H	BT Coal	C2	92.3	200	5.6		99.9	0.1
B10H	BT Coal	C2	43.6	250	5.6		95.9	3.1
B13H	BT Coal	C2	48.8	200	10.0	NaOH	99.1	0.7
B9R	V-1082	P1	31.0	50	8.0		99.7	0.0
B11R	V-1082	P1	36.8	50	8.0		99.9	0.0
B12R	V-1082	P2	27.3	~20	8.0		100.0	0.1
B14R	V-1082	P2	22.5	~20	9.5	Na_2CO_3 (0.5 wt %)	99.5	1.3

A = A indicates run made in the large agglomeration vessel, and B indicates run was made in the small agglomeration vessel (Parr autoclave), an H suffix indicates a high pressure run, and an R suffix indicates ashy resid was the feed to the run.

B = P1 - No. 6 fuel oil; P2 - white kerosene; C1 - V-1074 heavy distillate from Run 262; C2 - 25/75 wt % oil C1/V-1082 ashy resid from Run 262.

C = Natural (unadjusted) slurry pH was not measured in every run.

Note: Ash rejection basis differs from results presented last quarter. See text for details.

elevated pressure was completed. Seven pressure agglomeration runs with Black Thunder coal were made in the 300mL Parr Autoclave (Table 15). One was made with No. 6 fuel oil, and six with the Wilsonville 25/75 wt % distillate/ashy resid blend as the agglomerant. The viscosity-temperature data (see below) from various potential oils were used to select test conditions. Temperatures ranged from 150 to 250°C, and pressures ranged from about 50 to 650 psig. One run with the resid blend apparently did not produce agglomerates (Run B4H), one produced microscopic agglomerates, three produced very small agglomerates, and the product from one run was caked from over-oiling. The fuel oil run also produced agglomerates. One of the pressure agglomeration runs (Run B13H, Table 15) was made at a slurry pH of 10 (NaOH, pH measured at room temperature). In spite of physical agglomeration in several runs, no significant resid deashing occurred. Pressure agglomeration necessitated a change in the oil addition method. The runs were made by adding lumps of solid resid into the autoclave, with slow stirring, at about 95°C. The reactor was sealed and the contents were stirred at high-shear conditions after the run temperature of 150°C to 250°C was reached.

New Basis for Ash Rejections

In order to reduce uncertainties in physically-cleaned vs. water-solubilized ash rejection and problems associated with SO_3 retention in the feed, product, and reject subbituminous coal ash, we will report ash rejection on a different basis than in the past. The ash rejections we have reported from the start of this contract are based on ash in the feed which is not recovered in the agglomerate product. Ash rejection on this basis is generally an upper limit, because it accounts, as reject, water-soluble ash and any ash contained in lost material. The ash rejections reported here (Table 15) are based on ash actually recovered in the reject solids (filter cake), which does not include water-soluble ash. Ash rejection on this new basis represents the material actually physically cleaned from the feed, and can be considered a lower limit to ash rejection. This second type of ash rejection is not greatly influenced by differential retention of SO_3 in the feed, product, and reject ash (see below).

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

Old Ash Rejection = Ash Rejection (Unrecovered Product Basis) =
$[(M_1-M_2)/M_1]x100\%$, where

M_1 = Mass of Ash Charged (from all sources such as coal, oil, etc.), and M_2 = Mass of Ash in Agglomerate Product.

New Ash Rejection = Ash Rejection (Recovered Reject Ash Basis) =
$(M_3/M_1)x100\%$, where

M_1 = Defined as above, and
M_3 = Mass of ash recovered in solid reject.

Ash Balance (Excluding Water-Soluble Ash) = $[(M_2+M_3)/M_1]x100\%$, where

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

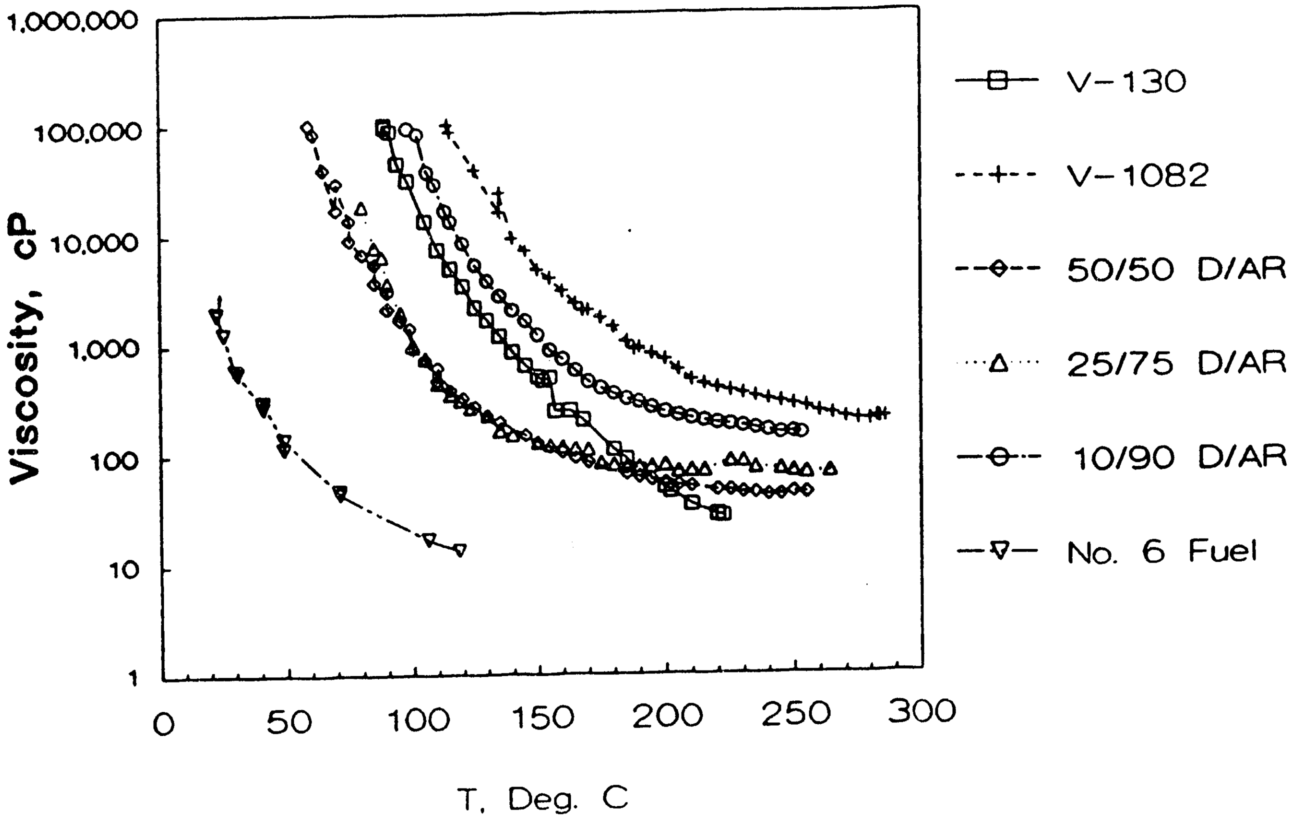
Ash Balance = New Ash Rejection - Old Ash Rejection + 100%.

The amount of SO_3 retained in the ash of agglomeration feeds, products, and rejects is highly variable, depending on ashing conditions and the sample characteristics. The few samples of feed and product ashes we analyzed ranged in ash SO_3 content from less than 5% to nearly 21%. Such variation will cause inconsistencies in the ash rejection, ash balance, etc., unless calculations are made on an SO_3-free basis. Adjusting our previously reported ash rejections to an SO_3-free basis is estimated to decrease the values by between 4 and 20% absolute and increase ash balances by a similar amount. It is likely that most of the ash rejection previously attributed to water solubilization[12] (at pH>5 only) is actually an artifact of the variation in SO_3 retention in the feed and product ashes.

The ash rejections based on recovered solid reject (Table 15) are not corrected for SO_3, but are less sensitive to ash SO_3 variation than the ash rejections previously used. When it is necessary to have highly accurate yield and balance information for economics, scale-up, etc., we will obtain the additional analyses needed and make the appropriate calculations on an SO_3-free basis.

Viscosity Measurements of Agglomerating Liquids

In order to use ashy resid as an agglomerating oil, dilution and/or high temperature are necessary to reduce the oil viscosity. We measured viscosities of liquefaction resids, resid/distillate mixtures, and other oils to guide selection of temperature and dilution ratio for agglomeration experiments. The viscosity vs. temperature profiles of No. 6 fuel oil, the V-130 deashed resid, the V-1082 ashy resid, and three blends of V-1074 distillate with the ashy resid, were measured with the Brookfield viscometer. The experimental procedure for obtaining viscosities of agglomerating oils at elevated temperatures is described in the Experimental section (below). Constant-temperature determinations could be made, if needed, for more accuracy. The viscosity profiles (Figure 11) will help select temperatures suitable for agglomeration. For all but the No. 6 fuel oil, the estimated actual temperature is ~30°C higher than the values shown. The viscosity vs. temperature profile measured for a 25/75 wt % blend of V-1074 distillate with the ashy resid was found to be nearly identical to that of the 50/50 blend. The



Note: All oils except No. 6 fuel oil are from Wilsonville Run 262. Blend ratios are wt % D/wt % AR, where D = V-1074 distillate and AR = V-1082 ashy resid.

Figure **11** Viscosity-Temperature Relationship for Various Oils. Note that the temperature shown is estimated to be 30°C lower than the actual temperature for all oils except fuel oil No. 6.

viscosity vs. temperature profile of a 10/90 wt % blend of V-1074 distillate with the ashy resid was closer to the ashy resid profile than to the 25/75 wt % distillate ashy resid profile. In a method for deashing tar sands using a flotation procedure,[13] it is recommended that the oil (i.e., tar sand) viscosity be 1500 cP or lower for the oil and mineral phases to separate. CONSOL's agglomeration practice suggests that oil viscosities of 200 cP or lower may be desirable for agglomeration.[14] We chose to use viscosities of 1000 cP and 200 cP as benchmarks. These results are summarized in Table 16. This provides an easy means to estimate temperatures for agglomeration with the oils tested. No additional viscosity measurements are planned at this time.

TABLE 16

VISCOSITY OF AGGLOMERATION OILS
Summary Table

Sample	Estimated Temp., °C[a] To Reach 1000 cP	To Reach 200 cP
No. 6 Fuel Oil	30[b]	50[b]
V-130	170[c]	200[c]
V-1082	220[c]	300[c]
10/90 wt % Dist/Ashy Resid	180[c]	230[c]
25/75 wt % Dist/Ashy Resid	130[c]	160[c]
50/50 wt % Dist/Ashy Resid	130[c]	160[c]

a) Estimated from plot of log viscosity vs temperature.
b) Based on actual temperature.
c) Based on temperature estimated by adding 30°C to the thermocouple temperature reading (see text).

Miscellaneous

A sample of CO-pretreated coal was received from UK/CAER for use in future agglomeration tests.

A sample of Black Thunder coal was sent to B. Slomka at Ames Lab. Dr. Slomka will determine the cleanability of this coal in column flotation tests. Tests will be conducted on the as-is -200 mesh coal and on micronized coal. Our agglomeration experience with this coal (pulverized) and reported[15] washabilities of several 14-mesh Wyodak seam coals from Campbell County, Wyoming, indicate that Black Thunder coal is not very cleanable by conventional techniques. The tests at Ames Lab should indicate how well ash is liberated from the pulverized and micronized coal.

Experimental

A description of the CONSOL system for agglomeration of coal at high pressure (Parr Benchtop Autoclave) follows. The Parr Benchtop Mini Reactor system (Model 4561M) has a nominal capacity of 300mL and is designed to operate on a benchtop. The reactor is normally operated on a benchtop with Plexiglas shielding to protect against the possible escape of steam or ejection of other material. Any work conducted above 250°C will be done in a steel barricade, however, because of increased system pressure. A separate control unit has the thermocouple readout and controllers for heating and stirring. The autoclave is constructed of Hastelloy C-276, and is rated for 3000 psig and 350°C operation. The minor reactor equipment modifications done for the current work consisted of construction of a six-bladed impeller and a removable baffle (four plates) and removal of a cooling loop and a dip tube (plugs or cap fittings were used to seal these ports). A non-standard drive pulley was used to obtain the desired stirring speed (about 2300 rpm with coal slurry present). The reactor is equipped with a pressure gauge for operation to 3000 psig and a rupture disk rated at 3050 psig.

For the current application, an aqueous slurry of coal is agglomerated using a petroleum-derived or liquefaction-derived oil. Experiments will generally be conducted at temperatures no higher than 250°C, at which the steam pressure is 562 psi. Tests may be run at strongly acidic or alkaline conditions (pH 1 to 13). Manufacturer recommendations were followed in calculating the maximum quantities of materials charged to the reactor: 175 mL water, 44 g coal, and 15 g oil. These quantities are limited because of the volumetric expansion of liquid water, which is 25% at 250°C. It is possible that a temperature of 300°C may be required for some runs. At this temperature, the steam pressure is 1230 psig and the volume expansion of liquid is 40%. At these conditions, we would reduce the quantities of materials charged to the autoclave by an appropriate amount, and conduct the experiments in a steel barricade.

The oil addition method is as follows: 1) the water and coal are heated in the reactor (unsealed) to 90-95°C, 2) the reactor is opened and the oil (which may be a solid at room temperature) is added, 3) the reactor is sealed and heated to the final temperature, and 4) after the appropriate time at temperature, the heating mantle is removed and a container of water is placed around the reactor to lower the temperature and pressure (monitored during quenching). The reactor is then moved to the hood and opened. Workup of the sample then follows our usual procedure for agglomeration.[14] A system for adding oil while the reactor is pressurized may be added at a later time.

The experimental procedure for obtaining viscosities of agglomerating oils at elevated temperatures was initially tested on No. 6 fuel oil and modified to accommodate problems associated with solids-containing resid. In the procedure eventually adopted, a covered stainless steel beaker containing about 120 g of the sample was heated by a mantle which covered the bottom half of the beaker. A temperature readout was provided by a thermocouple placed near the beaker wall, about halfway down from the top. An opening in the cover provided space for the thermocouple, the viscometer shaft, and a purge stream of nitrogen, which prevented the hot material from oxidizing. The measurements were conducted in a hood because of vapor emitted from the hot oil. Manual stirring was used until the material was heated to a fluid condition, and then the viscometer spindle was kept rotating to provide some agitation as the sample cooled. The oil was heated to the desired temperature and then viscosity measurements were recorded as the sample cooled ballistically. The viscometer was a Brookfield model LVT. The proper spindle selection and a range of eight speed settings allowed readings to be obtained from about 20 to 100,000 cP. At the conditions used for most determinations (cooling profile from the completely fluid sample), the recorded temperature near the container is estimated to have differed from that of the sample near the viscometer spindle by 30°C. Constant-temperature determinations can be made as needed for more accuracy. The reported values are uncalibrated; that is, the raw data were not referenced to a standard-viscosity oil.

SUBTASK 2.1.3 SOLVENT PRETREATMENT (SANDIA)

Solvent pretreatment work at Sandia involves using hydrogen from an in situ water-gas shift reaction to concurrently hydrogenate a solvent in a trickle-bed reactor. Previous demonstration and optimization experiments used a model compound mixture to test for catalyst activity and to test the effects of liquid space velocities. Experiments for the quarterly period from October 1992 to December 1992 used heavy distillate (V-1074), and V-1074 that had been dewaxed at -5°C and -35°C by CONSOL. For these purposes a larger catalyst bed was used. The larger reactor has 22 cm^3 of internal volume and consists of two 0.4" I.D by 7" long stainless steel tubes connected in series. This configuration allows for adequate reactor volume to achieve suitable liquid space velocities.

Three sets of tests were performed with Shell 324M (12.4% Mo, 2.8% Ni) as the catalyst to evaluate the baseline response of heavy distillate to low severity hydrogenation using the water-gas shift reaction. Additional tests were performed using the -5°C dewaxed V-1074 with a Pt HTO (5.4%Pt) catalyst and a coated NiMo HTO (8.1% Mo, 2.7% Ni) catalyst which had been synthesized at Sandia.

Shell 324M Testing

The catalyst was used as extrudate and packed in the 0.4" O.D. reactor tube. The catalyst bed was then sulfided at 390°C for four hours with a 9% H_2S in hydrogen mixture. A $50CO-50H_2$ mole% mixture was used with equimolar amounts of steam ($steam:CO:H_2$ = 1:1:1) to hydrogenate the concurrently flowing solvent. The Weight Hourly Space Velocity (WHSV) was varied over the range of 0.3 hr^{-1} to 0.8 hr^{-1}. The reactor system pressure was kept at 1000 psig and the tests were performed at two temperatures, 300°C and 325°C. Since both the V-1074 and the dewaxed solvent are semisolids at room temperature it was necessary to heat the feed reservoir and to heat-trace feed lines. Several modifications were made to the reactor to ensure smooth operations. Elemental analyses of products from these runs are presented in Tables 17 and 18.

Hydrogen content was increased from 9.9% to 10.7% using the V1074 feed and increased from 8.5% to 9.3% using the -5°C dewaxed solvent. Some decrease in hydrogenation amount was noticed during the first day of catalyst testing. This can be attributed to catalyst deactivation which seems to take place during the first several hours on-line. Catalyst deactivation is discussed

Table 17 Carbon and Hydrogen Content of Solvent (V-1074 and -5°C dewaxed V-1074)

Sample	**WHSV (hr^{-1})**	**Temperature C°**	**Carbon wt%**	**Hydrogen wt%**
V1074(feed)	NA	NA	89.5	9.9
9283	0.47	300	88.2	10.4
9284	0.44	300	88.6	10.7
9296	0.83	325	87.3	10.2
-5C Dewax (feed)	NA	NA	89.1	8.5
10223	0.30	300	89.3	8.9
10226	0.30	300	88.8	8.9
10228	0.29	325	89.1	9.3
10236	0.78	325	88.9	8.8
10237	0.76	325	89.1	8.9

Table 18 Carbon and Hydrogen Content of Solvent (-35°C dewaxed V1074)

Sample	W H S V (hr^{-1})	Temperature C°	Carbon wt%	Hydrogen wt%
-35C Dewax (feed)	NA	NA	90.6	8.0
11044	0.51	300	90.4	8.9
11045	0.56	300	90.9	8.5
11052	0.30	325	88.9	8.7
11058	0.80	325	91.4	8.1
11063*	0.73	325	91.1	8.4 (1000 psig)
11065*	0.74	325	91.2	8.3 (670 psig)
11067*	0.68	325	90.4	8.3 (330 psig)

* Hydrogen only for these experiments

in section 2.3.3. Overall, the maximum hydrogen increase was approximately 0.8 wt%. By way of comparison 4,5-dihydropyrene, a known hydrogen donor compound, has 1.0 wt% donatable hydrogen content. These increases should be sufficient to make notable improvements in coal liquefaction runs.

Hydrogen content in the product was increased from 8.0% to 8.9.% using the -35°C dewaxed solvent. In general the -35°C dewaxed solvent performed like the -5°C dewaxed solvent, except that the -35°C feed was more difficult to pump. Overall the maximum hydrogen content increase of the pretreated distillate is about 0.8 to 0.9 wt%.

Samples 11063, 11065, and 11067 were taken on the third day of operation and were hydrotreated with hydrogen as the sole gas reactant to test the effect of hydrogen partial pressure. The effect of reducing hydrogen pressure was not dramatic in these tests. This result could be due in part to catalyst deactivation during previous testing. Catalyst deactivation is discussed in task 2.3.3.

Gas samples taken during the combined water-gas shift solvent hydrogenation experiments using V1074, -5°C dewaxed V1074 and -35°C dewaxed V1074 showed that CO conversions were very high (95% at 300°C). There seems to be no problem achieving near equilibrium conversions to hydrogen and carbon dioxide at the conditions tested (300°C ,P_t=1000 psig and CO Gas Hourly Space Velocity = 150 hr^{-1}).

Platinum HTO Catalyst Testing

A batch of platinum HTO catalyst was prepared for use in the water-gas shift solvent hydrogenation reaction using -5°C dewaxed feed. The catalyst synthesis is described in subtask 2.3.3. Pretreatment of the catalyst consists of pressing into pellets, sizing to -10+20 mesh size, and calcining in air at 500°C to remove residual amine compounds from catalyst synthesis. The catalyst is next packed in the trickle-bed reactor and the platinum is reduced in flowing hydrogen gas for two hours at 200°C. The Weight Hourly Space Velocity (WHSV) was varied from 0.3 hr^{-1} to 0.8 hr^{-1}. The reactor system pressure was kept at 1000 psig and temperatures were tested at 300°C and 325°C.

Results in Table 19 show that hydrogen content of the solvent increases by a moderate 0.5% using the combined water-gas shift solvent hydrogenation reaction (experiments 11177, 11184 and 11186). The less than expected hydrogen content of these samples was due to lower hydrogen partial pressures since some of the carbon monoxide formed methane under these conditions. This side reaction reduces hydrogen partial pressure in the trickle-bed reactor. Previous tests using the model compound mixture and the Pt HTO catalyst (July 1992) showed very little methane formation. The current tests showed as much as 14 vol% methane in the exit gas at 325°C. The most plausible explanation for the high methane production in these runs is the lower gas hourly space velocity in this larger reactor (150 hr^{-1} compared to 400 hr^{-1} for the July runs). Future tests will aim at resolving this issue.

Table 19 Carbon and Hydrogen Content of Solvent (-5°C dewax/Pt catalyst)

Sample	**W H S V (hr^{-1})**	**Temperature C°**	**Carbon wt%**	**Hydrogen wt%**
-5C Dewax (feed)	NA	NA	89.1	8.5
11177	0.32	300	90.5	9.0
11184	0.32	325	90.4	9.0
11186	0.82	325	90.6	8.9
11193*	0.78	325	89.9	9.6 (1000 psig)
11195*	0.73	325	90.5	9.0 (670 psig)
11197*	0.74	325	90.9	8.6 (330 psig)

* Hydrogen only for these experiments

The product from the "hydrogen only" tests (samples 11193,11195, and 11197) showed a marked hydrogen concentration effect (unlike the tests using Shell 324M). An increase of 1.1% hydrogen was noted for the sample produced at 1000 psig of hydrogen. Although this is typical of noble metal catalysis, it is notable that this high activity was achieved after two days of operation with a rather "dirty" feed. The good performance after two days of experiments suggests that platinum HTO catalysts do not deactivate as rapidly as the Shell catalyst at these conditions, and may be a good candidate for other upgrading applications.

Coated HTO Nickel Molybdenum Catalyst Testing

Experiments reported in December used -5°C dewaxed solvent from CONSOL in the microflow trickle-bed reactor. The catalyst used in these tests was a hydrous titanium oxide coated onto an alumina substrate and contained 2.7% nickel and 8.1% molybdenum. The catalyst was used as -10+20 mesh size and packed in the 0.4" I.D. reactor tube. The catalyst bed was then sulfided at 390°C for four hours with a 9% H_2S in hydrogen mixture. The Weight Hourly Space Velocity (WHSV) was tested over a range of 0.4 hr^{-1} and 1.1 hr^{-1}. These WHSV numbers are slightly higher for this catalyst than for the Shell 324 tests because the packing density was approximately 72% as large as that for the Shell 324M tests. The reactor system pressure was kept at 1000 psig and temperatures used were 300°C and 325°C. Carbon and hydrogen contents of the starting and hydrogenated distillates are shown in Table 20.

Hydrogen content in the product was increased from 8.5% to 9.6% for the -5°C dewaxed solvent. The maximum hydrogen content increase of the pretreated distillate ranges from 0.8 wt% to 1.1 wt%. Gas samples taken during the combined water-gas shift solvent hydrogenation experiments showed that CO conversions were 95% at 300°C. Samples 121802, 121804, and 121806 were taken on the third day of operation and were hydrotreated with hydrogen as the sole gas reactant to test the effect of hydrogen partial pressure. The results are quite similar to previous test results using Shell 324M catalyst.

During November nine pretreated solvent samples produced from V1074, -5°C dewax, and -35°C dewaxed solvents were sent to CONSOL for solvent quality measurements.

Table 20 Carbon and Hydrogen Content of Solvent (-5°C dewaxed solvent NiMo HTO coated catalyst)

Sample	W H S V (hr^{-1})	Temperature	Carbon wt%	Hydrogen wt%
-5C Dewax (feed)	NA	NA	89.1	8.5
121503	0.37	300	90.4	9.4
121504	0.41	300	89.9	9.6
121603	0.42	325	90.4	9.6
121604	0.96	325	90.5	9.0
121802*	1.0	325	89.8	9.3 (1000 psig)
121804*	1.0	325	90.5	8.9 (670 psig)
121806*	1.1	325	90.5	9.1 (330 psig)

* Hydrogen only for these experiments

SUBTASK 2.2.3 MODIFIED REACTOR CONCEPTS (SANDIA)

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

Several coal liquefaction tests were run in November and December using autogenic reaction conditions (100 psig nitrogen). These tests were used to evaluate the solvent quality of hydrotreated distillates produced with the trickle bed reactor.

Results from these liquefaction experiments using two types of solvents: 1) baseline and hydrogenated V1074 heavy distillate and 2) baseline and hydrogenated dewaxed V1074 (dewaxed at -5°C) are shown in Table 21. In addition, a hydrogen donor (hexahydropyrene, H6PY) was added to the baseline solvents to evaluate a known hydrogen donor addition.

Table 21 shows that under these conditions coal conversion was increased from 59% with V1074 to 63% with hydrogenated V1074. Oil yield as measured by pentane solubility increases more substantially from 9% with V1074 to 25% for the hydrogenated V1074.

Table 21 Product Yield (%dmmf) for Microautoclave Tests with Wyodak Coal

Solvent	**Added Hyd. (wt%)**	**% IOM**	**% PA + A**	**% Oils**	**% Gases**	**% Conv.**
V1074	0	41	45	9	5	59
Hyd. V1074	0.7	37	32	25	5	63
V1074+H6PY	0.6	37	27	33	3	63
-5°C dewax	0	34	65	-5	6	66
Hyd. -5C dewax A	0.1	30	58	7	5	70
Hyd. -5C dewax B	0.8	32	41	23	5	68
-5°C dewax+H6PY	0.6	23	43	30	4	77

Coal conversion is equal to (100-%IOM Yield). Conditions: 400°C, 100 psig N_2, 30 minutes, No catalyst, Solvent:Coal=1.5:1, Assume feed solvent is 100% pentane soluble.

Coal conversion increased form 66% to 68% and oil yield increased from a negative value with dewaxed V1074 to 23% for the hydrogenated dewaxed V1074 (sample B). The substantial increase in oil yield for all hydrotreated solvents showed that the moderate coal conversions did not completely reflect the improved solvent quality. It is anticipated that Wyodak coal conversions at 425°C-450°C using these solvents will reflect the improved solvent quality in the coal conversion measurement. These tests will be undertaken in the next quarter. In addition the experiments with added H6PY showed a improved oil yields over the hydrogenated distillates possibly because all of the supplementary hydrogen from H6PY was effective donor hydrogen. CONSOL will evaluate hydrogen distributions on the hydrogenated samples using proton NMR spectroscopy.

Solvent Upgrading - Solvent upgrading using synthesis gas mixtures and the in situ water-gas shift reaction was indicated by the nitrogen and sulfur removal during low temperature solvent hydrogenation. Previous investigators have commented on the effectiveness of sulfur removal using the water-gas shift reaction for in situ hydrogen generation.[16] Results in Table 22 show that as much as half of the initial nitrogen can be removed at temperatures as low as 300°C.

Results in Table 22 show that solvent upgrading is closely tied to liquid feed rates and temperatures. Catalyst deactivation is measurable at these low severity conditions and will be addressed in longer term tests.

Table 22 Nitrogen and Sulfur Removal for WGS reaction (Shell 324M)

Sample	WHSV (hr^{-1})	Temperature	Nitrogen ppm	Sulfur ppm
V1074	NA	NA	4600	220
9284	0.44	300	2400	NM
9286	0.61	300	3000	80
9293 *	0.38	300	3200	150

-5°C Dewax	NA	NA	6400	490
10223	0.30	300	2100	210
10224	0.33	300	3300	310
10233	0.33	325	3900	210
10237	0.76	325	4500	140

* Sample showed that the catalyst bed was partially deactivated

NM = Not Measured   NA = Not Applicable

TASK 2.3.1 IRON BASED DISPERSED CATALYSTS (UK/CAER)

Liquefaction with Superfine Iron Oxide

Data were presented in the previous quarterly report showing the the catalytic effect of superfine iron oxide catalysts (SFIO) on liquefaction of Black Thunder coal in WRO.[17] Concentrations over a range of iron on dry coal up to 5 wt% were evaluated in a statistically designed experiment. From the data, a linear model was developed from which the centerpoint data were determined and compared with experimentally determined data. There was good agreement between the model and the experimental data at the midpoint.[18] However, comparisons of experimental data taken at the center-edgepoint did not agree well with predicted data.[19] Additional data have been taken in the region of the center-edgepoint to get a better understanding of conversions and yield structure at lower iron concentrations.

Although most of the data in the previous report were reported as iron concentrations on as-received coal, we are switching our reporting basis to a dry coal basis to relate more closely to plant operation practice. A number of runs made at various levels of iron on dry coal up to the midpoint 3.2 wt% Fe level are shown in Table 23. All of these runs were made at 415°C for 60 minutes.

The addition of SFIO to these samples is superimposed on an already sizable amount of iron concentration in the WRO-coal feed slurry. In the thermal run over 4 wt% iron on dry coal was already present in the feed. Mossbauer analysis on several of the residues from the liquefaction runs was used to characterize the form of the iron present in the product. The iron in the residue from the thermal run to which no iron was added (Run 139-1) was identified as 97-99% as $Fe_{1-x}S$ and most of the remaining (1-3%) as magnetite. In addition, a trace of super paramagnetic iron sulfide of a very fine particle size may also be present. A tentative Mossbauer analysis showed that of the Fe in the Black

Thunder coal 80% was present as pyrite, 13% as jarosite, 6% as clay/ferrous sulfate and 0.1% as pyritic sulfur. Therefore, the iron content in the mineral content of the coal appears to convert primarily to pyrrhotite with only a small amount of oxide remaining. It may be that the 1-3% magnetite remaining in the thermal liquefaction residue could be related to the oxide content of the mineral content of the coal.

Since 6.1 wt% of the iron in the feed slurry was derived from the coal ash, of which about 6% was present as clay/ferrous sulfate, a small portion of the iron identified as magnetite may have been derived from the coal ash fraction of the feed. The form of the molybdenum in the reaction IOM, which was present in the ashy resid fraction in the WRO, which was present at a level of about 400 ppm on dry coal, has not as yet been determined. Those results will be reported when they become available.

The addition of SFIO even at the level of 0.19 wt% iron (1900 ppm) resulted in a change in the oil yield going from 51.3 wt% up to 59.4 wt%. Although the sample at 1900 ppm was only a single run, the reproducibility of this value is evident by examining the other data collected at higher SFIO concentrations. The values at the higher concentrations all fall in the range from 57-61 wt% with an average of the 7 runs being 59.2 wt%. Although there are variations across the sample base, the trend in oil yield provides some verification of a catalytic effect of the SFIO. The magnitude of increase in THF conversion in the presence of added iron increases from the thermal baseline of 107 wt% up to 108-110% at the highest iron concentration. These increases provide strong support for an increased yield due to added SFIO.

What is so surprising about this result is that an extremely small amount of added iron oxide can cause a measurable increase in both oil yield and THF conversion when the level of iron

Table 23. Liquefaction of Black Thunder Coal in WRO with SFIO[a]

					Center-Edgepoint	Midpoint	Tetralin no WRO
Fe Added, wt% dry coal	none	0.19	0.31	0.65	1.4	3.2	1.3
Fe_2O_3 Added, wt% dry coal	none	0.27	0.44	0.93	2.0	4.5	1.8
Fe, wt% dry coal[c]	4.2	4.2	4.4	4.8	5.6	7.3	1.5
Mo, ppm wt maf coal	381	371	374	379	379	375	0
g-atm S/g-atm Added Fe[b]	-	2.4	2.5	2.4	2.3	1.9	1.2
Product Yields, wt% maf coal							
HC Gases	1.9	2.0	2.0	1.1	1.2	2.8	1.3
CO2+CO	5.0	5.1	5.1	4.8	5.0	4.7	4.7
Gases	6.9	7.1	7.1	5.9	6.2	7.5	6.0
Oils	51.3	59.4	59.7	61.2	57.0	59.1	44.9
PA + A	48.4	38.2	41.7	41.2	45.0	43.3	37.8
IOM	-6.6	-4.8	-8.4	-8.3	-8.2	-9.9	11.3[d]
THF Conversion	107	105	108	108	108	110	89
mg H2/g maf coal	57	56	51	58	54.8	60.1	47
wt % H2 consumed	35	43	39	44	42	48	36
Sample No.	139-1 /167-1 /337-1	336-1	316-1	272-2	272-1	174-2/ 190-1/ 190-3	316-3

a. Black Thunder coal with 20.8-22.0 wt% moisture, 5.2 wt% ash on as-received coal, 5.4 g WRO solvent, 3 g as-received coal, 415°C, 60 min, 1000 psig H2 (cold).

b. Added as dimethyldisulfide.

c. Fe in the coal ash contributes approximately 0.25 wt% to the total iron value.

d. Mossbauer analysis showed 75-80% of the Fe present as $Fe_{1-x}S$ and 20-25% of the Fe present as super paramagnetic oxide/oxyhydroxide.

already present in these samples is quite substantial. For the 1900 and 3100 ppm Fe addition levels, this amounts to only 4% and 7%, respectively, of the amount of iron already in the sample. At the higher end of the scale for the midpoint sample, addition of 3.2 wt% Fe is equivalent to 70% of the amount of iron already in the sample.

With this amount of iron already present in the sample, of which 90-95% was present as pyrrhotite, this increase in yield is puzzling. From prior work, pyrrhotite has always been assumed to be the major catalytic component in these reactions.

If indeed pyrrhotite is the active component, then adding pyrrhotite to the liquefaction run at the same level as addition as the SFIO should give a comparable result to the SFIO. Also, adding the pyrrhotite in a very finely divided form of a size comparable to the size of the pyrrhotite already present in the WRO should give even a more preferred reaction form. Fortunately, a very small particle size pyrrhotite that had been prepared by a laser pyrolysis technique was available for testing in this manner. Data from runs at two levels of addition of pyrrhotite to Black Thunder coal in WRO are shown in Table 24.

Pyrrhotite was added at a level of 0.7 and 1.4 wt% Fe to coal slurry already containing 4.2 wt% iron, most of which was present as pyrrhotite, as determined by Mossbauer analysis. Since the iron in the coal ash made up only 6.1% of the total iron content in the feed slurry (0.25 wt% absolute value), its contribution to the total amount of iron present was quite small. Even though, a tentative Mossbauer analysis showed that of the Fe in the Black Thunder coal 80% was present as pyrite, 13% as jarosite, 6% as clay/ferrous sulfate and 0.1% as pyritic sulfur. Overall, the overwhelming amount of iron present in the WRO ashy resid component was pyrrhotite that remained in that form during the reaction. Therefore, based on total iron present in the WRO and coal ash in the feed slurry, the pyrrhotite added at a level of 0.7 and 1.4 wt% amounted to an added iron to total iron concentration of 15% and 25%, respectively.

Table 24. Nanometer Pyrrhotite Catalysis of Black Thunder Coal Liquefaction in WRO[a]

Added Fe, wt% dry coal	0	0.73	1.4
Total Fe, wt% dry coal	4.2	4.8	5.5
Mo, ppm wt dry coal	381	369	370
Moisture in coal, wt%	21.9	19.7	20.2
Products, wt% maf Coal			
HC Gases	1.9	1.9	1.7
CO_2 + CO	5.0	5.5	5.5
Total Gases	6.9	7.4	7.2
Oils	51.3	52.0	55.8
PA + A	48.4	45.4	43.5
IOM	-6.6	-4.9	-6.6
THF Conversion	106.6	104.8	106.6
H_2 consumed, mg/g maf Coal	57	52	54
% H2 consumed	34.8	41.2	41.8
Run Number	139-1/ 167-1/ 337-1	310-1	309-1

a. 1.8 gram WRO/gram as-received coal, 415°C, 60 min, 1000 psig H_2 (cold), no added sulfur.

At these levels of addition of fresh pyrrhotite, oil yield increased over the range from 51.3 to 55.8 wt% at the highest pyrrhotite addition level while THF conversion remained steady at 107%.

These numbers suggest that adding pyrrhotite to an already abundant amount of pyrrhotite in this system does not cause any major effect. However, at the temperature of 415°C that was used here the effect of the pyrrhotite may be somewhat less than at the higher temperatures actually used in the plant, i.e., 425-440°C.

Iron Impregnated Coal by Incipient Wetness

The benefit of using smaller particle iron oxides as catalysts for coal liquefaction was observed by Anderson[20] who reported improved results when using 1 μm pyrite in SRCII processing. In recycle under SRCII conditions in the presence of pyrite which had been ground to 75 μm, total oil went from 17.8% up to 23% when using the smaller pyrite. Cugini, et al[21] used an incipient wetness technique to obtain small particle iron oxide catalysts. In this procedure coal was impregnated with an incipient volume of ferric nitrate solution followed by precipitation with ammonium hydroxide. Subsequently the coal was dried before subjecting it to liquefaction. Liquefaction activities of coals impregnated with 5000 ppm iron were determined in microautoclaves using Illinois #6 coal in tetralin. Comparisons were made with other iron catalyst precursors in the presence of hydrogen sulfide added as CS_2. These precursors included particulate Robena pyrite, ferrous sulfate and ferrous ammonium sulfate impregnated as a dilute solution on coal, and powdered 1 micron iron oxide. Results from continuous runs with a coal impregnated with FeOOH by the incipient wetness technique were almost identical to results on coals in the presence of ammonium heptamolybdate (AHM) and ammonium tetrathiomolybdate catalysts.

	No Cat	FeOOH 2500 ppm	AHM 1500 ppm
C_5-950	71.8	82.9	81.5
950+ C_7 Sol	10	6.2	8.6
C_7 Insols	15.3	8.3	8.6

Microautoclave results with H_2S present were:

a. FeOOH prepared by precipitating from ferric nitrate solution with ammonium hydroxide and drying as a powder is slightly better than Fe_2O_3.

b. FeOOH added to coal (Mukherjee) by suspending the coal in a dilute solution of ferric nitrate and adding base to precipitate on coal[22] was about the same as Fe_2O_3.

c. FeOOH impregnated by the incipient wetness technique is as good as AHM.

d. Addition of H_2S makes a big improvement over no H_2S being present.

The yields of both methylene solubles and heptane solubles from incipient wetness impregnated FeOOH followed the order:

incipient wetness > Mukharjee = physically mixed Fe_2O_3

In continuous runs under staged temperature conditions, Cugini, et al. reported exceptionally high 950°F$^+$ conversion and very high yields of heptane solubles. Conversion data from these runs are shown below:

Reactor #1	Reactor #2	950°F$^+$ Conv	C_7 Sol.
275	435	85	85.8
350	435	88	79.4

Evidence that pyrrhotite was not completely formed at temperatures below 275°C was suggested from the continuous runs. Pyrrhotite was not observed in the XRD in FeOOH impregnated carbons which were treated at temperatures below 350°C, whereas for materials treated at 350°C, pyrrhotite having a particle size of 40 nm was observed. The data suggest that at the lower temperatures the particle size is small and very active while at higher temperatures the crystals are larger and less active.

Metals were determined by SEM to be primarily on the surface[23] of coals that had been impregnated by the incipient wetness technique using $FeCl_3$ hexahydrate, ammonium tetrathiomolybdate, or Ni(II) nitrate hexahydrate. After hydropyrolysis where about one-half the coal had converted, the metals had migrated into the THF insoluble products. For Wyodak coal the incipient wetness impregnation technique was noticeably better than an ultrasound technique, although for several other cases the IW method was apparently no better.

Impregnating Coals by IW Technique - The results of Cugini, et al.,[21] indicate that the IW method for dispersing iron onto coal is very promising for increasing liquefaction activity. These results suggest this approach should be evaluated as one catalyst alternative in this program. Presumably, the higher the dispersion of the metal on and within the coal particle, the greater the contact of the metal during the liquefaction process. Because this is a multi-step process, understanding the individual steps in the sequence will be important for optimizing the metal deposition process. In the first step optimal distribution of the metal solution on the coal must occur since in the second step in which base is added, presumably oxide formation will occur at the point of contact with the base material.

The IW preparative method involves a number of independent steps that can affect the performance of the resulting coal-catalyst combination. A flow chart showing the general synthesis method for preparing IW impregnated coals is shown in Figure 12. Preparation proceeds through a series of operations involving coal preparation, metals impregnation, base precipitation, filtration, washing, and drying, all of which can be altered in

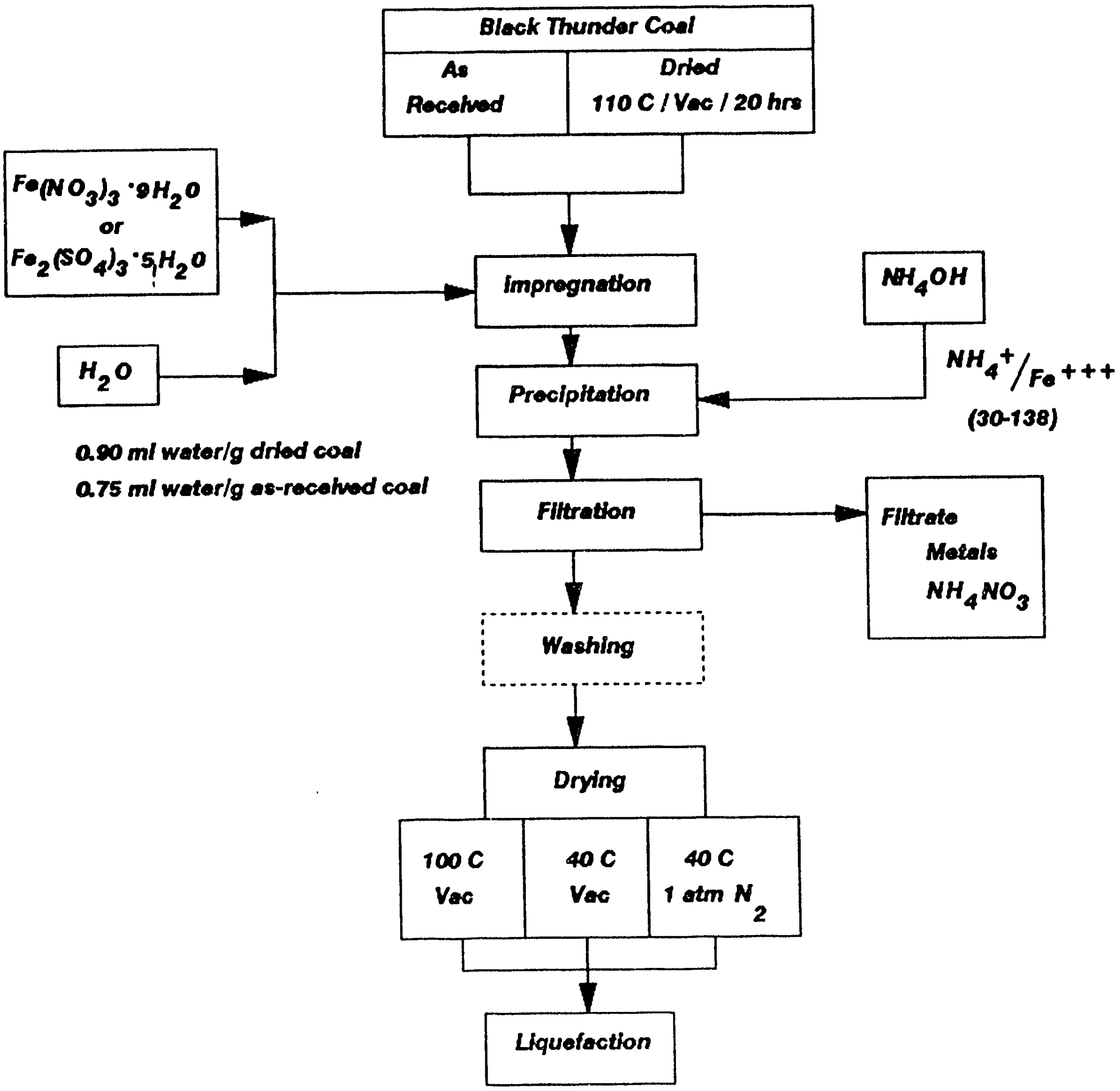


Figure 12. Outline for Preparation of Fe IW-Impregnated Coal

various ways. Following is a discussion of these individual steps and how they have been addressed thus far in the experimental program.

IW Point - For any coal the first step in the preparation is to determine the volume of water required to cause the onset of incipient wetness. This volume is important since it defines the maximum level of water that can be used to transport the metal impregnating agent in the metal dispersion step. Of course, less water can be used, if so desired. Incipient wetness as a preparative technique has been extensively used for preparing supported metal catalysts. D. R. Milburn, et al.,[24] described "incipient wetness" as the point where unbound moisture is about to become available. At the IW point the onset of particulate bridging or agglomeration occurs as well as the volume of the material begins to expand significantly, i.e., the apparent density begins to decrease. The IW number will vary according to the porosity of a coal, the particle size to which a coal is ground and the level to which it has been dried.

Moisture Content of Coal - Thus far coals having only two different levels of moisture have been impregnated by the IW method. One was the starting Black Thunder coal received from CONSOL which contained slightly more than 20 wt% moisture. The other was essentially a dry coal having 2-3 wt% moisture. The moisture content of the as-received Black Thunder coal is apparently very close to the moisture content of run-of-mine Black Thunder coal, which reportedly is about 20-25 wt%.

The amount of water that had to be added to the undried as-received -200 mesh ground Black Thunder coal to reach the IW point was in excess of 2-times the moisture content in as-received coal as shown in Table 25. In our test 3/4 milliliters of water was required per gram of coal to reach the IW point of the as-received material which corresponds to a moisture content in the impregnated coal of 55 wt%. Coal that had been predried at 100°C at 10 Torr for 20 hours required 0.9 milliliters per gram material, which corresponds to 48 wt% moisture on a dry coal basis. This value is only slightly smaller than the IW moisture value of the as-received coal, assuming good reproducibility of this value.

Table 25. Moisture Content of Starting Coal Plus IW[a]

	"As Received"	Predried[b]
Starting Coal, wt% moisture	21	2-3
IW Water, ml/gram	0.75	0.90
IW water, wt% dry coal	55	48

a. IW = Incipient wetness water

b. Predried at 100°C, 1 Torr, 20 hours.

Because the chemical form of moisture in coal is very uncertain, especially for the lower rank coals, to ascribe the difference in the IW values of the dried and as-received coal samples to an internal volume within the coal that is accessible to water is probably overly simplistic. Likewise, to assume the remaining volume is related to surface moisture is also presumptuous. Since the difference in the IW values is only 1/6th of the total moisture contained in the coal at the IW point, these two moisture values may have some importance to metal deposition by the IW method. The smaller value, assuming it is accurate and can be reproducibly observed in repeated experiments, may influence how water absorbs on coal and effects metal dispersion and final deposition. This, of course, depends on the mechanism by which the metal containing solution absorbs and how metal diffusion occurs. If the initial water added to the coal evenly wets the surface or fills the voids, by limiting the amount of metal solution added to the coal to an amount that is equivalent to the difference between the two IW values, an opportunity for obtaining better metal intrusion into the coal may occur. However, if the initial water adsorbs in a uneven manner both on the surface and within the inner voids, the amount of water necessary to obtain maximum metal distribution may require using the entire IW value.

Impregnation Compound - An important factor in applying the IW method is the selection of the particular compound to serve as the impregnating carrier of the metal. This is important for attaining high dispersion of the metal onto the coal without adversely affecting the coal itself. For iron, the first requirement in selecting a metal carrier is finding compounds that are soluble in water at the level necessary to attain the desired concentration in the defined volume of water. At the 1 wt% iron on dry coal, which is equivalent to an iron oxide loading of 1.4 wt%, as described in Table 25, the concentration of the two iron salts used in studies thus far, both using the IW volume of water, are shown in Table 26.

Table 26. Concentration of Impregnating Salt in IW Water for 1 wt% Fe Loading

	Dried Coal	"As Received" Coal
$Fe(NO_3)_3 \cdot 9H_2O$	7.5 wt%	8.8 wt%
$Fe_2(SO_4)_3 \cdot 5H_2O$	8.1 wt%	10.4 wt%

The concentrations for the nitrate salt can be increased because of its high solubility. Such is not true for ferric sulfate whose solubility is far more limited. Of course, at lower metal loadings the concentrations will be less allowing for more flexibility. These concentration values suggest that using volumes of water far below the IW values will be feasible only when the loading on the coal will be at lower levels. This assumes, of course, that using smaller volumes would provide some benefit, such as if intraparticle penetration or more even surface wetting occurs in preference to uneven liquid surface accumulation.

Co-deposition of molybdenum by the IW method is also being investigated. Simultaneous versus sequential addition procedures are possibilities for attaining high dispersions of the metals. For both approaches the affect of pH on stability of the soluble metal compounds in the impregnating solution and the possibility of metal removal during the precipitation process must be considered.

Method of Mixing - To achieve highly dispersed metal on the coal by the IW procedure will, in all likelihood, be dependent on the method of mixing during addition of the water. A priori, the larger the volume of metal solution to be added to the coal, the less the problem will be for attaining better dispersion. In the experiments that have been conducted thus far using the IW volume, a considerable amount of metal deposition on the surface, as opposed to deposition within the cracks, crevices and pores, of the coal particles has been observed. We will be determining whether diminishing the amount of water below the IW level is feasible from the standpoint of metal dispersion and liquefaction performance. Although mixing problems may not be observed at our current scale, which were all approximately 20 grams, we anticipate at the larger scale the method of achieving uniform mixing will require careful attention.

Base Precipitation - In order to convert the soluble metal containing species to a precipitated form of iron oxide, base is added which promotes the formation of the iron oxyhydroxide. Ammonium hydroxide is typically used in order to keep the coal free of added metal ions. Although recipes for preparing FeOOH are well documented, the ratio of Fe^{+3} to NH_4^+ that will be effective in a coal particle has not been investigated. Likewise, the impact of ion exchange when base is added to the coal matrix must be considered. Some recipes involve addition of ammonium hydroxide to the metal impregnated coal after which the coal is separated from the filtrate and dried. The concentration of iron and other cations, such as calcium, that is removed from the coal plus the amount of nitrate removed in alkaline solution was addressed by examining the filtrate from several preparations. Data are shown in Table 27 for several samples for which the NH_4OH filtrate was collected.

These data show that in the NH_4OH filtrate, the amount of iron that was solubilized ranged from 0.1-0.09 wt%. The amount, though negligible, was sufficient to give a greenish tint to the filtrates. The amount of calcium present in the starting coal that was solubilized was also negligible ranging from 0.0038-0.0093 wt%. The amount of nitrate recovered in the NH_4OH filtrate appeared to be quantitative ranging in absolute value upward from 83% for sample CH-3.

Under basic conditions, many of the carboxylic acid groups will presumably exchange with the base resulting in the formation of the corresponding ammonium carboxylates. The extent to which this occurs has not been determined, although this could impact on the performance of the coal during liquefaction.

Water Washing - Washing of the coal may not be necessary where ammonium nitrate is used, since most of the nitrate appears to be removed in the NH_4OH filtrate. However, any residual NH_4^+ that might be left would be decomposed at the higher temperatures used in drying. Therefore, if ferric nitrate is used, washing is optional. In the case of ferric sulfate salts, however, water washing will be necessary in order to remove the sulfate ion, which will not decompose under subsequent drying conditions. The option of using the sulfate is of interest because of the much lower cost of the sulfate salts versus the nitrate.

Filtrates collected from water washing of two particular coal preparations (CH-22 and CH-4) are included in Table 27. In both cases the iron and calcium recoveries were not significantly different from the levels shown in the NH_4OH filtrates indicating these values are negligible. Nitrate concentrations were not monitored since the concentrations in these filtrates became extraordinarily low.

Drying - Because of the addition of a significant amount of water during the impregnation, precipitation and washing steps, drying may be necessary at one or more places in this procedure. Coals having several different moisture levels are being evaluated in this process, of which, two will be discussed here. One had been dried at 110°C at 1 Torr for 20 hours and the other was an "as-received" sample which contained 20+% moisture. The latter sample had been ground in air at ambient temperature having a moisture content apparently close to that of run-of-mine coal.

Fe Distribution

Chemical analysis of the materials that have been prepared by iron impregnation with ferric nitrate is shown in Table 28. The X-ray Photoelecton Spectroscopic (XPS) analysis of several of the materials provides data on surface composition versus bulk concentration of elements. By this technique the amount of metal deposited within the coal particle can be determined relative to the amount deposited on the surface. The surface composition of carbon, oxygen, nitrogen and sulfur was determined in addition to the relative amounts of metals, including iron, calcium, aluminum, silicon, and magnesium. For ease of comparison, tables having a common format for the bulk and surface compositions are presented in Table 29 and Table 30.

Table 27. FILTRATE ANALYSIS BY DIRECT CURRENT PLASMA EMISSION SPECTROMETRY (DCP)

	NH_4OH Filtrate					Washwater Filtrate	
Coal Sample No.	CH-1	CH-3	CH-13	CH-15	CH-21	CH-22[a]	CH-4[b]
Dry coal, grams	20	15	15	15	15	8	4.08
Fe^{+3}, wt% dry coal	0.275	1	0.275	1	0.55	0.55	1
Fe Added, grams	0.055	0.15	0.04125	0.15	0.0825	-	-
N added as NO_3, grams	0. 0414	0.113	0.031	0.113	0.0621	0.00224	-
Ca in dry coal, grams	0.20	0.15	0.15	0.15	0.15	-	-
Washing	NO	NO	NO	NO	NO	YES	YES
Filtrate, g	77.6	188	73.9	242.8	144.7	195	166.5
Fe							
ppm	0.67	0.01	0.33	0.32	0.17	0.13	0.24
Recovery % ($\times 10^2$)	9.4	0.1	5.9	5.2	3.0	3.1	9.8
Nitrogen as NO_3							
wt%	0.050	0.050	0.050	0.050	0.040	-	-
Recov %	94	83	119	108	93	-	-
Calcium							
ppm	1.5	0.86	1.56	0.88	1.24	0.17	0.31
Recovery, wt%	0.06	0.10	0.07	0.14	0.11	0.02	0.12

a. CH-22 originated from CH-21.
b. CH-4 originated from CH-3.

Generally the concentrations of surface iron increased as the order of IW-added iron increased with the 1 wt% Fe samples having the highest surface concentrations. For the sample to which no iron was added, CH-BT, the surface concentration was similar to the bulk concentration of the coal itself. The concentration of carbon on the surface fluctuated around the bulk composition. Oxygen concentration on the surface appeared to be consistently higher than the bulk concentration. Presumably the chemical combination of the oxygen plus the added iron could account for the increase in the corresponding oxygen. In all the samples, aluminum and silicon, interestingly, appear to be enriched at the surface relative to their bulk concentrations, even though the only reliable Si concentration was on as-received coal. However, the magnitude was sufficiently great to remove any question as to its enrichment above the background level. Generally, sulfur concentrations were lower at the surface relative to the bulk sample, except for CH-0/8 where the sulfur concentration was significantly higher than the bulk. This is unexpected since the only variation in the preparation of this 0.765 wt% Fe on as-received coal was using a lower NH_4^+/Fe^{+3} ratio (31/1).

Peak deconvolution of the XPS data provides information regarding the components of the different bonding energies within the individual element peak envelopes. These values compared to reference values and the relative intensities of the deconvoluted peaks provides information on the chemical state of the individual elements on the surface. The data on iron and oxygen are presented in Table 31.

The binding energy position of the $Fe_{2p\,3/2}$ peak of the Black Thunder coal dried at 110°C at 10 Torr for 20 hours (CH-BT) is consistent with uniform distribution of iron in the mineral matter in a form such as sulfides, silicates and aluminosilicates. Samples to which IW iron was added to the surface both broadened and shifted the peak to higher energy.

Table 28. Proximate, Ultimate and Metals Analysis of Fe IW-Impregnated Coals

	Black Thunder		Fe IW-Impregnated Coal Samples					
	CAER	CONSOL	CH-BT	CH-1	CH-2	CH-3	CH-0/8	CH-5[a]
Proximate, as-received basis								
Moisture	20.98	22.4	2.63	5.94	4.1	6.47	4.92	5.96
Ash	4.82	5.46	5.66	6.58	5.83	6.25	5.93	17.17
Volatile Matter	34.4	-	45.47	44.4	43.88	45.1	43.51	50.4
Fixed Carbon	39.8	-	46.2	43.08	46.2	42.2	45.6	26.5
Ultimate, Dry								
Carbon	69.97	70.32	72.15	71.61	65.95	69.89	71.64	57.25
Hydrogen	4.78	4.68	4.34	4.32	4.32	4.63	4.18	3.47
Nitrogen	1.43	1.04	1.23	1.62	1.68	1.75	1.94	1.21
Sulfur	0.56	0.50	0.53	0.46	0.45	0.49	0.45	5.67
Chlorine		0.035						
Oxygen	17.16	16.74	15.93	15.00	21.52	16.55	15.55	14.13
Ash	6.10	6.69	5.81	7.00	6.08	6.68	6.24	18.26
Ash Composition, wt%								
Fe_2O_3	-	5.48	-	-	-	-	-	-
CaO	-	21.34	-	-	-	-	-	-
Al_2O_3	-	15.76	-	-	-	-	-	-
SiO_2	-	31.48	-	-	-	-	-	-
MgO	-	4.3	-	-	-	-	-	-
Na_2O	-	0.48	-	-	-	-	-	-
K_2O	-	0.49	-	-	-	-	-	-
TiO_2	-	1.14	-	-	-	-	-	-
P_2O_5	-	0.96	-	-	-	-	-	-
SO_3	-	17.26	-	-	-	-	-	-

a. Contains 0.485 wt% added vanadium and no added iron.

Table 29. Bulk Elemental Analysis of As-Received Samples

	Black Thunder Coal		Fe IW-Impregnated Coal Samples					
	CAER	CONSOL[a]	CH-BT	CH-1	CH-2	CH-3	CH-0/8	CH-5
Carbon	55.29	57.84	70.25	67.36	63.25	65.37	68.12	53.84
Oxygen	32.21	29.60	17.85	19.39	24.28	21.23	19.16	18.59
Nitrogen	1.13	1.18	1.2	1.52	1.61	1.64	1.84	1.14
Iron	-	0.193	-	-	-	-	-	-
Calcium	-	0.75	-	-	-	-	-	-
Aluminum	-	0.56	-	-	-	-	-	-
Silicon	-	1.11	-	-	-	-	-	-
Magnesium	-	0.15	-	-	-	-	-	-
Sulfur	0.44	0.46	0.52	0.43	0.43	0.46	0.43	5.33

a. See Table 4, July-Sept Quarterly Report, DOE/PC/91040-17, p19

Table 30. Surface Concentration of IW Impregnated Coal Samples[a]

	CH-BT	CH-2	CH-3	CH-4	CH-0/8	CH-5[b]
Added Fe	none	0.275	1.0	1.0	0.765	none
Carbon	71.10	62.81	52.65	55.94	66.81	57.19
Oxygen[c]	20.57	27.14	29.47	26.96	20.17	25.58
Nitrogen	1.31	1.28	1.01	1.00	0.75	1.30
Iron	0.33	2.17	7.78	8.87	3.18	0.24
Calcium	0.51	0.34	0.73	0.96	0.69	0.11
Aluminum	1.95	2.88	4.78	2.84	1.88	2.32
Silicon	3.99	3.29	3.22	2.98	4.58	3.04
Magnesium	-	-	-	-	-	4.85
Sulfur	0.23	0.09	0.34	0.44	1.93	5.10

a. As-received basis.
b. Also contains 0.31 % Vanadium; 0.455 % V added to sample.
c. Includes oxygen associated with moisture in sample.

Deconvolution indicates major contribution from the Fe-O structural type plus a higher energy component consistent with some contribution from Fe-(OH) type structures. The oxygen band shows essentially three components, two of which were likely related to the iron at approximately 530 ev and 531 ev and an unidentified band at 533 ev. From these relative contributions, for the three IW Fe-impregnated samples shown, the final high temperature drying appears to diminish the FeOOH structure, probably through growth in crystallite size, giving rise to more Fe_2O_3 type structures. The oxygen data suggest a strong contribution from the OH structure in the three IW Fe-samples, indicating that oxygen, giving rise to a higher energy band than that associated with the OH, is making a major contribution to this distribution. Interpretation of the oxygen bonding states is still quite tentative.

Since we are just beginning to analyze this data, at present we have no explanation for several of these observations. However, as more samples are evaluated and better understanding of the chemistry of the deposited metals on these coals develop, these differences in surface versus bulk compositions will be determined.

Liquefaction of IW Impregnated Coals

The effect of the variables associated with the preparation of these IW impregnated coals on liquefaction is being determined. Since there are a number of variables involved in the preparation, the discussion will center first on results that are currently available on direct comparison of the effect of these variables on yields and distributions. Evaluations are being made in both WRO and tetralin and results on several of these materials have been completed.

Effect of Fe Concentration - Available results on a series of as-received coals impregnated with different levels of iron are

Table 31. XPS Analysis of IW Fe-Impregnated Coal Samples

				C_{1s} Binding Energy (ev)		$Fe_{2p3/2}$ Binding Energy (ev)		$Fe_{2p3/2}$ Peak Deconvolution			O_{1s} Peak Deconvolution		
	Fe Conc wt%	Pre-dried °C[a]	Final Dry °C[a]	Line Position	Static Charge	Line Position	Value (Corr)	P_1 (ev)	P_2 (ev)	P_1/P_2 Inten	P_1 (ev)	P_2 (ev)	P_1/P_2 Inten
CH-2	0.27%	110	115	287.63	3.03	714.3	711.27	710.71	713.44	4.26	530.97	532.97	1
CH-3	1%	110	40	287.68	3.08	714.3	711.22	710.52	712.82	2.24	530.20	531.92	0.58
CH-8	0.76%	None	40	286.80	2.20	713.4	711.2	710.60	712.60	2.30	531.50	533.10	4.2
CH-BT		110	None	286.40	1.80	711.1	709.3						
CH-CO	CO Pre-treat			286.17	1.57	711.9	710.33						
Literature Data													
FeO							709.5± 0.2				530.0 ±0.2		
Fe_2O_3							711.0± 0.15				529.8 ±0.1		
FeOOH							711.9± 0.2				531.4 ±0.2 530.3± 0.2		

a. At indicated temperature, 10 Torr, 20 hours.

shown in Table 32. These samples were unwashed and dried at 40°C at 10 Torr. Liquefaction data on a sample of as-received Black Thunder coal, which had not been subjected to either of the drying steps, and one which had been dried at a somewhat higher final drying temperature than the iron impregnated samples are included for comparison.

Comparison of the two blank runs suggest that the 90°C drying has a possible detrimental effect on the subsequent liquefaction of the coal. At present, our comparison is limited to this higher temperature run. However, data are presently being obtained on a sample dried at the lower 40°C at 10 Torr. Since all of the iron impregnated samples had been subjected to the final drying step, the "blank dried" sample may provide the best baseline, suggesting that drying has a detrimental effect that is recovered by the addition of iron. The 0.15 wt% iron sample apparently does not contain sufficient iron to recover activity since its activity is much closer to the "blank dried" sample in oils yield, THF conversion and H_2 consumption. For the 0.275 and 0.77 wt% Fe samples and the blank undried sample THF conversions range from 85 to 88 wt%, which shows a direct, though small, response to iron concentration. For these samples constant oil yields of 44 wt% and hydrogen consumptions of 36-37 mg H_2/gram maf coal were observed. The increase in conversion in the presence of iron is quite similar to what was observed at similar concentrations of SFIO in tetralin.

Liquefaction results on a separate preparation of 0.77 wt% Fe IW impregnated as-received coal is shown in Table 33. These samples were all dried at in the final drying step shown in Figure 12 at 90°C/125 Torr.

As reaction time increased, the iron containing samples showed a steady increase in THF conversion, oil yield and hydrogen consumption. Compared with the 0.77 wt% Fe sample in Table 32, the conversion was slightly higher and oil yield slightly lower, the latter being essentially the same as the "blank dried" sample in run 279-1 in Table 33. In both cases, the THF conversion was greater than for either the undried as-received coal (160-1) or the as-received coal which was subjected to a final dry at 90°C (279-1). In general, these 0.77 wt% Fe coal samples provide higher conversion than coals subjected to any pre-drying but similar in magnitude to undried as-received coals.

Comparing these data on thermal liquefaction of coal to which IW Fe-impregnated catalysts were added with as-received coal to which no Fe was added shows a clear advantage in conversion at all residence times from 15-60 minutes.[25] These data are shown in Table 34. However, no clear cut effect on oil yield is observed. However, there is a definite trend in the HC and $CO+CO_2$ yields. The HC gases yield appears to increase in the presence of the iron by 0.3-0.5 wt% while the $CO+CO_2$ yield decreases by 0.9-1.5 wt%. Most of the other runs made thus far have generally had almost no impact on the $CO+CO_2$ yields with several having some effect on HC yields.

Only limited Mossbauer data are available at this time on residues from the various liquefaction runs. However, the iron in the residue from the 15 minute run described above (Run 226-1) contained 60-70% super paramagnetic oxide/oxyhydroxide and 30-40% pyrrhotite. Although a molar ratio of sulfur to iron of 3.7 was used in the run, the iron was only partially converted to the pyrrhotite form. Residues from the longer term runs as well as other samples from this run are being evaluated to check and expand on this result.

Effect of NH_4^+/Fe Ratio - The effect of using two different levels of ammonium hydroxide in the iron oxide formation step on liquefaction was evaluated . In both cases the as-received coal

Table 32. Liquefaction of Iron IW Impregnated As-Received BT Coal[a,b]

Coal Sample ID	Blank	Blank dried[e]	CH-10	CH-12	CH-31
Added Fe, wt% dry coal	0	0	0.15	0.275	0.77
Added Fe_2O_3, wt% dry coal	0	0			
pH Filtrate	-		10.4		10.8
Final moisture in coal	21.4	1.5	1.3		1.2
S/Added Fe in Cat	-	-	1.2	2.6	1.4
Products, wt% maf coal					
HC Gases	1.0	1.0	1.1	1.1	1.2
CO_2+CO	4.9	4.3	4.3	4.0	4.4
Total Gases	5.9	5.3	5.4	5.1	5.6
Oils	43.4	39.1	37.7	44.0	43.0
PA + A	35.8	38.2	39.0	36.7	39.2
IOM	14.9	17.4	17.8	14.2	12.2
THF Conv	85.1	82.6	82.2	85.8	87.8
mg H_2 Consumed/g maf coal	36[c,d]	29	30	37	37
Run Number	160-2	279-1	15-3	3-7-1	3-15-2

a. Metal added as $Fe(NO_3)_3\cdot 9H_2O$ in 0.75 ml water/grams as-received coal; impregnated coal treated with 1.54 M NH_4OH solution at a ratio of 138 moles NH_4OH/mole Fe; samples were unwashed and all were dried at 40°C for 20 hours at ~10 Torr.
b. Liquefaction conditions: 415°C, 60 min, 5.4 g tetralin/3 g coal sample, 1000 psig hydrogen (cold).
c. Corresponds to 23 wt% conversion of total H_2 in feed.
d. Corresponds to 8.7 mg H_2 consumed/g total maf feed.
e. Dried at 90°C for 20 hrs at 25 Torr.

Table 33. Liquefaction of 0.77 wt% Iron IW Impregnated As-Received BT Coal[a]

Liquefaction Time, min[b]	60	15	30	60	60[d]
Moisture, wt% IW Coal	1.5[c]	6.2	4.6	6.2	2.2
Added Fe, wt% dry coal	0	0.77	0.77	0.77	0
Added Fe_2O_3, wt% dry coal	0	1.1	1.1	1.1	0
S/Added Fe, m/m	-	3.7	3.7	3.7	-
Products, wt% maf coal					
HC Gases	1.0	0.9	1.1	1.3	1.0
CO_2+CO	4.3	3.3	3.5	3.4	3.8
Total Gases	5.3	4.1	4.5	4.7	4.8
Oils	39.1	18.6	28.5	38.9	37.4
PA + A	38.2	49.4	48.6	46.1	37.6
IOM	17.4	27.9	18.4	10.4	20.2
THF Conv	82.6	72.1	81.6	89.7	79.8
mg H_2 Consumed/g maf coal	29	37	40	45	23
Run Number	279-1	226-1	227-1	226-2	280-1

a. Metal added as $Fe(NO_3)_3 \cdot 9H_2O$ in 0.66 ml water/grams as-received coal; impregnated coal treated with 1.54 M NH_4OH solution at a ratio of 138 moles NH_4OH/mole Fe; samples were washed and were then dried at 40 °C for 20 hours at 125 Torr.
b. Liquefaction conditions: 415°C, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).
c. Dried 90°C, 20 hours at 125 Torr.
d. As-Received coal washed with same volume NH_4OH as used for 0.77 wt% Fe samples. Sample then dried at 40°C, 20 hours at 125 Torr.

Table 34. Comparison of Fe IW-Coal with As-Received BT Coal

Reaction Time, min[a]	15		30		60	
IW-Fe, wt% dry coal[b]	0	0.77	0	0.77	0	0.77
Ratio S/Fe, m/m	-	3.7	0	3.7	0	3.7
Products, wt% maf coal						
HC Gases	0.4	0.9	0.6	1.1	1.0	1.3
CO_2+CO	4.2	3.3	4.5	3.4	4.9	3.4
Total Gases	4.6	4.1	5.1	4.5	5.9	4.7
Oils	20.7	18.6	28.0	28.5	43.4	38.9
PA + A	40.9	49.4	43.7	48.6	35.8	46.1
IOM	33.7	27.9	23.3	18.4	14.9	10.4
THF Conv	66.3	72.1	76.7	81.6	85.1	89.7
mg H_2 Consumed/g maf coal	30	37	28	40	36	45
Run Number	154-2[c]	226-1	154-1[c]	227-1	160-2[c]	226-2

a. Liquefaction conditions: 415°C, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).
b. Metal added as $Fe(NO_3)_3 \cdot 9H_2O$ in 0.66 ml water/gram to as-received coal; impregnated coal treated with 1.54 M NH_4OH solution at a ratio of 138 moles NH_4OH/mole Fe; samples were washed and were then dried at 40 °C for 20 hours at 25 Torr. Fe concentrations apply only to added iron.
c. Quarterly Report, July-Sept. 1992, Advanced Direct Liquefaction Concepts for PETC Generic Units, DOE/PC/91040-17, November 1992, p11.

was subjected to IW impregnation to an iron level of 0.77 wt% Fe. Samples were then treated with 1.54 M NH_4OH solution at ratios of either 31 or 138 moles NH_4OH/mole Fe and then dried at 40°C for 20 hours at 10 Torr. The higher ratio was chosen from the recipe of Cugini, et al.[21] Liquefaction data are presented in Table 35. The oil yield and THF conversion are slightly better for the sample using the lower ratio of ammonium hydroxide to iron.

performance of this ammonium hydroxide washed sample was determined (Run 280-1, Table 33). It appears that the ammonium hydroxide washed coal gives somewhat poorer performance than the as received coal both in THF conversion, oil yield and hydrogen consumption.

Effect of Washing - When ferric nitrate is used as metal carrier in the impregnation step, nitrogen is removed during the drying step, as pointed out above. Such will not be the case for preparations using the ferric sulfate salt, which will require washing to remove the sulfate ion. Results on the sulfate salt preparations are not available at this time. However, the effect of washing on liquefaction of samples prepared using the nitrate salt was determined for two coals containing 0.55 wt% iron. Data are shown in Table 36. These two samples were both subjected to a 100°C final dry. The oil yield and THF conversion for the washed sample were slightly higher than for the unwashed sample.

Effect of Final Dry - The effect on liquefaction of drying in an inert atmosphere, i.e., nitrogen, versus in a vacuum was determined on as-received coal containing 0.275 wt% added iron. This will be especially important for devising a larger scale production scheme for these impregnated coals since vacuum drying will not likely be feasible on a commercial scale. The data on these two coal samples are shown in Table 37. The moisture level in the nitrogen dried sample (9 wt%) was somewhat higher than for the vacuum dried sample (2 wt%) indicating that either more than 20 hours or a higher temperature will be necessary to reduce the moisture to the same level as in the vacuum sample. In these two samples the liquefaction performance of the sample dried in vacuum was somewhat better than the one prepared in flowing nitrogen. The vacuum dried sample had 5.8 wt% higher oil yield and 2.1 wt% higher THF conversion.

Table 36. Effect of Washing on Liquefaction of 0.55 wt% Iron IW Impregnated As-Received BT Coal[a]

Catalyst Sample No.	CH-21	CH-22
Washing	No	Yes
Final Drying Temperature	100	100
Added Fe, wt% dry coal	0.55	0.55
Added Fe_2O_3, wt% dry coal	0.79	0.79
S/Added Fe in Cat	1.17	1.17
Products, wt% maf coal[b]		
HC Gases	1.2	1.1
CO_2+CO	4.3	4.2
Total Gases	5.5	5.3
Oils	41.7	45.8
PA + A	40.3	38.2
IOM	12.6	10.5
THF Conv	87.4	89.5
mg H_2 Consumed/g maf coal	41	39
Run Number	13-1	13-2

a. Metal added as $Fe(NO_3)_3 \cdot 9H_2O$ in 0.75 ml water/grams as-received coal; impregnated coal treated with 1.54 M NH_4OH solution at a ratio of 138 moles NH_4OH/mole Fe; samples were washed as indicated and then dried at 100°C for 20 hours at 10 Torr.

b. Liquefaction conditions: 415°C, 1 hour, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).

Table 37. Effect of Drying Conditions on Liquefaction of 0.275 wt% Iron IW Impregnated As-Received BT Coal[a]

Catalyst Sample No.	CH-12	CH-13
Drying Conditions	Vac[b]	N_2[c]
Moisture, wt%	2	9
Added Fe, wt% dry coal	0.28	0.28
Added Fe_2O_3, wt% dry coal	0.39	0.39
S/Added Fe, m/m	2.6	1.3
Products, wt% maf coal[d]		
HC Gases	1.1	1.1
CO_2+CO	4.0	4.1
Total Gases	5.1	5.2
Oils	44.0	38.2
PA + A	36.7	40.3
IOM	14.2	16.3
THF Conv	85.8	83.7
mg H_2 Consumed/g maf coal	37	37
Run Number	7-1	15-1

a. Metal added as $Fe(NO_3)_3 \cdot 9H_2O$ in 0.75 ml water/grams as-received coal; impregnated coal treated with 1.54 M NH_4OH solution at a ratio of 138 moles NH_4OH/mole Fe; samples were unwashed and dried as indicated.
b. Dried at 40°C, 20 hours at 10 Torr.
c. Dried at 40°C in 140 ml/min flowing N_2 at 1 atm.
d. Liquefaction conditions: 415°C, 1 hour, 5.4 g tetralin/3 g coal, 1000 psig hydrogen (cold).

Overview - The data base is still incomplete on the series of iron samples that have been prepared. Since there are so many independent variables involved in the preparation, comparison of this data as an integrated group is certainly questionable since the interactions of these variables on performance have not been defined. However, grouping the data on these IW Fe-impregnated catalysts and comparing their relative THF conversions, oil yields and hydrogen consumptions, all factors that should reflect process severity. These data are graphically presented in Figure 13. Most of the data used in the figure were presented in the previous tables, however, data that were not previously presented are included in Table 38.

These data show a steady increase in coal conversion up to about 0.77 wt% added Fe where it levels out. Additional Fe up to 1.26 wt% appears not to give any added advantage in conversion. Oil yields also show the same trend with the molybdenum catalyst giving a sizable increase over the level of Fe that had apparently leveled out. Generally, hydrogen consumption parallels conversion by giving higher values at the higher conversion and oil yield levels.

The maximum levels for each of the prime process parameters are:

THF conversion - 91%
Oil yield - 50 wt% maf coal
H_2 consumption - 49 mg/gram maf coal.

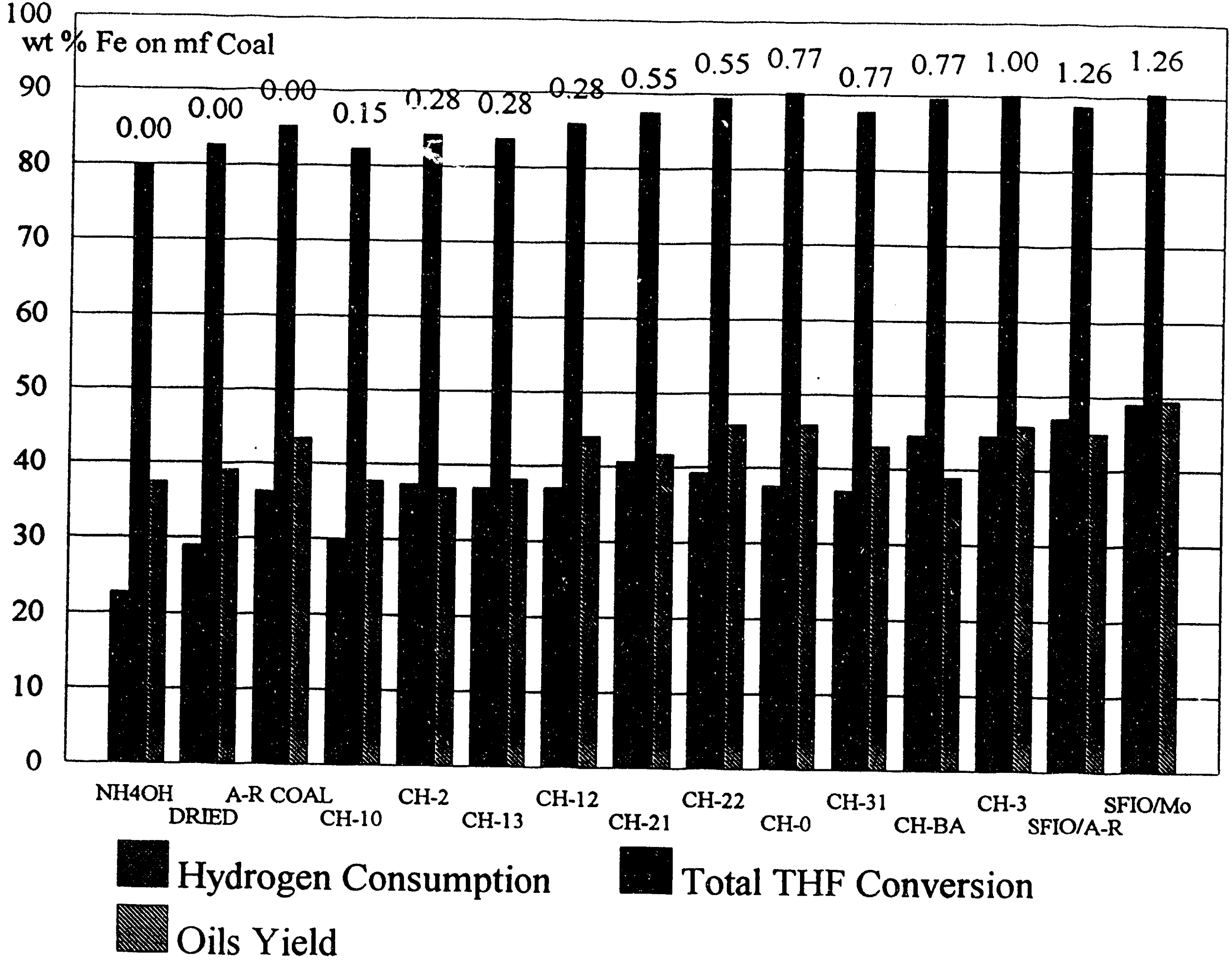
These data suggest that Fe concentration may be the dominating influence in the overall preparation scheme with other variables being much less important. As more data become available, this trend may be further confirmed. One factor that does standout in this data is that the addition of Mo causes a step jump in the yield of oils, although, at this level, it has little effect on THF conversion.

Thus far in this program, the highest values for oil yield when using WRO were observed for Shell 324 added at a ratio of 1.37 wt% Mo plus 0.26 wt% Ni on dry coal (11.0 wt% S-324/dry coal).[26] Results on the liquefaction of the iron IW-impregnated coal to which powdered $NiMo/Al_2O_3$ was added at a concentration of

Figure 13

EFFECT OF Fe ON LIQUEFACTION

60 minute reactions in tetralin



415 C, 5.4 g tetralin, 3.0 g Coal
1000 psig H2 (cold)

approximately 8 wt% on dry coal are shown in Table 39. The S-324 catalyst gives the highest oil yield and hydrogen consumption observed in tetralin, along with a THF conversion that is comparable to the iron catalysts. Addition of the S-324 to the IW-impregnated Fe coals resulted in a slight drop in oil yield with the magnitude still remaining

Table 38. Miscellaneous Liquefaction Runs in Tetralin

	As-Received	CH-2	CH-3	Nanocat	Nanocat/ MoNaph
Fe, wt% dry coal	0	0.27	1.0	1.3	0.88
Fe_2O_3, wt% dry coal		0.39	1.4	1.8	1.3
Molybdenum, ppm on dry coal	0	0	0	0	1890[b]
g atom S/g atom Metal	0	1.2	1.2	1.2	1.2
% moisture in the coal	21.4	3.9	3.9	20.8	20.7
Products, wt% maaf Coal					
HC Gases	1.0	1.1	1.1	1.3	1.3
CO_2 + CO	4.9	4.4	3.7	4.7	4.4
Total Gases	5.9	5.5	4.8	6.0	5.7
Oils	43.4	36.8	46.0	44.9	49.4
PA + A	35.8	41.9	39.3	37.8	35.3
IOM	14.9	15.8	9.9	11.3	9.5
THF Conversion	85.1	84.2	90.1	88.7	90.5
H_2 consumed, mg/g maf coal	36.2	37	45	47	49
% H_2 consumed	23.2			36.4	38.1
Run Number	160-2	325-1	324-1	316-3	328-1

a. 1.8 grams tetralin/gram coal, 415°C, 60 min, 1000 psig H_2 (cold).
b. Molybdenum added as molybdenum napthenate containing 6.07 wt% Mo.

Table 39. Effect of NiMo/Al_2O_3 on Liquefaction of Fe-IW Impregnated Coal in Tetralin[a]

	As-Received	Dry Coal[b]	S-324[c]	S-324 &IW	S-324 &IW
Fe, wt% dry coal	0	0	0	0.76	0.38
Molybdenum, wt% dry coal	0	0	1.0	1.0	0.5
Nickel, wt% dry coal	0	0	0.2	0.2	0.1
S-324, wt% dry coal	0	0	8.2	8.5	8.8
g atom S/g atom Metal	0	0	1.9	1.6	1.6
% moisture in the coal	21.4	1.5	1.5	4.6	8.1
Products, wt% maf Coal					
HC Gases	1.0	0.9	0.8	0.9	0.7
CO_2 + CO	4.9	4.4	3.5	2.9	3.8
Total Gases	5.9	5.3	4.3	3.7	4.5
Oils	43.4	39.1	59.4	56.6	50.5
PA + A	35.8	38.2	24.1	27.9	34.8
IOM	14.9	17.4	12.1	11.8	10.1
THF Conversion	85.1	82.6	87.9	88.2	89.9
H_2 consumed, mg/g maf coal	36.2	17.5	45	51	47
% H_2 consumed	23.2	16.8	43.6	46.8	42.2
Run Number	160-2	279-1	262-1	261-1	265-2

a. Black Thunder Wyodak coal, 1.8 g tetralin/g coal, 415°C, 60 min, 1000 psig H_2 pressure (cold).
b. Dried at 40°C, 20 hours, 125 Torr.
c. Shell 324 contains 12.4 wt% Mo and 2.8 wt% Ni on alumina.

over 50 wt%. The data indicate that the H_2 consumption was generally the same being accompanied by a small increase in conversion.

Cation-Exchanged Iron Containing Coals

The ion-exchange process, in which iron was exchanged primarily for calcium, would yield a highly dispersed catalytic iron species for coal liquefaction. The coal samples were first ground to <200 mesh under a nitrogen atmosphere. The ion-exchange experiments were carried out in a 10 liter fermenter equipped with temperature and pH controller. A freshly made 0.05M aqueous solution of ferric acetate was kept at a controlled pH of about 2.8 using sulfuric acid and a constant temperature of 333K. A slurry made from a 10:1 ratio by weight of dry coal to ferric acetate was stirred under a nitrogen atmosphere for 20 hrs. At the completion of the procedure, the ion-exchanged coals were repeatedly washed with distilled water until the pH value of the filtrate for two consecutive washes was constant. ^{57}Fe Mössbauer and x-ray absorption fine structure (XAFS) spectroscopies were used to characterize this iron species after both the ion-exchange and the liquefaction processes. The results indicate that added iron is initially present in bimodal form, with most present as highly dispersed goethite (α-FeOOH) particles 50-100Å in diameter, but with a significant fraction of the iron in particles finer than 30Å in diameter, which may represent molecularly dispersed ferric ions at the ion-exchange (carboxyl) sites. Particles larger than 50Å may be due to the hydrolysis of iron acetate or ion-exchanged iron forming iron oxyhydroxide.

Production of Small Particle Sulfated Iron Oxides

Several groups have investigated the use of sulfated hematites (Fe_2O_3/SO_4^{2-}) for use as both coal liquefaction and coprocessing catalysts with promising results. It is important to note that this formula does not represent a stoichiometric relationship between the sulfate and the iron but rather the sulfate may be considered as SO_3 chemisorbed on the surface of Fe_2O_3. Tanabe et al.[27] found that the sulfated hematite exhibited the highest activity, similar to that of a $Co/Mo/Al_2O_3$ catalyst, for the liquefaction of a bituminous coal. A study by Yokoyama, et al.,[28,29] showed that the activity of the sulfated hematite was independent of the rank of the coal, yielding high activities for both bituminous and subbituminous coals. In addition to a high conversion, these catalysts also showed a relatively high selectivity to oils.[30] These materials were identified by Mossbauer and XAFS spectroscopy to have particle sizes from 20-100 angstroms.[31]

More recent work by Pradhan et al.[32,33] has shown the high activity of sulfated hematite for both direct coal liquefaction and coprocessing of coal with a Maya resid. The addition of up to 2 wt% molybdenum as a promoter metal was found to further increase the activity of the catalyst. The highest conversions were achieved in the presence of added elemental sulfur with the catalyst. The high activities reported were achieved at very low catalyst loadings of <0.4 wt% Fe. The high activity is, in part, associated with the high dispersion due to the small particle size. XRD and TEM have both shown that the average particle diameter is 10-30 nm. The small size of these particles allows better contact with the coal. In addition, the presence of the sulfate group on the surface may inhibit the tendency of the particles to sinter during the liquefaction process. The increased acidity associated with the sulfate group also enhances the activity of the catalyst for certain reactions.

The technique used for production of the sulfated hematite involves the aqueous precipitation of an iron salt in the presence of a source of sulfate ion. There are several techniques used for this purpose. For this project, a urea precipitation of ammonium ferric sulfate was utilized. In this process 25 g of urea were mixed with 17.5 g of $(NH_4)Fe(SO_4)_2 \cdot 12 H_2O$ in 500 ml of distilled deionized water. The initial pH of the solution was ~3. The solution, stirred continuously during the process, was heated to ~95°C and kept at temperature for ~2 hrs. During this time the urea caused the gradual precipitation of the iron. After ~1.5 hrs the pH increased and after 2 hrs reached ~7 indicating the completion of the reaction.

The precipitate was removed from the solution by vacuum filtration and washed with distilled deionized water to remove unbound sulfate groups. The filter cake was dried to remove any residual moisture. The original technique called for calcination of the filter cake in air at 500°C for ~1 hr. Subsequent testing showed that for the small samples (~3g) generated in each batch calcining at ~475°C for ~10 minutes was sufficient.

Promoter metals may be added to the sulfated hematite by addition of metal containing salts to the solution. Molybdenum has been used, in the form of ammonium molybdate, to produce a sulfated hematite doped with molybdenum. Various concentrations of molybdenum have been added to determine the optimum loading. This procedure may be modified to add multiple promoter metals to the sulfated hematite. A combination nickel/molybdenum promoted sulfated hematite has been produced by this technique (Table 40).

XRD was utilized to identify the phase of the precipitated iron particles, both before and after calcination. As shown in Figure 14 the XRD spectra of the as-formed particles closely matches the reported spectra of goethite (α-FeOOH). Also shown in the spectra are the 44.7° and 65.0° peaks identified with α-Fe. The relatively poor resolution in the XRD spectra is due to both the extremely small size and poor crystallinity of the particles. After calcining, the XRD spectra of the particles, shown in Figure 15, is consistent with the spectra of hematite (α-Fe_2O_3) with the presence of the α-Fe peaks at 44.7° and 65°. The sharpness of the peaks in the calcined particles may be attributed to an increase in both the crystallinity and average particle size.

The chemisorbed sulfate group has been reported to have several effects on the catalytic properties of the particles.[33] One of the proposed functions is the attainment and maintenance of high dispersion. The sulfate group may inhibit particle agglomeration and sintering. The quantity of sulfur present was determined by elemental analysis to be 3-5 wt %. There was little effect of calcination on the sulfur content. The slight increase in concentration is easily accounted for by the mass loss which occurs during calcination.

The average crystallite diameter of the particles may be estimated from the XRD spectra using the Debye-Sherrer equation. Utilizing this equation, the average particle sizes were shown to be in the 5 - 30 nm range with most particles ranging from 15-20 nm. SEM on the particles reveal that the particles exist as an agglomeration of very small particles below the resolution of the instrument. While this does not directly confirm the estimates made from the XRD spectra, neither does it refute them. TEM on the particles will establish the validity of the XRD derived estimates.

Table 40. Sulfated Hematite Sample Data

Sample	Description	Phase, XRD	Diameter, nm (XRD)	Surface Area, m2/g	Sulfur wt%	SO4, wt%	Promoter Metal	Conc., wt%
SH1	FeOOH/SO4	Goethite		31				
SH1C	Fe2O3/SO4	Hematite		70				
SH2	FeOOH/SO4	Goethite		130				
SH2C	Fe2O3/SO4	Hematite		38				
SH3	FeOOH/SO4	Goethite		103	2.32	5.8		
SH3C	Fe2O3/SO4	Hematite		84	2.77	6.925		
SH4	FeOOH/SO4	Goethite		60??	4.72	11.8		
SH4C10	Fe2O3/SO4	Hematite		71	5.54	13.85		
SH4C20	Fe2O3/SO4	Hematite			5.41	13.525		
SH4C30	Fe2O3/SO4	Hematite			5.47	13.675		
SH4C60	Fe2O3/SO4	Hematite		62	5.49	13.725		
SH5	FeOOH/SO4	Goethite	14±4	121	2.58	6.45		
SH5C	Fe2O3/SO4	Hematite	19±2	101	3	7.5		
SH6	10%Mo/FeOOH/SO4	Goethite			0.9	2.25	Mo	9.8
SH6C	10%Mo/Fe2O3/SO4	Hematite	15±2	200	1.08	2.7		
SH7	5%Mo/FeOOH/SO4	Goethite			1.61	4.025		
SH7C	5%Mo/Fe2O3/SO4	Hematite	16±3	182	1.59	3.975		
SH8	2%Ni/2%Mo/FeOOH/SO4	Goethite	8	152	1.54	3.85	Mo/Ni	2.20/1.24
SH8C	2%Ni/2%Mo/Fe2O3/SO4	Hematite	17±2	130	1.69	4.225	Mo/Ni	2.45/1.35
SH9	1%Mo/FeOOH/SO4			190	1.93	4.825	Mo	1.65
SH9C	1%Mo/Fe2O3/SO4			129	2.11	5.275	Mo	1.21
SH10	FeOOH/SO4		20±3	110	1.16	2.9		
SH10C	Fe2O3/SO4		21±4	91	1.32	3.3		
SH11	FeOOH/SO4			115	1.4	3.5		
SH11C	Fe2O3/SO4			87	1.57	3.925		
SH12	Co/Mo/FeOOH/SO4			199			Mo/Co	
SH12C	Co/Mo/Fe2O3/SO4			133			Mo/Co	

Figure 14. As-formed Particles with Goethite and alpha Fe

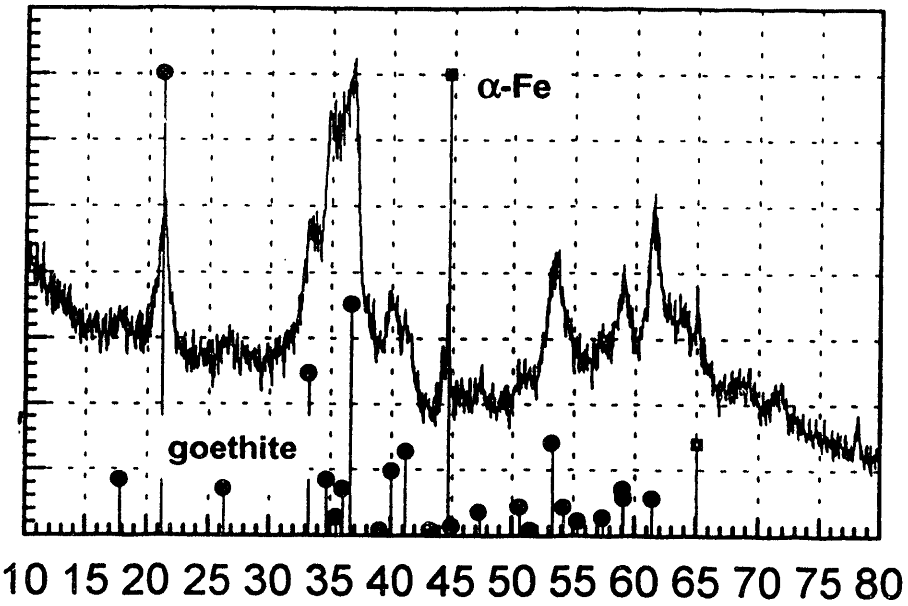


Figure 15. Calcined Particles with Hematite and alpha Fe

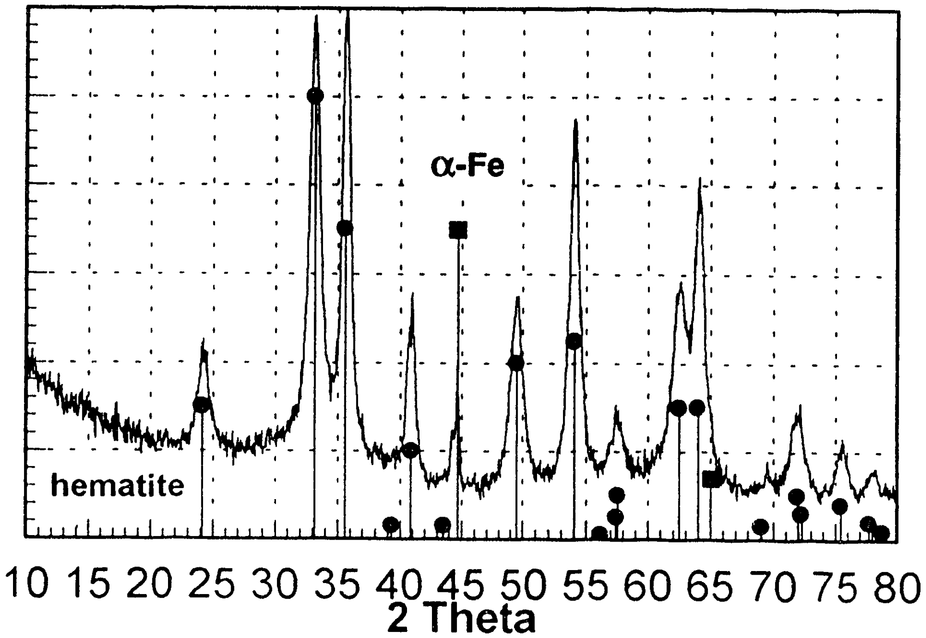
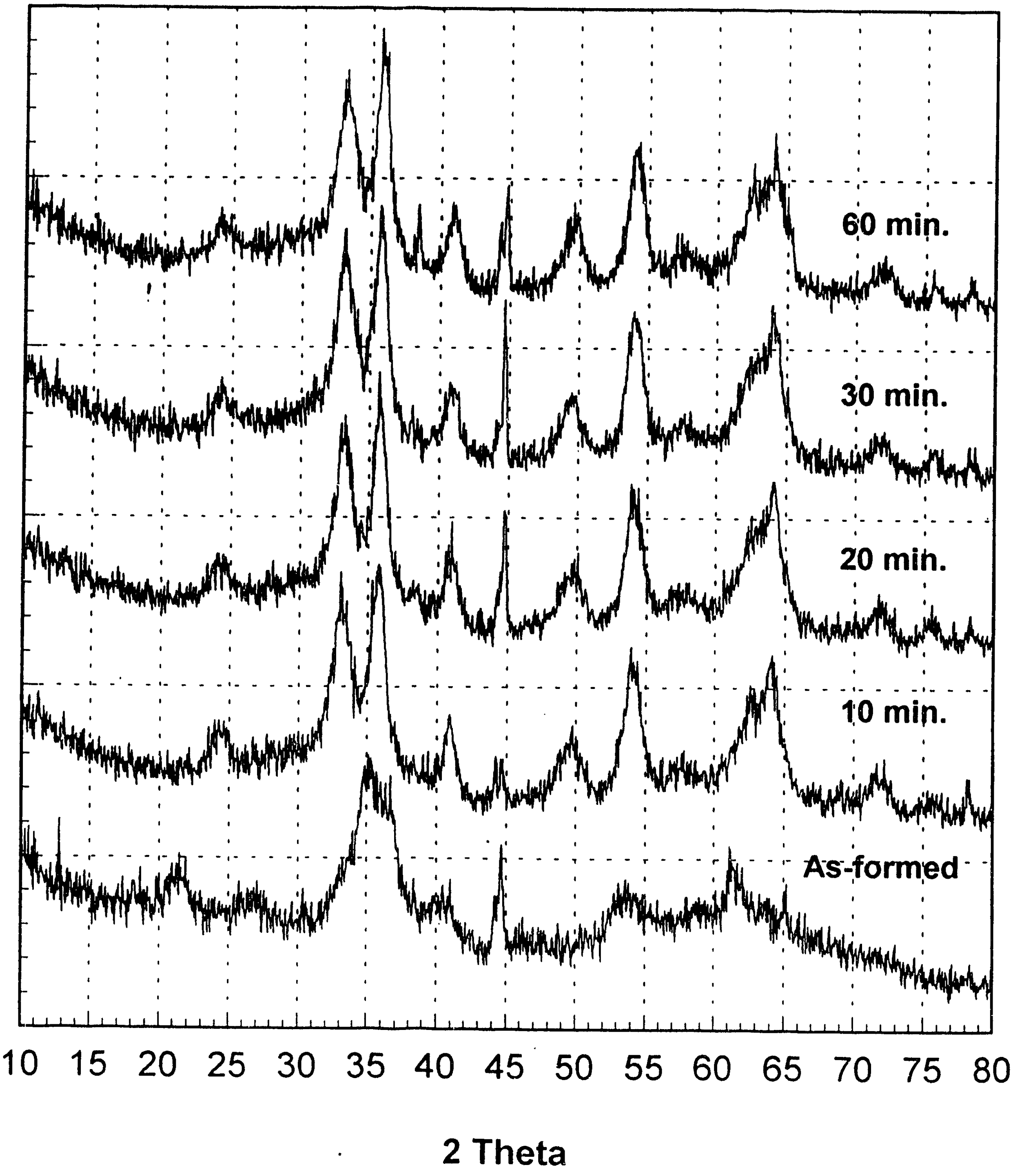


Figure16. Effect of Time of Calcination on XRD

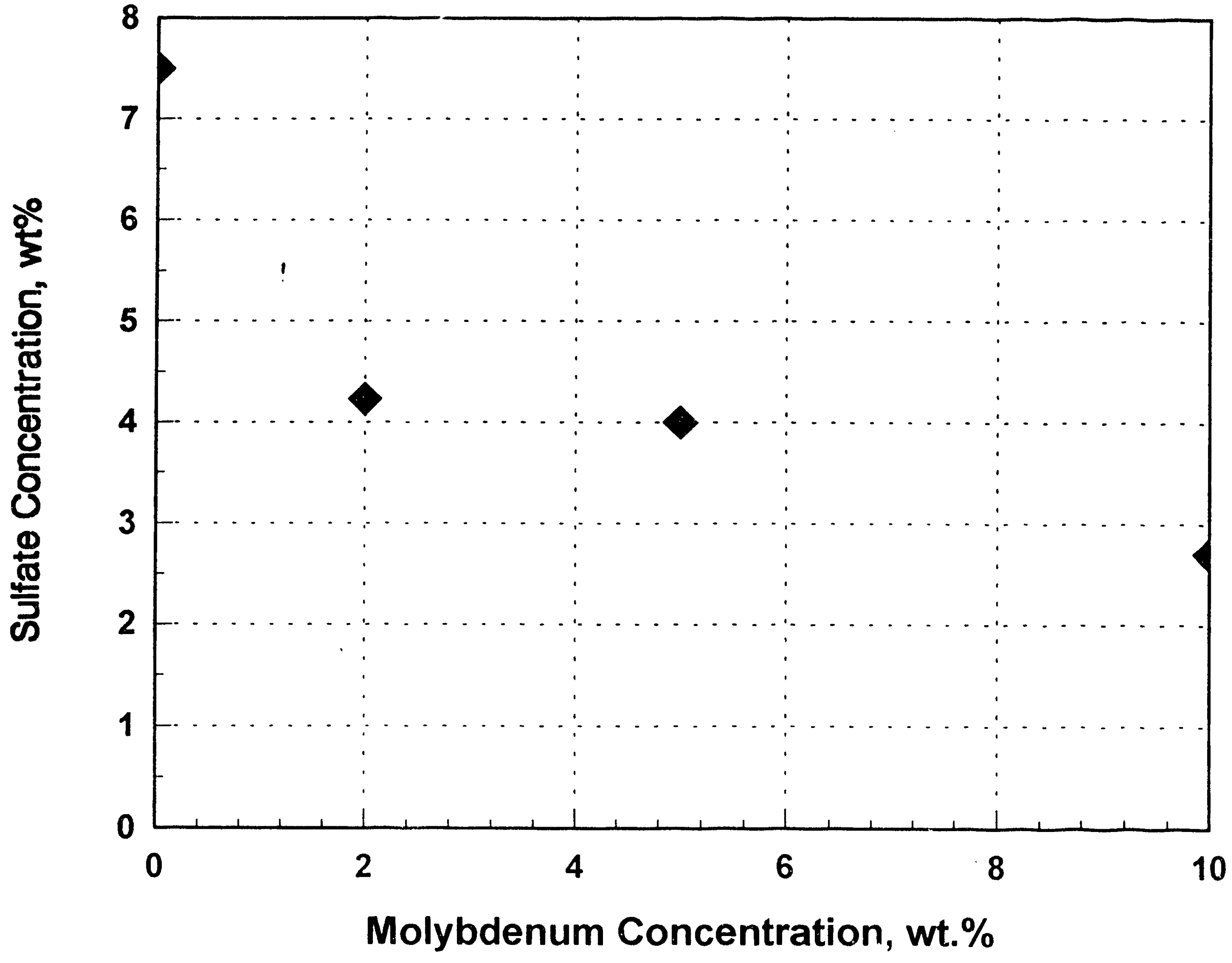


In order to determine the effect of residence time at temperature during calcination on the particle phase and size, a single batch of goethite was split into 4 samples. Each sample was calcined for between 10 and 60 minutes. The resulting catalysts were analyzed by XRD and the spectra were compared to determine phase and particle size. As Figure 16 clearly indicates, the transformation from goethite to hematite is complete within 10 minutes. However, the continued exposure to this temperature appeared to have little effect on the average diameter of the particles. There is some loss of surface area associated with the calcination process. Nitrogen BET measurements showed a decrease of the surface areas of ~18% during the calcination process.

The addition of molybdenum to the sulfated hematite as a promoter metal has been reported to improve the activity of the catalyst.[33] It was therefore decided to attempt to add varying amounts of molybdenum to the sulfated hematite to act as a promoter metal. The doping of the sulfated hematite with molybdenum was achieved by addition of ammonium molybdate to the iron alum/urea solution. Elemental analysis of both the product and the waste water indicate that all but a trace amount of the molybdenum is incorporated in the catalyst.

The role of the molybdenum in the catalyst structure is unclear. However, elemental analysis shows that as the amount of molybdenum has a strong effect on the amount of sulfur. As Figure 17 indicates the effect of molybdenum on the sulfur concentration is to decrease the amount present. Since the sulfate group is located primarily on the surface, this may indicate that the molybdenum displaces the sulfate group on the surface of the hematite. This speculation is further supported by the XRD spectra which indicate that, even at concentrations

Figure17. Effect of Molybdenum Concentration on Sulfate Concentration



up to 10 wt% molybdenum, only the hematite and α-Fe spectra were identified. This indicates that the molybdenum is present either in an amorphous phase or on the surface.

The addition of molybdenum had a moderate effect on the particle diameter as determined from XRD spectra. As shown in Figure 18, the increase in the amount of added molybdenum led to a gradual decrease in the particle diameter. However, as the error bars indicate, this trend is somewhat dubious. The significant error is due to inaccuracies associated with the estimation of particle diameter from XRD spectra and also to the amount of noise present in the spectra. The molybdenum promoted sulfated hematites also appear as a loose agglomeration of particles whose size was below the resolution of the SEM.

Surface areas of the molybdenum promoted sulfated hematites were measured by the nitrogen BET method. The effect of increasing molybdenum concentration was to increase the surface area of the particles, as shown in Figure 19. Since there is little to no porosity associated with these particles, the trend in surface area agrees with the trend seen in the particle diameter estimation. This increase in surface area may also support the proposal of molybdenum displacing the sulfate on the surface. As mentioned earlier, one of the proposed function of the sulfate on the hematite is the inhibition of the agglomeration of the particles. The replacement of the sulfur with molybdenum may lead to further inhibition of agglomeration due to the relative size of the atoms. This would agree well with both the surface area measurements and particle diameter estimations. To confirm this theory, XPS will be performed on the particles to determine the nature of the molybdenum near the surface.

Figure18. Effect of Molybdenum Concentration on Particle Diameter Estimated from XRD

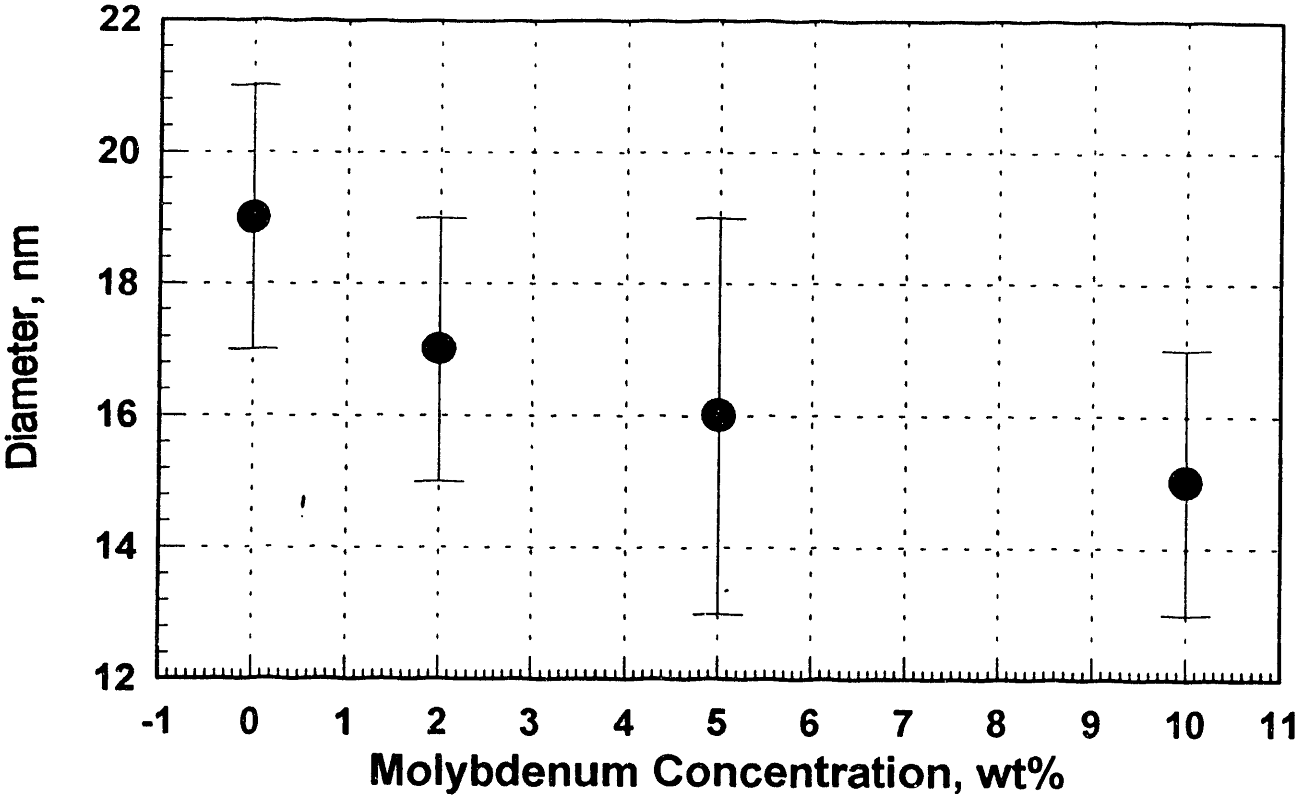
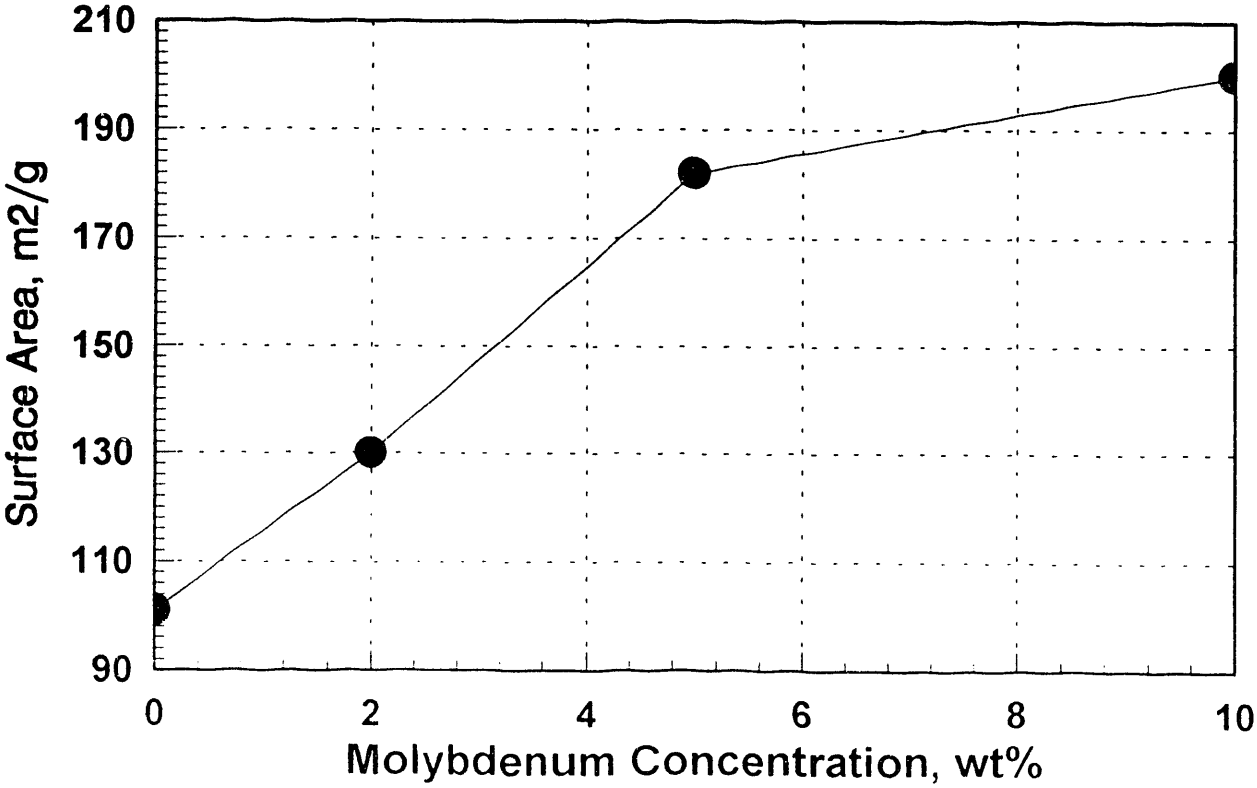


Figure 19. Effect of Molybdenum Concentration on Surface Area



Task 2.3.2 - CATALYST STUDIES (CONSOL)

We received a sample of Nanocat superfine iron oxide catalyst from UK/CAER for use in agglomeration tests. The iron oxide we received is untreated, but it is likely that the version eventually used will be modified by some additional treatment. No experimental work was performed on this task.

SUBTASK 2.3.3 CATALYST STUDIES (SANDIA)

Platinum HTO Synthesis

A large batch of Hydrous Titanium Oxide catalyst was prepared with platinum as the active metal. This catalyst was made by exchanging platinum ammonium nitrate onto a bulk HTO support. The HTO is prepared from tetraisopropyl titanate and tetraethyl orthosilicate in a sodium hydroxide methanol solution. The solution is hydrolyzed with acetone and water to precipitate the sodium form of the HTO. Platinum content on the catalyst was 5.4wt%.

Coated HTO NiMo Catalyst Synthesis

An alumina supported HTO catalyst was synthesized by coating the titanate onto an alumina support (Amocat 1C blank extrudate). Molybdenum was ion exchanged onto the coating and nickel was added by contacting the catalyst with a known amount of nickel in solution. This catalyst was then calcined in air at 500°C and crushed and sieved to a -10+20 mesh size. The molybdenum content was 8.1 wt% and the nickel content was 2.7 wt%. After solvent pretreatment the catalyst was removed from the reactor, washed with tetrahydrofuran, and tested for catalyst deactivation.

Catalyst Deactivation

The solvent pretreatment reactor is a fixed bed reactor consisting of two 0.4" I.D. tubes packed with catalyst connected by a short 0.125" O.D. connecting tube. The two-reactor configuration is necessary to achieve the desired Weight Hourly Space Velocities for the liquid feed. Post test carbon content was measured for catalyst at the feed end of reactor tube one as well as the exit end of reactor tubes one and two. Table 41 shows the carbon content of the catalysts which were removed from the trickle bed reactor after three days of reaction (eight hours of reaction time is considered a "day" in this reactor since the reactor cannot be operated unattended). All catalysts were removed and washed with copious amounts of tetrahydrofuran before carbon content was determined.

Table 41 Carbon content of catalysts (wt%)

Catalyst	Feed	Feed end reactor 1	Exit end reactor 1	Exit end reactor 2
Shell 324M	V1074	4.8	4.1	4.0
Shell 324M	-5°C dewax	8.9	8.3	7.4
Shell 324M	-35°C dewax	7.0	7.2	7.0
Coated HTO NiMo	-5°C dewax	9.3	8.1	7.5
Pt HTO	-5°C dewax	5.9	5.4	4.4

Results in table 41 show that the more aromatic dewaxed feeds deposited more carbon on the alumina supported Shell 324M than did the more paraffinic V1074. This is to be expected since they have a higher concentration of coke forming compounds. The coated HTO NiMo catalyst carbon content was similar to the Shell 324M post test carbon result. This is not surprising since the alumina support is acidic and would allow carbon deposition under these conditions. The platinum catalyst, however, had a relatively low amount of carbon possibly because of the less acidic bulk HTO support. This may be an important consideration in long term catalyst testing. Future tests will use a surface area analysis to determine the effects of carbon deposition on catalyst activity.

Catalyst deactivation can also be measured using a model compound hydrogenation test on the used catalyst.[2] Table 42 presents results from pyrene hydrogenation tests with fresh and aged NiMo HTO and a fresh and aged bulk platinum HTO.

Table 42 Pyrene hydrogenation results for fresh and used catalysts

Compound	**Coated NiMo HTO**	**Used Coated NiMo HTO**	**Platinum HTO**	**Used Platinum HTO**
Pyrene (wt%)	61.0	97.9	51.3	96.5
H_2Pyrene (wt%)	28.9	2.1	29.1	3.5
H_6Pyrene (wt%)	7.1	0	15.0	0
H_4Pyrene (wt%)	2.9	0	4.6	0
Rate constant*	0.19	0.008	0.26	0.012

* Pseudo first order rate constant (sec^{-1}) per gram of catalyst.[2] (Conditions: Reaction time 10 minutes, hydrogen pressure=500 psig, Temperature = 300°C.)

Results from pyrene hydrogenation tests show that both the coated NiMo HTO and the platinum HTO show catalyst deactivation at 300°C. Residual activity on the platinum HTO is slightly better than the coated NiMo HTO however the initial Pt HTO activity was higher (k=0.26 sec^{-1} for Pt and k=0.19 sec^{-1} for NiMo HTO). Carbon content of the commercial alumina supported catalyst (see Table 41) indicated high levels of carbon deposition indicating that residual hydrogenation activity may be very low in these catalysts as well. The pyrene test will be used with these catalysts in January.

Task 2.4.2 - Solids Separation (CONSOL)

Summary

Two approaches were taken to deashing liquefaction bottoms (resid) by agglomeration. These were: 1) to use the resid as the agglomerating oil, and 2) to use the resid as the hydrophobic solid (instead of or along with coal). The first approach is described under Task 2.1.2.2. The second strategy for rejecting ash from ashy resid is to grind it (it is solid at room temperature) and treat it as the agglomeration feed. An oil is used which allows agglomeration at low temperature, so that no melting of the resid occurs. Four runs were made with ball-milled ashy resid as the feed. There was agglomeration, but no substantial deashing in the four runs.

Discussion

Two approaches to deashing liquefaction bottoms (resid) by agglomeration are: 1) to use the resid as the agglomerating oil, and 2) to use the resid as the hydrophobic solid (instead of or along with coal). The first approach is used in the agglomeration runs at elevated pressure, described under Task 2.1.2.2. We also began exploring the second approach to rejecting ash from the ashy resid. This strategy for rejecting ash from ashy resid is to grind it (it is solid at room temperature) and treat it as the agglomeration feed. An oil is used which allows agglomeration at low temperature, so that no melting of the resid occurs. A similar flotation method has worked for rejecting ash from tar sands.[13] Although both approaches have resulted in physical agglomeration, neither one produced substantial deashing.

A ball mill is used to grind V-1082 ashy resid for 2 hr to 20 hr in water (50 wt % slurry, paste-like texture). A portion of the ground resid slurry is agglomerated at low temperature (room temperature to 50°C) with agglomerating oil (No. 6 fuel oil or white kerosene). Initially, the resid charge to agglomeration was quite low because the slurry was extensively diluted as a consequence of washing the material out of the ball mill. We have improved our technique for recovering milled material from the jar and we typically obtain a charge of about 30 to 40 g of resid in 175 mL of slurry. Four runs were made with ball-milled ashy resid as the feed. These were (Table 15) B9R, B11R, B12R, and B14R. Two runs used No. 6 fuel oil at 50°C as the agglomerating liquid; the others used white kerosene at room temperature. One of the kerosene runs, Run B14R, was made at a pH of 9.5 (Na_2CO_3 added, 0.5 wt % of the MF coal). Na_2CO_3 was used as an additive because it successfully promoted ash rejection in a tar sands flotation deashing technique.[13] There was agglomeration, but no substantial deashing in any of the four runs.

Task 2.6.1 FLUIDIZED COKING (UK/CAER)

Since the last reporting period, seven shakedown runs were completed using the CAER 3-inch fluid bed reactor system. The objectives of these runs were to 1) test the mechanical systems of the modified fluid bed reactor, 2) develop a tar sample preparation procedure, and 3) produce small (less than 50 g) "scouting" samples for subsequent analysis by CONSOL.

Shakedown Run Experiences

The original 3-inch reactor system was designed for batch-flow fluidized bed combustion sorbent tests. For the fluid coking tests, the reactor was modified for a continuous flow operation; this required the addition of a pressurized screw feeder. Initially, a screw feeder system fabricated at the CAER was utilized for the first shakedown tests.

Shakedown Run SR-1 - During the first shakedown run , a 3:1 alumina/resid mixture was prepared for use as the reactor feedstock material. This 3:1 mixture had a high angle of repose and tended to "rat-hole" in the feed hopper. As a result of the irregular flow in the hopper, the flow rate from the screw feeder was very erratic. Leaks in the screw feeder hopper and a blockage in the feeder transport line eventually forced the run to be aborted. For the next run, the alumina/resid mixture was increased to a 10:1 ratio and the seals in the screw feeder system were upgraded.

A thick aerosol formed in the condenser section of the sample recovery stream which tended to foul the steam condenser units. The 0.1 μM ceramic filter in the hot section of the sample train was ineffective in capturing the aerosol, since it appeared to form in the cooler condenser and ice bath sections. Subsequent analysis of the aerosol particulate revealed that it was a condensed hydrocarbon.

Shakedown Run SR-2 - The purpose of this run was to test the alumina/resid injection system with the 10:1 alumina/resid feedstock. The flow properties of this mixture ratio appeared to be greatly improved over the 3:1 mixture used in run SR-1. However, the flow of the feedstock material into the reactor was still erratic due to leaks in the feed system. After about 30 minutes of feeding, the alumina/resid mixture into the reactor, the feed nozzle injector became occluded and the run was aborted. The feed nozzle occlusion was caused by the resid material sticking to the hot sections of the nozzle tube near the entrance of the reactor.

Shakedown Runs SR-3 to SR-5 - The objective of these runs was to produce a series of scouting coker tar samples for subsequent analysis by CONSOL. A modified feed nozzle clean-out port was installed so that the feed tube could be cleared during the run.

The operating conditions and approximate tar yields for the scouting samples are displayed in Table 43. Only the resid flow rate was varied during these test while the steam rate was held constant (i.e. the fluidizing velocity was a constant 0.3 M/s). The tar yield appears to proportional to the steam/resid ratio. All of the samples were initially dissolved in methylene chloride and subsequently filtered to remove any alumina particulate matter that may have been present.

Table 43. Scouting Sample Run Conditions

Sample Number	Steam/Resid Ratio (lb/lb)	Coking Temperature, °C	Tar Yield, % (tentative)
SR-3	8.52	500	44
SR-4	12.34	500	46
SR-5	13.01	500	53

Due to the relatively short duration of these runs (less than 35 minutes), an accurate material balance of the resid and coker products were not possible. The duration of the reactor runs were still limited by the deposition of resid on the feed tube nozzle. Cleaning the feed tube during a run proved to be impractical since the deposited resid was difficult remove. The pressure drop across the cool section of the sample recovery train increased steadily throughout each run; this is due to deposition of tars and the nuisance aerosol particles.

Shakedown Run SR-6 - The purpose of this run was to test the new Technetics screw feeder system. The new system contained a one-piece, neoprene hopper and screw housing. The construction of the housing provided an improved pressure sealing surface as compared to our in-house feeder. A pressure regulator was also installed on the feed hopper to equalize the pressure difference between the feeder and the reactor.

Resid deposition in the feed tube continued to be a hinderance to maintaining longer duration runs. This deposition appeared to be caused by the rapid heating and subsequent softening of resid. To correct this problem, a water cooled injector nozzle was designed and fabricated for testing in run SR-7.

Shakedown Run SR-7 - The purpose of this run was to test the feasibility of using a cooled injector nozzle for transporting the resid mixture into the reactor. The water-cooled injector nozzle was placed in the lowest bed port of the 3-inch reactor. The nozzle consisted of three concentric tubes (1/2", 3/8", and 1/4") with swagelock heat exchanger connectors. Cooling water flowed through the heat exchanger fittings between the outer and middle tubes. Inside the 1/4" tube, the resid was transported to the reactor with nitrogen gas. The 1/2" tube and the 1/4" tube were welded together on the reactor end of the nozzle to seal the cooling water cavity. The 3/8" tube (or middle tube), was cut

1/2" shorter on the end to open a flow path for the cooling water.

A schematic of the modified reactor used for this run is shown in Figure 20. The ceramic filter used in run SR-1 was moved the exit of the sample recovery train; this was to capture the aerosol particulate before the non-condensible gases entered the wet test meter.

The resid inject nozzle remained clear throughout the entire run period of 30 minutes. However, the run was aborted due to the accumulation of tars in the ice bath and condensers in the sample recovery section of the apparatus; this created an excessive back pressure in the reactor vessel.

Project Status

A series of reactor runs, for the production of 500 to 1000 g of coker tar, are scheduled for late February. The production sample will be shipped to Sandia for use in their hydrotreating study. A small portion of this sample will be sent to CONSOL for characterization.

The capacity of the current sample recovery train is not sufficient to handle the quantity of steam and tars condensed. The condensers become fouled quickly from the resulting emulsion. Therefore, a separate sample recovery section will be added in parallel to the existing one. A two-way valve ahead of the parallel recovery trains will isolate each section so that they can be cleaned on-line.

TASK 3.4 PRELIMINARY TECHNICAL ASSESSMENT

Baseline Economic Assessment - Preparation of the baseline economic assessment, based on Wilsonville Run #263J, continued. This baseline study will serve as the reference against which the results of this program will be compared.

During the quarter detailed heat and material balances were calculated for both the coal and ash concentrate gasification units. Shift unit design data for both gasification systems was obtained from United Catalysts, Inc. Technical and economic data relating to the ROSE unit were obtained from the Kerr McGee Corporation. As a result of the above, the hydrogen, fuel gas and steam balances were recalculated. An error in the higher heating value of the Black Thunder coal was also corrected. The revised technical data for the baseline case is shown in attached Tables 43 to 51 and Figure 21.

The economic portion of the baseline assessment was begun. Investment cost for the oxygen plant, which serves both gasification units, was determined on a mid-1991, Wyoming plant location basis.

Slack Wax Upgrading - An earlier preliminary evaluation had indicated that dewaxing of the distillate portion of the process solvent might be beneficial. This evaluation was based on upgrading the slack wax (paraffinic reject from dewaxing) to a premium-value, fully refined paraffin wax. However, in a multi-plant scenario it is probable that wax supply would exceed demand. Therefore, it became necessary to consider alternate slack wax upgrading routes. At the September DOE Contractors Conference it was learned that AMOCO is working on a DOE sponsored program to selectively, catalytically crack paraffinic materials derived from Fischer-Tropsch synthesis. The products from this selective cracking are high value gasoline and gasoline precursors. AMOCO was contacted and indicated their willingness to conduct small scale cracking tests on our highly paraffinic slack wax material, provided the respective DOE Program Managers approve. At the December Quarterly Review Meeting our DOE Program Manager was asked to determine the procedural mechanism for conducting such tests. As a preliminary step before conducting such tests, CONSOL was requested to perform additional analytical characterization tests on the available slack waxes.

Upgrading of Dewaxed Oil - Several discussions were held with SANDIA personnel on the merits of various approaches to hydrotreatment of the dewaxed oil.

Fluid Coking - An unpublished summary report of ABB Lummus Crest's work in fluid coking of coal liquefaction residues was obtained from Burns and Roe and passed on to CAER personnel.

TABLE 43
BLACK THUNDER COAL PROPERTIES

ELEMENTALS, WT% MF

• CARBON	68.50
• HYDROGEN	4.80
• OXYGEN	18.90
• NITROGEN	1.00
• SULFUR	0.50
• ASH	6.30
Total	100.00

MOISTURE, AS-RECEIVED	30%

HEATING VALUE, Btu/lb.

•LHV, As-Rec'd	7,746
•HHV, MF	11,495

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TABLE 44
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
LIQUEFACTION SYSTEM YIELDS

INPUTS:

• MF COAL	100.00
• DISPERSED CATALYST	0.12
• SULFIDING AGENTS	1.43
• MAKEUP DAS	0.52
• HYDROGEN	5.88
Total =	107.95

OUTPUTS:

• WATER	14.82	
• HYDROGEN SULFIDE	0.34	
• AMMONIA	0.61	
• CARBON MONOXIDE	0.95	
• CARBON DIOXIDE	5.04	
• C1 to C3 GASES	7.89	
• C4+ DISTILLATE	58.32	
• ASH CONCENTRATE	19.98	(37.1% Ash)
Total =	107.95	

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TABLE 45
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED C4+ DISTILLATE PRODUCT PROPERTIES

• YIELD, Wt% on MF COAL	58.32
• 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

TABLE 46
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED FIRST STAGE REACTOR PARAMETERS

- Six Once-Thru Reactors in Parallel, 803 Tons Each
- 9 Feet ID. (12" Wall Thk.) x 100 Feet Height
- MF Coal Space Rate = 29.3 lb/ hr-ft^3 of Reactor
- MF Coal Concentration in Slurry = 30%
- Process Solvent Composition :

- Distillate	39.1%
- Resid	40.5%
- UC	9.1%
- Ash	11.3%

- Dispersed Catalyst(Molyvan L) 100 ppm Moly on MF Coal & Sulfiding Agents (Iron Oxide & H2S) Used
- Temperatures :
    - Reactor Inlet = 767° F
    - Reactor Outlet = 877° F
    - Reactor Effective = 840° F
    - Reactor Design = 905° F
- Average Hydrogen Partial Pressure = 2,185 psig
- Operating/ Design Pressure = 2,910 / 3,200 psig
- MAF Coal Conversion = 89.6%
- Net Resid Yield = 32.4% on MF Coal

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TABLE 47
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED SECOND STAGE REACTOR PARAMETERS

- Six Ebullated Reactors in Parallel, 349 Tons Each
- 12 Feet ID. (11" Wall Thk.) x 32 Feet Height
- Resid + UC Conversion = 19.0% of Feed
- Operating/ Design Temp. 825 / 850° F
- In-Bed Exotherm = 30° F
- Average Hydrogen Partial Pressure = 2,220 psig
- Operating / Design Pressure = 2,760 / 3,035 psig
- WHSV = 5.5 lb_{feed}/ hr-lb of cataylst
- Criterion 324 Catalyst
- Catalyst Replacement Rate = 3.0 lb / ton MF Coal
- Total Catalyst Inventory = 593,000 lbs.

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TABLE 48
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED DEASHING UNIT PARAMETERS

- MAF Coal Conversion = 93.6%

- Fiowrates,T/SD :
  - Vacuum Bottoms Feed = 4,780 (37.7% solids)
  - Makeup DAS = 70
  - Clean Resid Product = 2,165 (72% recovery)
  - Ash Concentrate = 2,685 (67.2% solids)

- Organic Rejection = 12.6% of MF Coal

- Energy Rejection = 17.1% of Coal HHV

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TABLE 49
BASELINE CASE STUDY : BLACK THUNDER COAL HYBRID CONFIGURATION - W'VILLE RUN# 263J
OVERALL UPGRADING YIELDS

INPUTS (Wt.% on MF Coal):

• C_4+ DISTILLATE	58.32
• HYDROGEN	1.29
Total =	59.61

OUTPUTS:

• WATER	1.27
• HYDROGEN SULFIDE	0.02
• AMMONIA	0.41
• C_1 to C_3 GASES	2.20
• C_4's	6.88
• LIGHT NAPHTHA	5.28
• REFORMATE	43.55
Total =	59.61

TABLE 50
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
HYDROGEN AND FUEL GAS BALANCES

HYDROGEN BALANCE (MMSCFD):

- CONSUMPTION

- LIQUEFACTION UNIT	313.8
- UPGRADING	144.2
Total =	458.0

- PRODUCTION

- GASIFICATION OF ASH CONC.	107.8
- GASIFICATION OF COAL	201.1
- PRODUCED IN CAT. REFORMING	71.1
- STEAM REFORMING OF HC GASES	78.0
Total =	458.0

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

- CONSUMPTION

- SLURRY PREHEATER	973
- STEAM REFORMER FEED	754
- CAT. REFORMER	661
- STEAM REFORMER	617
- DISTILLATE HYDROPROCESSING	217
- VACUUM UNIT	188
- GASIFICATION COAL, DRYING	156
- ROSE UNIT	89
- SULFUR RECOVERY UNIT & MISC.	20
Total =	3,675

- PRODUCTION

- LIQUEFACTION OFF GAS	2,065
- DISTILLATE HYDRO. OFF GAS	1,553
- CAT. REFORMING OFF GAS	57
Total =	3,675

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TABLE 51
BASELINE CASE STUDY : BLACK THUNDER COAL HYBRID CONFIGURATION - W'VILLE RUN# 263J
THERMAL EFFICIENCY

• INPUTS (Billions of Btu/D):

- MF COAL, 17,004 T/D	390.9
- MAKEUP DAS	2.6
- SULFIDING AGENTS	0.9
- ELECTRICAL POWER*, 257 MW	61.7
Total =	456.1

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

• OUTPUT (Billions of Btu/D):

- GASOLINE, 50,000 BPSD	262.7

OVERALL THERMAL EFICIENCY = 57.6 %

LIQUEFACTION UNIT ONLY = 70.0 %

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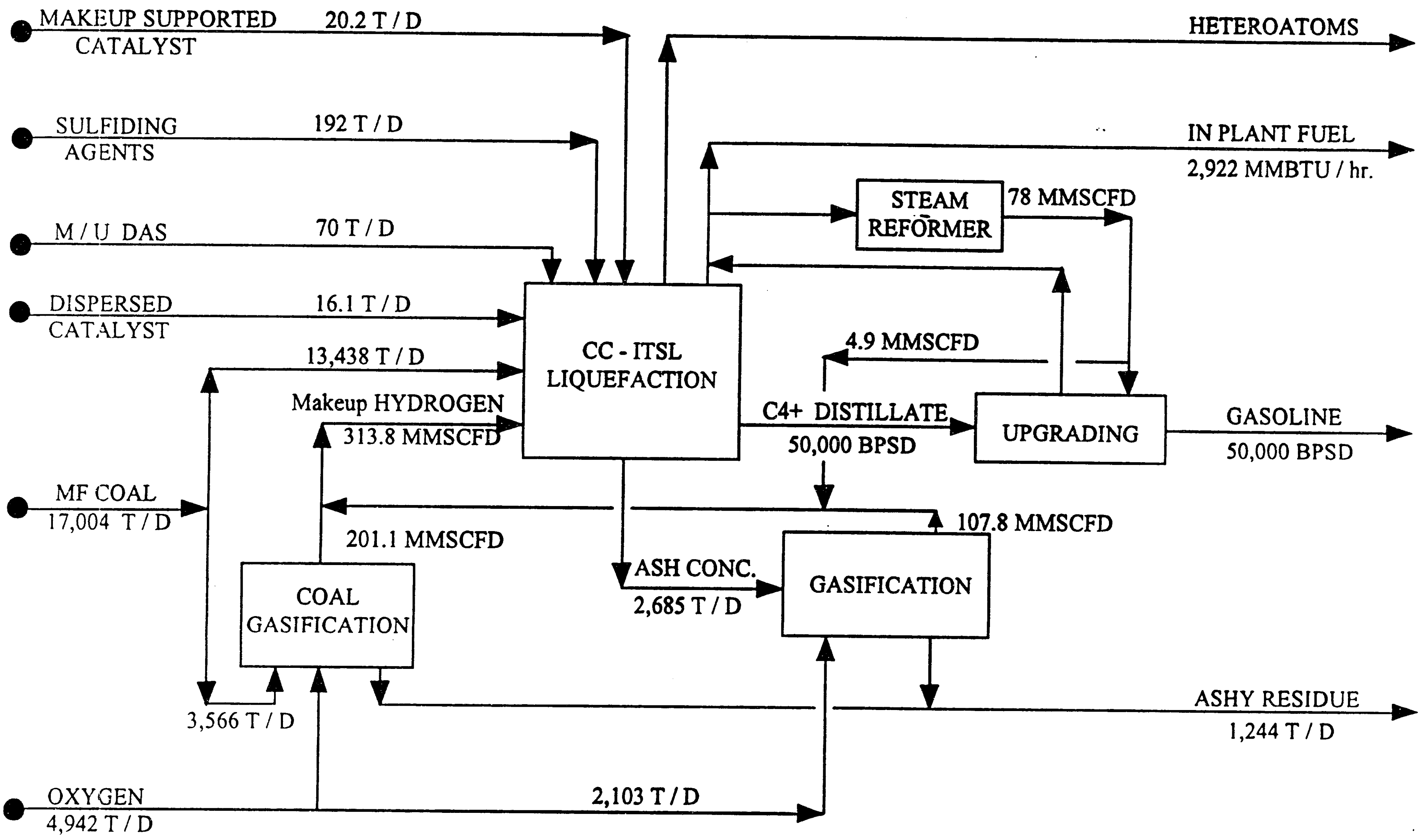

FIGURE 21
BLACK THUNDER LIQUEFACTION STUDY - HYBRID MODE
SIMPLIFIED BLOCK FLOW DIAGRAM
CONCEPTUAL COMMERCIAL PLANT BASED ON WILSONVILLE RUN #263J

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