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CATALYSTS AND PROCESS DEVELOPMENTS FOR TWO-STAGE LIQUEFACTION

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EXECUTIVE SUMMARY

Research under way in this project centers upon developing and evaluating catalysts and process improvements for coal liquefaction in the two-stage, close-coupled catalytic process. The project is being carried out under contract to the United States Department of Energy.

As discussed in the previous quarterly report, the results showed that C/T liquefaction is not a good option for Black Thunder subbituminous coal.

In this quarter, the liquefaction of Black Thunder coal was continued. The studies showed that the combination of Wender's sulfated iron oxide with molybdenum is the most effective catalyst for this liquefaction. Compared with other iron/molybdenum catalysts, distillate yields were increased and the catalyst deactivation was not as severe as for the supported (extruded) catalysts.

BACKGROUND

National energy policy requires that a reliable supply of reasonable-cost transportation fuels be available for both national and economic security. Unfortunately, the United States is importing about 50% of its petroleum supplies. Projections suggest an even greater reliance on imported oil in the future. An alternative to imported oil must be found if the United States is to achieve energy independence. Synthetic fuel from other fossil fuels is an alternative to imported oil. Coal is the most abundant of all fossil fuels, and the United States has one of the largest reserves of coal deposits in the world. The conversion of coal to transportation fuels would thus appear to be a necessary element of a serious synthetic fuels energy policy.

The conversion of coal to synthetic fuels through both direct and indirect routes was practiced commercially in Germany during World War II. Currently, South Africa produces transportation fuels through the indirect liquefaction of coal. Both technologies are uneconomic compared with producing transportation fuels from crude oil, but are or were practiced because of political considerations. Current assessments are that direct liquefaction offers the best chance for producing transportation fuels from coal at an economically viable cost.

There are no commercial direct coal liquefaction plants in operation anywhere in the world. However, several direct coal liquefaction technologies, such as the H-coal and the Exxon donor solvent processes, have been extensively studied. Currently, the most promising direct coal liquefaction route is the two-stage, close-coupled catalytic liquefaction process being studied at the Advanced Two-Stage Coal Liquefaction Facility at Wilsonville, Alabama. This facility serves as a research and demonstration plant to test new process options and catalysts for converting coal on a 6 tons of coal per day scale. Projected costs for direct coal liquefaction have dropped from over \$90 per barrel in 1981 to about \$36 per barrel today primarily because of improvements tested and demonstrated at Wilsonville. While the cost is still high, direct coal

liquefaction by the two-stage process continues to show improving economics and viability as a commercial technology.

The two-stage, close-coupled liquefaction process is a hydrotreating process that is conducted in two reactors in series with minimal residence time between reactors. This has been designated as "close-coupling." The first reactor is the primary coal conversion reactor where coal, a recycled coal-derived solvent, and hydrogen react to produce a hydrogenated coal product slate. The first reactor may be operated as either a catalytic or a thermal (non-catalytic) stage. The second reactor is operated with catalyst and serves to upgrade the first stage products by removing oxygen, nitrogen, and sulfur heteroatoms, increasing the hydrogen content of the products, and further reducing the boiling point of the products. The process is optimized to produce a maximum distillate product slate, optimum hydrogen utilization, high coal conversion, and sufficient coal-derived solvent for recycle. While the reactions taking place in both reactors are similar, each reactor sees a different feedstock because of the ongoing conversion. It is thus probable that each reactor will need to be optimized to produce the best overall liquefaction process. Two obvious areas for improvement to the two-stage process are improved catalysts and improved process options to reduce hydrogen consumption.

In view of the aforementioned considerations, the Department of Energy funds research programs designed to improve the economics and viability of direct two-stage coal liquefaction processes. This Department of Energy-funded research program is directed toward finding better catalysts and alternative process options to improve the overall liquefaction process. Better catalysts would improve liquefaction performance by increasing coal conversion, distillate yields, and/or hydrogen utilization. Ideally, catalysts should have both good hydrogenation activity and good activity maintenance. Process improvements include the removal of heteroatoms from coal before liquefaction to reduce hydrogen requirements and beneficiation before liquefaction to remove unreactive ash and other components from the coal.

PROGRAM OBJECTIVES

The overall objectives of this program are to develop and evaluate new catalyst formulations and process improvements for use in two-stage, close-coupled coal liquefaction. Improved catalysts are needed that can lead to higher coal conversion, distillate yields, or better hydrogen utilization. First stage catalysts are optimized primarily for enhanced coal conversion, and second stage catalysts for coal-resid upgrading. Process improvements include pretreatment to lower the oxygen content and unreactive components in coal before liquefaction. The program requires close cooperation between Amoco Oil and other Department of Energy-sponsored research efforts, particularly the Wilsonville Advanced Two-Stage Coal Liquefaction Facility.

PROJECT DESCRIPTION

Our technical approach to this project includes developing first and second stage coal liquefaction catalysts and testing the effects of selected pretreatment procedures on subsequent liquefaction. The procedures to be evaluated are methods for removing oxygen from coals and the beneficiation of coals to reduce ash and unreactive components prior to their liquefaction. Partially removing oxygen from coals prior to liquefaction has the potential of reducing hydrogen requirements and prolonging catalyst life. Beneficiation and pretreatment to reduce ash and unreactive components increases reactor throughput, improves catalyst life, and reduces the losses of product carried along with the unconverted coal and mineral matter rejected from the process.

Our overall approach to catalyst development is to prepare new formulations and modify existing refinery catalysts as candidates for either first or second stage coal liquefaction catalysts. First stage catalysts need to be accessible to large coal fragment molecules and promote both further fragmentation and hydrogen transfer to radical

fragments. Second stage catalysts need to promote aromatics saturation and heteroatom removal as well as reduce molecular weight to produce usable distillable liquids.

Coal liquefaction catalysts serve to promote both molecular weight reduction and hydrogen transfer to coal. We will screen candidate catalysts in fixed-bed reactors for upgrading a coal-resid and Panasol mixture. The fixed-bed unit allows accurate measurements of catalyst aging. Catalysts that show good second stage activity and activity maintenance for upgrading the coal-resid mixture will also be good candidates for further testing as first stage catalysts. Coals to be used as feedstocks are Illinois No. 6 (bituminous), Black Thunder (subbituminous), and Martin Lake (lignitic) coals. Resids are coal-derived liquids from the Wilsonville Coal Liquefaction Facility. Panasol (byproduct from naphtha reforming) is used as a solvent. Base case runs using a standard catalyst combination are being done to provide meaningful comparisons. Our approach allows accurate comparison of the relative effects of various pretreatments, coals, solvents, or catalysts on the liquefaction process.

Seven tasks have been identified to bring about the above objectives. Task 1 called for the completion of a detailed project management plan, which was issued. Task 2 is a general laboratory support task for the coal liquefaction tests. It provides the analytical support for characterizing most of the liquefaction samples and catalysts being tested. It includes microautoclave tests to more fully understand the results of larger scale experiments and qualification of solvents used or produced during liquefaction. Task 3.1 is directed toward determining the liquefaction behaviors of standard coal samples and comparing them with the beneficiated or pretreated samples. Pretreatment procedures emphasize methods for oxygen removal and beneficiation to remove ash and inert materials.

Catalyst development and testing are being done under the three parts of Task 3.2. Task 3.2.1 is used to test a series of candidate first stage

catalysts and the best second stage catalysts as first stage catalysts with Illinois No. 6 bituminous and Black Thunder subbituminous coals in our continuous pilot plant unit. The objective is to identify a high-activity first stage catalyst.

In Task 3.2.2 up to 50 candidate catalysts were evaluated with an Illinois No. 6 coal-resid and Panasol mixture to identify the five best second stage catalysts. Novel and conventional catalysts have been prepared and tested. Several of Sandia's hydrous metal oxide catalysts have been tested, and two additional tests are planned under Task 3.2.3. Consultation to Sandia on preparing their catalyst in a suitable form is also being provided.

Other process developments are being evaluated under Task 3.3. Decarboxylation of low-rank coals by hydrothermal and caustic- or catalyst-aided treatments will be tested.

RESULTS AND DISCUSSION

During this fifteenth quarter of the contract, experimental work on Task 3.2.1 (first stage catalyst) continued by liquefying Black Thunder bituminous coal using dispersed iron and molybdenum catalysts. A run was also made with Sandia hydrous titanate catalysts under Task 3.2.3; results are included in the Appendix and will be discussed in the next quarterly. Under Task 3.1, a continuous pilot plant test was completed of a pretreatment stage for rejection; results are included in the Appendix and will be discussed in the next quarterly. Other detailed reports of the results and efforts for this quarter are given by task below.

Task 2: Laboratory Support and Microautoclave Runs

No activity limited to this task was undertaken; results of laboratory analyses are reported under the remaining tasks when applicable.

Task 3.1: Feedstock Effects

Analyses are complete from a run aimed at oxygen rejection/conversion with Black Thunder coal feed in a low pressure pretreatment stage. Process conditions are in Table A-1 of the Appendix. Product analyses are in Tables A-2 and A-3, and net yields from coal and hydrogen consumptions are given in Table A-4 of the Appendix. Results will be discussed in detail in the next quarterly report.

Task 3.2.1: First Stage Catalysts

The objective of experimentation in this subproject was to evaluate first stage catalysts for liquefaction of Illinois No. 6 coal and Black Thunder subbituminous coal using a two-stage, continuous-flow unit.

First Stage Catalyst Tests with Black Thunder Coal

This series of tests used dispersed iron plus molybdenum catalysts for liquefaction of Black Thunder subbituminous coal. Initial tests with Molyvan L dispersed molybdenum catalyst plus iron oxide gave good results at long residence times, but high resid yields at residence times similar to those used at Wilsonville. To increase resid conversion, the more active hydrogenation catalysts AMOCAT™ 1C or AMOCAT™ 1B were tested in the first stage (Quarterly Report 56), but rapid and severe catalyst deactivation was seen. Different forms of dispersed iron plus molybdenum catalysts might be more active for hydrogenation but not be susceptible to deactivation by pore plugging like supported catalysts. Earlier work with Illinois No. 6 coal has shown that Molyvan L is a reactive dispersed molybdenum catalyst. This series of runs tested Molyvan L together with ferrous sulfate or Professor I. Wender's sulfate iron oxide catalyst,

which are both more active catalysts than iron oxide. Wender's sulfated iron oxide was also tested as a support for molybdenum and also without addition of a sulfiding agent to retain higher catalyst acidity, which could be beneficial.

EXPERIMENTAL: FEEDSTOCK DESCRIPTIONS AND TEST CONDITIONS

Analyses of the Black Thunder subbituminous coal feed, obtained from the mine and ground at the University of North Dakota, are given in Table 1. Different batches of coal were used in the Black Thunder reference test (FCL-126) and first stage catalyst tests (FCL-135). Liquefaction solvent was a blend of V-1074 and V-203 liquids from Wilsonville Run 258. The analyses of the Black Thunder solvent used in these studies, FSN-136, are given in Table 2. The bench-scale liquefaction runs were made in AU-135L continuous, two-stage pilot plant with 1-liter stirred autoclave reactors. Feed slurries consisted of 33/67 mixtures of coal/liquefaction solvent. Dispersed iron or molybdenum plus iron catalysts were added directly to the feed. Ferrous sulfate was dissolved in a minimum amount of distilled water before addition to the feed tank. Standard amounts of 100 ppm Mo/coal and 0.7% Fe/coal were used (Molyvan L contains 0.8% Mo). Sulfated iron oxide was precipitated from a solution of ferrous sulfate with ammonia¹, dried at 125°F, ground to -100 mesh, and used without calcining. TPS-20, an oil-soluble sulfiding agent containing 20% sulfur, was added directly to the feed for all except two of the test periods. Illinois No. 6 solvent was used in the last period to study effects of solvent composition. The analyses of Illinois No. 6 solvent are given in Table 2 (FSN-109).

Nominal residence times were 1-1.5 hours, which are similar to Wilsonville. These shorter residence times were achieved by operation of the first stage at reaction temperature (780-820°F) and operation of the second stage at 500°F (little reaction in the second stage).

Product solubility was determined by millipore filtration, distillate yields were determined by modified D-86 and D-1160 distillation, and

distilled fractions were analyzed for C, H, S, N, O, and aromatic carbon by ^{13}C NMR. Unconverted solids were analyzed for metals by ICP (inductively coupled plasma spectroscopy).

Black Thunder Coal: Dispersed Iron and Molybdenum Catalysts

In earlier tests, Black Thunder coal was liquefied with Molyvan L dispersed molybdenum catalyst, Molyvan L/red mud (iron oxide) or molybdenum octoate/red mud at 3.0 hours nominal residence time (Quarterly Report 52). At this relatively long residence time, performance was good, giving over 88% coal conversions to THF solubles at 800-820°F, and less than 5% resid. Periods with iron oxide gave no resid in the net product from coal. Residence times at Wilsonville are about 1.0-1.5 hours. At the end of the run, one period was included at 1.5 hours residence time and 820°F with Molyvan L (no iron oxide). Coal conversion was good (88%), but the resid yield was very high (17%). This was much different from results from Illinois No. 6 coal, where the results were similar at 800°F/3.0 hours and at 820°F/1.5 hours. Catalyst requirements for liquefaction of Black Thunder subbituminous coal and Illinois No. 6 coal are clearly different.

Batch autoclave liquefaction of Black Thunder coal in tetralin showed that impregnation of the coal with ferrous sulfate in methanol or water gave better results than red mud. Autoclave liquefaction studies also showed good performance from an iron oxide catalyst precipitated in the presence of sulfate, developed by Wender and Pradhan¹. Ferrous sulfate or sulfated iron oxide catalysts, used in combination with molybdenum, might give sufficient hydrogenation activity for good conversion of Black Thunder resid at reasonably short residence times.

Ferrous Sulfate and Molyvan L

Process conditions are given in Table A-5 of the Appendix, product analyses are given in Tables A-6 and A-7 of the Appendix, and net yields from coal are given in Table A-8 of the Appendix.

The effects of temperature on the liquefaction yields from ferrous sulfate plus Molyvan L catalysts at 1.5 hours residence time are summarized in Table 3. Liquefaction at 820°F gave 87% conversion, compared with 84.5% conversion at 800°F, and the resid yield dropped to 9% from 21%, but distillate yields actually decreased to 40% from 45% because hydrocarbon gas yields nearly doubled at the higher temperature. The high gas yield also contributed to 1% higher hydrogen consumption. Analyses of the heavy distillate and resid, Table 4, showed that 650°F- product from the higher temperature was hydrogen-poor, which would make it difficult to upgrade. Ferrous sulfate/Molyvan L catalysts gave better performance at 1.5 hours residence time than Molyvan L, but coal conversions were still too low and gas yields were too high.

Sulfated Iron Oxide and Molyvan L

Physical and chemical analyses of the sulfated iron oxide catalyst are given in Table 5, and the pore size distribution is shown in Figure 1. The surface area was 189 m²/g, more than twice as high as reported by Wender and Pradhan, and surface areas of 400 m²/g should be possible because of the small average pore radius (16Å).

Without a sulfiding agent, product yields from sulfated iron oxide catalyst and Molyvan L were about the same as from ferrous sulfate and Molyvan L, Table 6. With added sulfiding agent TPS-20, resid yields dropped from 18% to 12-13%, giving more 650-935°F distillate. Reaction temperatures were kept low (800°F) to avoid high hydrocarbon gas yields, which were slightly lower in the presence of the sulfiding agent. Hydrogen consumptions were 1.2% higher with sulfiding agent, indicating that improved performance was from increased hydrogenation.

Instead of Molyvan L, molybdenum was directly supported on the sulfated iron oxide catalyst, which was used for liquefaction in the presence of a sulfiding agent. Yields were identical to those from sulfated iron oxide plus Molyvan L (Table 6, right-hand columns). The sulfated iron oxide is a good surface for dispersion of molybdenum, and the dispersed molybdenum

does not appear to benefit from any unusual interaction between molybdenum and iron.

Product analyses, Table 7, showed all product fractions were more hydrogen-rich if the catalyst contained sulfated iron oxide, molybdenum, and a sulfiding agent. Good hydrogenation activity is the key to good performance of this catalyst combination. The small pore size of the sulfated iron oxide does not contribute any special cracking activity, because essentially all porosity is lost in the liquefaction reaction. The sulfated iron oxide particles probably disintegrate during sulfiding, giving well-dispersed, reactive iron sulfides.

The combination of Wender's sulfated iron oxide with molybdenum is the most effective catalyst for liquefaction of Black Thunder coal at relatively short residence times. Compared with other Fe/Mo catalysts, distillate yields were increased from less than 40% to 47-48%. Because ammonium molybdate impregnation onto the sulfated iron oxide would be less expensive than Molyvan L, the molybdenum form of Wender's catalyst is preferred.

Liquefaction of Black Thunder Coal in Illinois No. 6 Solvent

Coal conversion and distillate yields from Black Thunder coal were still relatively low compared with those from Illinois No. 6 coal at 1.5 hours residence time, in spite of the catalyst improvements. Relatively poor liquefaction performance of Black Thunder coal could be from the hydrogen-poor ($H/C = 1.11$) nature of the solvent compared with that from Illinois No. 6 coal ($H/C = 1.19$). In batch autoclave tests, conversion of Black Thunder coal increased from 67% to 78% when the hydrogen content of the 650-935°F Black Thunder liquefaction solvent was increased from $H/C=1.11$ to $H/C=1.22$ (Quarterly Report 56). To test the effect of solvent composition in a continuous pilot plant, Black Thunder coal was liquefied in Illinois No. 6 solvent using ferrous sulfate plus Molyvan L catalysts.

Product yields are given in Table 8. Illinois No. 6 solvent gave 23% more distillate, 18% less resid, and 5% higher conversion than Black Thunder

solvent at the same conditions (800°F and 1.5 hour residence time). Pre-hydrogenation of Black Thunder solvent could give comparable improvements, which would have a large beneficial effect on process economics.

CONCLUSIONS

Sulfated iron oxide plus molybdenum and a sulfiding agent is the most effective catalyst for liquefaction of Black Thunder coal. Ammonium molybdate impregnated onto sulfated iron oxide is the most economical form of the catalyst. Results are better than from supported catalysts like AMOCAT™ catalysts because the supported catalysts deactivate rapidly with this coal. Good performance of the sulfated iron oxide catalysts is linked to high hydrogenation activity, which may upgrade the primary product from coal and the liquefaction solvent. Liquefaction of Black Thunder coal improved in Illinois No. 6 solvent, which is relatively hydrogen-rich, indicating that prehydrogenation of Black Thunder solvent may improve liquefaction performance.

Task 3.2.2: Second Stage Catalysts

No activity in this task during the quarter.

Task 3.2.3: Hydrous Metal Oxide Catalysts

Analyses are complete from a test of a powdered version of Sandia's hydrous metal titanate catalyst and a powdered nickel/molybdenum on alumina catalyst. Process conditions are in Table A-9 of the Appendix. Product analyses are in Tables A-10 and A-11, and net yields from coal are given in Table A-12 of the Appendix. Results will be discussed in detail in the next quarterly report.

CONCLUSIONS AND FUTURE WORK

A dispersed catalyst consisting of molybdenum on sulfated iron oxide is the most effective for liquefaction of Black Thunder subbituminous coal. Deactivation is not as severe as for supported (extruded) catalysts, and relatively good resid conversion can be achieved at reasonable space velocities. Liquefaction of Black Thunder coal improved markedly in Illinois No. 6 solvent, which is more hydrogen-rich. Prehydrogenation of liquefaction solvent may dramatically improve liquefaction of Black Thunder coal.

Future work will examine the use of molybdenum on sulfated iron oxide for liquefaction of Illinois No. 6 coal. A test of beneficiated Spring Creek subbituminous coal is planned. The final test in this contract will use a Sandia hydrous metal oxide catalyst supported on alumina.

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REFERENCES

1. V. R. Pradhan, J. W. Tierney, I. Wender, and G. P. Huffman,
"Catalysis in Direct Coal Liquefaction by Sulfated Metal Oxides,"
1991, *Energy and Fuels*, 497.

TABLE 1

COAL ANALYSES

		Black Thunder Subbituminous	
Coal			
Batch Number	FCL-126	FCL-135	
As Received, Wt% H ₂ O	23.60	23.31	
Dry, Wt%			
C	69.60	69.05	
H	5.01	5.23	
N	1.07	.90	
S	.46	.50	
O (Difference)	17.14	17.64	
Ash	6.72	6.68	
Wet, Wt%			
Fe	.13	.18	
Na	.03	.05	
K	.03	.02	
Ca	.88	.88	
Mg	.11	.15	
Al	.31	.42	
Ti	.02	.03	
Si	.33	.57	

TABLE 2
SOLVENT ANALYSES

Wilsonville Run	257	258
Wilsonville Coal	Illinois No. 6	Black Thunder Subbituminous
Batch Number	FSN-109	FSN-136
Elemental Analyses, Wt%		
C	89.26	89.25
H	8.83	8.26
N	.57	.75
S	.08	.05
O	1.26	1.69
Distillation, Wt%		
IBP-650°F	1.45	8.55
650-935°F	52.94	49.92
935+°F	46.16	41.52
Solubility, Wt%		
THF Insolubles	.12	.22
Toluene Insolubles	1.07	.99
Hexane Insolubles	7.96	4.31

TABLE 3

LIQUEFACTION OF BLACK THUNDER COAL WITH FERROUS SULFATE AND MOLYVAN L:
EFFECT OF TEMPERATURE ON PRODUCT YIELDS

Residence Time, Hours	1.5	1.5
Temperature, °F	800	820
Yields, Wt% MAF Coal		
C1-C3	10.4	19.2
C4-360°F	4	7
360-650°F	25	31
650-935°F	6	2
935°F+	21	9
C ₄ -935°F	35	40
Conversion	84.5	87.0
Hydrogen	-4.2	-5.1

Catalysts were Molyvan L (100 ppm Mo:coal) and ferrous sulfate (0.7% Fe:coal).

TABLE 4

LIQUEFACTION OF BLACK THUNDER COAL WITH FERROUS SULFATE AND MOLYVAN L:
EFFECT OF TEMPERATURE ON PRODUCT ANALYSES

Residence Time, Hours	1.5	1.5
Temperature, °F	800	820
Wt% Analysis		
360-650 Aromatic C	43	45
H/C	1.42	1.47
N	.41	.40
O	2.9	3.2
650-935 Aromatic C	55	60
H/C	1.20	1.15
S	.04	.05
N	.54	.65
O	1.4	1.4
935°F+, Solids		
H/C	.80	.75
S	.57	.66
N	1.25	1.25

TABLE 5

ANALYSES OF SULFATED IRON OXIDE CATALYST

	Sulfated Iron Oxide	Red Mud
<u>Elemental Analyses</u>		
Fe	39.7	58.9
S	--	0.0
O (calc. for Fe ₂ O ₃)	17.1	25.3
Moisture	37.4	--
<u>Pore Properties</u>		
BET Surface Area, m ² /g	189	<1
Pore Volume, cc/g	.15	.04
Average Pore Radius, Å	16	96

TABLE 6

LIQUEFACTION OF BLACK THUNDER COAL WITH DISPERSED Mo/Fe:
YIELDS FROM DIFFERENT CATALYST TYPES

Nominal Residence Time, Hours	1.5	1.5	1.5	1.5
Temperature, °F	800	800	800	800
Molyvan L, ppm Mo:Coal	100	100	100	0
Wender's, ppm Mo:Coal	0	0	0	100
Wt% Fe:Coal	0	0.7	0.7	0.7
FeSO ₄ /H ₂ O, Wt% Fe:Coal	0.7	0	0	0
TPS-20, Wt%	0	0	5.0	5.0
Yields, Wt% of MAF Coal				
C1-C3	10.4	10.6	8.9	8.4
C4-360°F	4	6	4	6
360-650°F	25	29	29	29
650-935°F	6	5	14	14
935°F+	21	18	13	12
C ₄ -935°F	35	39	47	48
Conversion	84.5	84.9	86.0	85.6
Hydrogen	-4.2	-4.2	-5.4	-5.4

TABLE 7

**LIQUEFACTION OF BLACK THUNDER COAL WITH DISPERSED Mo/Fe:
PRODUCT ANALYSES FROM DIFFERENT CATALYST TYPES**

Nominal Residence Time, Hours	1.5	1.5	1.5	1.5
Temperature, °F	800	800	800	800
Molyvan L, ppm Mo:Coal	100	100	100	0
Wender's, ppm Mo:Coal	0	0	0	100
Wt% Fe:Coal	0	0.7	0.7	0.7
FeSO ₄ /H ₂ O, Wt% Fe:Coal	0.7	0	0	0
TPS-20, Wt%	0	0	5.0	5.0
Wt% Analysis				
360-650°F				
Aromatic C	43	43	42	41
H/C	1.42	1.40	1.43	1.44
N	.41	.42	.46	.40
O	2.9	2.7	2.8	2.6
650-935°F				
Aromatic C	55	56	53	54
H/C	1.20	1.19	1.22	1.22
S	.04	.04	.04	.04
N	.54	.56	.55	.57
O	1.4	1.4	1.3	1.2
935°F+, Solids				
H/C	.80	.80	.84	.84
S	.57	.54	.52	.41
N	1.25	1.19	1.20	1.19

TABLE 8

LIQUEFACTION OF BLACK THUNDER COAL WITH FERROUS SULFATE AND MOLYVAN L:
EFFECT OF SOLVENT TYPE ON PRODUCT YIELDS

Residence Time, Hours	1.5	1.5
Solvent	Black Thunder	Illinois No. 6
Temperature, °F	800	800
Yields, Wt% MAF Coal		
C1-C3	10.4	9.6
C4-360°F	4	4
360-650°F	25	37
650-935°F	6	17
935°F+	21	3
C ₄ -935°F	35	58
Conversion	84.5	89.3
Hydrogen	-4.2	-4.6

Catalysts were Molyvan L (100 ppm Mo:coal) and ferrous sulfate (0.7% Fe:coal).

Property of Amoco Oil Company
Proprietary--To Be Maintained in Confidence

FIGURE 1
PORE SIZE DISTRIBUTION

APPENDIX

Property of Amoco Oil Company
Proprietary--To Be Maintained in Confidence

TABLE A-1

Black Thunder Coal: Pre-rejection of Oxygen, Process Conditions

Pretreatment temperature F	650	-----700-----				750
Pretreatment H2 SCFB	1000	500	----- 0-----			
SAMPLE PERIOD	1	2	3	4	6	7
HOURS ON STREAM	18.2	41.9	65.8	89.5	112	118
WT FRACTION COAL IN FEED .	0.33	0.33	0.33	0.33	0.33	0.33
1ST-STAGE TEMPERATURE, F .	650	700	700	700	700	750
SPACE TIME, MIN.	75.8	103	89.8	77.5	63.5	72.7
SEVERITY, STTUS.	0.20	1.60	1.39	1.20	0.98	5.59
COAL,CAT LHSV ..	.	.	.	.	.	.
SOLVENT,CAT LHSV	.	.	.	.	.	.
2ND-STAGE TEMPERATURE, F .	800	800	800	800	800	800
SPACE TIME, MIN.	75.8	103	89.8	77.5	63.5	72.7
SEVERITY, STTUS.	25.5	34.8	30.3	26.1	21.4	24.5
COAL,CAT LHSV ..	.	.	.	.	.	.
SOLVENT,CAT LHSV	.	.	.	.	.	.
COMBINED SEVERITY, STTUS .	25.7	36.4	31.7	27.3	22.4	30.1
SYSTEM PRESSURE, PSIG	2500	2500	2500	2500	2500	2500
1000 SCFH H2 PER BBL FEED.	5.29	5.26	5.01	4.55	4.63	4.93

Pre-rejection of oxygen in the first stage was accomplished by cutting hydrogen flow and heating. Catalytic liquefaction occurred in the second stage which had an independent hydrogen supply. Hydrogen flow to the first stage was estimated.

TABLE A-2

Black Thunder Coal: Pre-rejection of Oxygen. Product Analyses

Pretreatment temperature F	650	-----700-----	750			
Pretreatment H2 SCFB	1000	500	-----0-----			
SAMPLE PERIOD	1	2	3	4	6	7
HOURS ON STREAM	18.18	41.93	65.78	89.5	112	118.1
PRODUCT GAS ANALYSES (VOL%)						
C1	0.913	1.120	1.050	1.050	1.050	1.030
C2	0.380	0.506	0.424	0.424	0.424	0.421
C3	0.250	0.337	0.254	0.254	0.254	0.277
C4	0.150	0.190	0.152	0.152	0.152	0.145
C5	0.036	0.058	0.040	0.040	0.040	0.082
C6	0.036	0.058	0.040	0.040	0.040	0.082
CO	0.152	0.175	0.128	0.128	0.128	0.116
CO2	0.524	0.544	0.651	0.651	0.651	0.593
H2S	.	.	.	.	.	.
FEED AND PRODUCT WATER (WT%)						
H2O IN FEED	7.930	7.120	.	.	.	.
FEED H2O LOSS G HR	0.000	0.000	0.000	0.000	0.000	0.000
H2O IN PRODUCT	8.860	8.860	.	7.740	.	6.490
SOLUBLE OR SLURRY CATALYSTS (WT%)						
SOL-SLURRY CAT	0.333	0.333	0.333	0.333	0.333	0.333
ASH IN CATALYST	100	100	100	100	100	100
S IN CATALYST	5.000	5.000	5.000	5.000	5.000	5.000
PRODUCT SLURRY SOLUBILITY, WT % INSOLUBLE						
THF	4.930	5.060	4.650	.	.	5.290
TOLUENE	9.000	10.71	11.27	.	.	13.13
HEXANE	15.71	18.35	18.36	.	.	17.55
ASH	1.960	1.970	1.840	.	.	1.810
PRODUCT DISTILLED FRACTIONS, WT%						
WT% NAPHTHA	8.740	.	7.100	.	.	5.600
WT% DISTILLATE	15.25	.	12.19	.	.	11.92
WT% VACUUM DISTILLATE	36.22	.	36.41	.	.	35.64
WT% RESID+UNCONV COAL	39.24	.	42.61	.	.	44.56

TABLE A-3

Black Thunder Coal: Pre-rejection of Oxygen, Elemental Analyses

Pretreatment temperature F	650	-----700-----	750			
Pretreatment H2 SCFB	1000	500	0-----			
SAMPLE PERIOD	1	2	3	4	6	7
DIOXANE-FREE DISTILLATE (360-650 F), WT%						
C				84.1		
H				10.3		
S				0.01		
O				4.00		
N				0.43		
TOTAL				98.8		
VACUUM DISTILLATE (650-RESID), WT%						
C				89.5		
H				9.08		
S				0.04		
O				1.39		
N				0.49		
TOTAL				100		
RESID + UNCONV COAL, WT%						
C				86.4		
H				5.75		
S				0.49		
O (DIFFERENCE)				1.90		
N				1.15		
TOTAL				98.1		
THF INSOLUBLES						
RESID THF INSOLUBLES, WT%						
ASH						
K				2100		
SI				83E3		
AL				58E3		
CA				11E4		
FE				13E4		
MG				21E3		
MO				2090		
NA				7800		
NI				230		
TI				5000		
V				236		

TABLE A-4

Black Thunder Coal: Pre-rejection of Oxygen Elemental Analyses

Pretreatment temperature F	650	-----700-----	750			
Pretreatment H2 SCFB	1000	500	-----0-----			
SAMPLE PERIOD	1	2	3	4	6	7
HOURS ON STREAM	18.2	41.9	65.8	89.5	112	118
NET PRODUCT YIELDS (WT% MAF COAL OR EQUIVALENT)						
OILS.....	.	32.8	17.2	24.5	.	28.2
ASPHALTENES.....	.	16.8	20.6	18	.	7.22
PREASPHALTENES.....	.	13.8	20.2	23.5	.	27.6
H2S	.	.	.	-1.5	.	.
NH3	.	.	.	0.29	.	.
CO + CO2.....	5.01	5.22	5.60	5.08	5.18	5.03
H2O	.	.	.	15.6	.	.
C1 TO C3	6.78	8.67	7.07	6.42	6.54	7.08
C4 TO 360	.	3.65	.	2.39	.	3.66
360 TO 650	.	33	.	23.5	.	19.1
650 TO 935	.	8.05	.	8.74	.	7.05
935 +	.	19.8	.	32.6	.	34.3
C4 TO 650	.	36.6	.	25.9	.	22.8
C4 TO 935	.	44.7	.	34.6	.	29.8
UNCONVERTED COAL	.	11	11.6	10.3	.	12.6
ASH	.	-86	-76	-1.4	.	-1.7
HYDROGEN	.	.	.	-3.5	.	.
PRODUCT MATERIAL BALANCES						
% OVERALL BALANCE.....	109	111	67	112	113	105
% ASH BALANCE	.	89.9	91.1	83.5	.	80.4
HETEROATOM REMOVAL (% OF HETEROATOMS IN FEED)						
SULFUR	.	.	.	-19	.	.
OXYGEN	.	.	.	.	.	.
NITROGEN	.	.	.	7.68	.	.

TABLE A-5

Black Thunder Coal: Dispersed Iron and Molybdenum Catalysts, Process Conditions

SAMPLE PERIOD	-----FeSO ₄ /H ₂ O-----						-----Wender-----				Mo/Wender		FeSO ₄ /H ₂ O	
	-----800-----		-820-	-780-	-800-		-Molyvan L		-Molyvan L		-Sulfiding		Molyvan L	
	2	4	5	7	9	11	13	14	16	17	19	20	22	23
HOURS ON STREAM	64.4	86.1	110	156	166	189	237	259	300	324	346	393	416	440
WT FRACTION COAL IN FEED .	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
1ST-STAGE TEMPERATURE, F .	800	800	800	820	780	800	800	800	800	800	800	800	800	800
SPACE TIME, MIN.	90.3	84.3	87	92.4	86.1	75.1	87.9	76.8	89.8	89.3	82.2	73.7	87	94.3
SEVERITY, STTUS.	30.4	28.4	29.3	54.4	16.3	25.3	29.6	25.9	30.3	30.1	27.7	24.8	29.3	31.8
COAL,CAT LHSV ..	.	.	.	.	.	.	.	.	.	.	.	.	.	.
SOLVENT,CAT LHSV	.	.	.	.	.	.	.	.	.	.	.	.	.	.
2ND-STAGE TEMPERATURE, F .	500	500	500	500	500	500	500	500	500	500	500	500	500	500
SPACE TIME, MIN.	90.3	84.3	87	92.4	86.1	75.1	87.9	76.8	89.8	89.3	82.2	73.7	87	93.9
SEVERITY, STTUS.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
COAL,CAT LHSV ..	.	.	.	.	.	.	.	.	.	.	.	.	.	.
SOLVENT,CAT LHSV	.	.	.	.	.	.	.	.	.	.	.	.	.	.
COMBINED SEVERITY, STTUS .	30.4	28.4	29.3	54.4	16.3	25.3	29.6	25.9	30.3	30.1	27.7	24.8	29.3	31.8
SYSTEM PRESSURE, PSIG	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500	2500
1000 SCFH H ₂ PER BBL FEED.	7.70	8.54	8.78	9.43	8.61	7.60	8.80	7.72	7.40	7.31	8.03	7.05	8.35	8.84

All periods where temperature is not indicated were at 800 F. Wender's catalyst is sulfated iron oxide powder. Mo/Wender catalyst is sulfated iron oxide impregnated with ammonium molybdate. Iron levels were 0.7% Fe/coal except for period 11 with 1.4% Fe/coal. Molybdenum levels were 100 ppm Mo/coal. Sulfiding agent was TPS-20, an oil-soluble disulfide containing 20% S. Period 9 at 780 F was not stable.

TABLE A-6

Black Thunder Coal: Dispersed Iron and Molybdenum Catalysts, Product Analyses

	-----FeSO ₄ /H ₂ O-----						-----Wender-----				--Mo/Wender--		-FeSO ₄ /H ₂ O-	
	-----800-----		--820--		--780--		--800--		--Molyvan L--		--Molyvan L--		--Sulfiding--	
	-----No S-----		--Sulfiding--										Ill 6 Liquid	
SAMPLE PERIOD	2	4	5	7	9	11	13	14	16	17	19	20	22	23
HOURS ON STREAM	64.42	86.15	109.9	156.1	165.6	189.1	236.7	259.4	299.9	323.5	346.3	392.8	415.8	439.5
PRODUCT GAS ANALYSES (VOL%)														
C1	0.808	0.999	0.999	1.470	0.884	0.884	0.953	0.953	0.827	0.851	0.815	0.815	0.807	0.807
C2	0.320	0.416	0.416	0.586	0.365	0.365	0.402	0.402	0.348	0.357	0.351	0.351	0.336	0.336
C3	0.198	0.277	0.277	0.393	0.245	0.245	0.280	0.280	0.245	0.245	0.249	0.249	0.228	0.228
C4	0.085	0.123	0.123	0.161	0.129	0.129	0.155	0.155	0.139	0.132	0.123	0.123	0.112	0.112
C5	0.046	0.042	0.042	0.078	0.064	0.064	0.069	0.069	0.044	0.054	0.040	0.040	0.047	0.047
C6	0.046	0.042	0.042	0.078	0.064	0.064	0.069	0.069	0.044	0.054	0.040	0.040	0.047	0.047
CO	0.124	0.143	0.143	0.177	0.133	0.133	0.153	0.153	0.132	0.147	0.150	0.150	0.145	0.145
CO ₂	0.437	0.541	0.541	0.541	0.473	0.473	0.492	0.492	0.364	0.399	0.353	0.353	0.396	0.396
H ₂ S														
FEED AND PRODUCT WATER (WT%)														
H ₂ O IN FEED														
FEED H ₂ O LOSS G HR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H ₂ O IN PRODUCT	10.7	5.700	5.200	6.190	10.5	7.400	11.25	6.210	5.090	8.770	7.030	1.940	7.190	9.970
SOLUBLE OR SLURRY CATALYSTS (WT%)														
SOL-SLURRY CAT	1.160	1.160	1.160	1.160	1.160	2.320	0.330	0.330	0.330	0.330	0.330	0.330	1.160	1.160
ASH IN CATALYST	29	29	29	29	29	29	100	100	100	100	100	100	29	29
S IN CATALYST	12	12	12	12	12	12	5.000	5.000	5.000	5.000	5.000	5.000	12	12
PRODUCT SLURRY SOLUBILITY, WT % INSOLUBLE														
THF	5.920	6.390	6.970	6.090	5.500	6.300	5.900	6.790	5.930	5.800	5.690	5.900	4.960	4.960
TOLUENE	11.64	14.41	14.52	13.87	11.57	13.48	12.15	13.6	9.550	9.570	9.790	9.050	7.520	6.530
HEXANE	16.99	18.24	17.46	21.52	17.78	24.01	22.03	22.23	16.95	16.84	17.93	19.23	15.23	10.1
ASH	2.140	1.730	2.540	2.350	1.980	2.950	2.100	2.310	2.080	1.970	1.780	1.710	2.390	1.760
PRODUCT DISTILLED FRACTIONS, WT%														
WT% NAPHTHA	9.430	3.960	4.010	5.960	8.460	6.140	10.12	4.070	4.370	7.780	6.040	3.270	5.930	8.980
WT% DISTILLATE	12.94	13.55	14.97	15.36	15.12	14.39	13.6	15.33	14.85	14.23	14.12	15.43	11.65	10.85
WT% VACUUM DISTILLATE	35.69	36.47	33.99	36.3	35.57	34.91	34.14	34.97	38.13	36.24	39.76	39.66	40.63	39.56
WT% RESID+UNCONV COAL	39.58	43.19	45	40.16	39.06	42.58	39.66	43	40.47	38.78	39.27	40.51	39.43	38.81

TABLE A-7

Black Thunder Coal: Dispersed Iron and Molybdenum Catalysts, Elemental Analyses

SAMPLE PERIOD	-----FeSO ₄ /H ₂ O-----						-----Wender-----				Mo/Wender		FeSO ₄ /H ₂ O	
	-----800-----		-820-	-780-	-800-		-Molyvan L	-Molyvan L	-Sulfiding		-Sulfiding		Molyvan L	
	2	4	5	7	9	11	13	14	16	17	19	20	22	23
DIOXANE-FREE DISTILLATE (360-650 F), WT%														
C	86.5	.	.	84.1	.	.	86.3	.	88.2	.	85.8	86.3	.	.
H	10.2	.	.	10.5	.	.	10.1	.	10.5	.	10.3	10.4	.	.
S	0.01	.	.	0.01	.	.	0.01	.	0.01	.	0.01	0.01	.	.
O	2.88	.	.	3.21	.	.	2.74	.	2.77	.	2.60	3.32	.	.
N	0.41	.	.	0.40	.	.	0.42	.	0.46	.	0.40	0.41	.	.
TOTAL	100	.	.	98.3	.	.	99.6	.	102	.	99.1	100	.	.
DIOXANE	9.06	5.00	5.00	1.92	5.00	5.00	5.00	4.40	5.00	2.75	5.00	3.52	5.84	5.00
VACUUM DISTILLATE (650-RESID), WT%														
C	90.1	.	.	90.2	.	.	89.8	.	89.8	.	90.2	89.7	.	.
H	8.99	.	.	8.68	.	.	8.90	.	9.12	.	9.14	9.37	.	.
S	0.04	.	.	0.05	.	.	0.04	.	0.04	.	0.04	0.03	.	.
O	1.44	.	.	1.39	.	.	1.35	.	1.32	.	1.23	1.09	.	.
N	0.54	.	.	0.65	.	.	0.56	.	0.55	.	0.57	0.46	.	.
TOTAL	101	.	.	101	.	.	101	.	101	.	101	101	.	.
RESID + UNCONV COAL, WT%														
C	86.6	.	.	86.2	.	.	85.3	.	85.8	.	86.5	86.7	.	.
H	5.74	.	.	5.39	.	.	5.72	.	6.03	.	6.04	6.55	.	.
S	0.57	.	.	0.66	.	.	0.54	.	0.52	.	0.41	0.75	.	.
O (DIFFERENCE)	0.39	.	.	0.63	.	.	1.84	.	1.37	.	1.60	0.00	.	.
N	1.25	.	.	1.25	.	.	1.19	.	1.20	.	1.19	1.02	.	.
TOTAL	99.6	.	.	99.4	.	.	98.2	.	98.6	.	98.4	101	.	.
THF INSOLUBLES														
RESID THF INSOLUBLES, WT%														
ASH	.	.	.	.	.	.	.	.	.	.	.	.	.	.
K	1710	.	.	1740	.	.	2180	.	2080	.	1630	1310	.	.
SI	74E3	.	.	81E3	.	.	77E3	.	86E3	.	94E3	85E3	.	.
AL	39E3	.	.	35E3	.	.	56E3	.	36E3	.	44E3	42E3	.	.
CA	11E4	.	.	94E3	.	.	12E4	.	88E3	.	11E4	92E3	.	.
FE	13E4	.	.	13E4	.	.	12E4	.	11E4	.	10E4	14E4	.	.
MG	17E3	.	.	19E3	.	.	20E3	.	19E3	.	20E3	17E3	.	.
MO	860	.	.	1240	.	.	1730	.	1820	.	1880	1440	.	.
NA	5700	.	.	6000	.	.	6000	.	6500	.	6600	5800	.	.
NI	221	.	.	214	.	.	240	.	279	.	307	191	.	.
TI	4600	.	.	4800	.	.	4600	.	5000	.	5500	4400	.	.
V	188	.	.	193	.	.	249	.	230	.	234	197	.	.

TABLE A-8

Black Thunder Coal, Dispersed Iron and Molybdenum Catalysts, Net Yields

SAMPLE PERIOD	-----FeSO ₄ /H ₂ O-----						-----Wender-----				Mo/Wender		-FeSO ₄ /H ₂ O	
	-----800-----						-----Molyvan L-----				-Sulfiding		-Molyvan L	
	2	4	5	7	9	11	13	14	16	17	19	20	-Ill 6 Liq	22 23
HOURS ON STREAM	64.4	86.1	110	156	166	189	237	259	300	324	346	393	416	440
NET PRODUCT YIELDS (WT% MAF COAL OR EQUIVALENT)														
OILS	24	22	27.2	3.95	23.2	4.85	4.75	9.88	30.9	26.6	24.4	21.9	43.3	62.7
ASPHALTENES	11.4	4.48	1.31	18.3	14.4	30.7	29.2	22.3	18.1	18.4	21.3	27.3	9.74	-5.3
PREASPHALTENES	20.2	27.2	25.7	26.2	21.3	25.3	22.3	23	11.4	12.3	13.4	9.27	6.97	3.47
H ₂ S	0.33	.	.	0.22	.	.	.	-0.19	.	-0.11	.	0.07	0.18	.
NH ₃	0.15	.	.	0.13	.	.	.	0.20	.	0.23	.	0.30	0.14	.
CO + CO ₂	6.09	8.28	8.51	9.46	7.37	6.58	7.89	6.93	5.05	5.48	5.48	4.80	6.25	6.61
H ₂ O	20	.	.	15.3	.	.	.	15.7	.	19.5	.	18.8	19.7	.
C1 TO C3	8.38	12.1	12.4	19.2	10.8	9.62	12.1	10.6	8.82	8.87	9.59	8.40	9.61	10.2
C4 TO 360	3.27	4.10	4.21	7.12	5.28	4.72	6.05	5.32	3.84	4.09	3.74	8.10	4.05	4.29
360 TO 650	22.2	23.3	28.7	31	31.7	28.5	26.8	30.2	28.9	29.3	26.9	30.1	37.2	36.2
650 TO 935	14.3	7.35	-3.3	2.16	8.16	4.78	7.01	1.98	14.4	13.1	17.1	10.7	17.3	16.5
935 +	17	20.1	25.8	9.28	14.9	24.1	17.5	18.8	14.4	12	12.4	10.7	1.45	3.87
C4 TO 650	25.5	27.4	32.9	38.1	36.9	33.2	32.8	35.5	32.7	33.4	30.7	38.2	41.3	40.5
C4 TO 935	39.8	34.8	29.7	40.3	45.1	38	39.8	37.5	47.1	46.5	47.8	48.9	58.5	57
UNCONVERTED COAL	14.2	16.5	15.8	13	13	12.2	14.3	15.9	13.8	14.1	14.2	14.6	9.33	12.1
ASH	-1.9	-2.2	0.82	-0.1	-0.91	1.31	-0.31	-0.02	-0.76	-0.97	-1.8	-2.3	0.42	-1.7
HYDROGEN	-4.2	.	.	-5.1	.	.	.	-4.2	.	-5.4	.	-5.4	-4.6	.
PRODUCT MATERIAL BALANCES														
% OVERALL BALANCE	102	120	119	113	149	85.2	104	100	102	104	112	115	98.1	103
% ASH BALANCE	97.8	74	110	99.9	89.3	113	96.4	99.8	91.1	88.7	78.9	72.6	105	80.2
HETEROATOM REMOVAL (% OF HETEROATOMS IN FEED)														
SULFUR	24.5	.	.	16.4	.	.	.	-24	.	-14	.	8.57	12.7	.
OXYGEN	.	.	.	.	.	.	.	.	.	.	.	.	.	.
NITROGEN	3.99	.	.	3.49	.	.	.	5.37	.	6.25	.	8.00	4.63	.

TABLE A-9

Black Thunder Coal: NiMo on Hydrous Titanate, Process Conditions

	-----.1% NiMo-----				--.1% NiMo--		--.2% NiMo--	
	-----Al2O3-----				---TiO2---		---TiO2---	
SAMPLE PERIOD	2	3	4	5	7	8	10	11
HOURS ON STREAM	46.5	69.2	93	117	140	164	211	225
WT FRACTION COAL IN FEED .	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
1ST-STAGE TEMPERATURE, F .	800	800	800	800	800	800	800	800
SPACE TIME, MIN.	104	113	92.4	89.3	83.5	80.2	90.3	89.8
SEVERITY, STTUS.	35.1	38.2	31.1	30.1	28.1	27	30.4	30.3
COAL,CAT LHSV ..	.	.	.	.	.	.	.	.
SOLVENT,CAT LHSV	.	.	.	.	.	.	.	.
2ND-STAGE TEMPERATURE, F .	500	500	500	500	500	500	500	500
SPACE TIME, MIN.	104	113	92.4	89.3	83.5	80.2	90.3	89.8
SEVERITY, STTUS.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
COAL,CAT LHSV ..	.	.	.	.	.	.	.	.
SOLVENT,CAT LHSV	.	.	.	.	.	.	.	.
COMBINED SEVERITY, STTUS .	35.1	38.2	31.1	30.1	28.1	27	30.4	30.3
SYSTEM PRESSURE, PSIG	2500	2500	2500	2500	2500	2500	2500	2500
1000 SCFH H2 PER BBL FEED.	10	11.1	9.32	9.18	8.44	8.27	9.34	8.77

Powdered catalysts were added to the feed slurry at 0.1-0.2% catalyst to coal. An oil-soluble sulfiding agent, TPS-20, was also added.

TABLE A-10

Black Thunder Coal: NiMo on Hydrous Titanate, Product Analyses

	-----.1% NiMo-----				--.1% NiMo--		---.2% NiMo--	
	-----Al2O3-----				-----TiO2----		-----TiO2----	
SAMPLE PERIOD	2	3	4	5	7	8	10	11
HOURS ON STREAM	46.51	69.16	93.03	116.6	140.1	163.9	211	224.8
PRODUCT GAS ANALYSES (VOL%)								
C1	1.060	1.060	0.820	0.908	0.886	0.954	0.885	0.885
C2	0.429	0.429	0.335	0.359	0.346	0.383	0.381	0.381
C3	0.294	0.294	0.229	0.233	0.209	0.241	0.271	0.271
C4	0.177	0.177	0.151	0.138	0.213	0.156	0.159	0.159
C5	0.052	0.052	0.049	0.038	0.035	0.040	0.079	0.079
C6	0.052	0.052	0.049	0.038	0.035	0.040	0.079	0.079
CO	0.111	0.111	0.091	0.090	0.081	0.099	0.078	0.078
CO2	0.319	0.319	0.272	0.182	0.147	0.354	0.143	0.143
H2S	.	.	.	.	.	.	.	.
FEED AND PRODUCT WATER (WT%)								
H2O IN FEED	.	.	.	.	.	.	.	.
FEED H2O LOSS G HR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H2O IN PRODUCT	3.780	3.170	2.440	1.470	2.770	1.410	1.350	2.140
SOLUBLE OR SLURRY CATALYSTS (WT%)								
SOL-SLURRY CAT	0.100	0.100	0.100	0.100	0.100	0.100	0.200	0.200
ASH IN CATALYST	100	100	100	100	100	100	100	100
S IN CATALYST	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PRODUCT SLURRY SOLUBILITY, WT % INSOLUBLE								
THF	6.330	6.070	6.400	6.470	6.560	6.130	6.550	6.640
TOLUENE	11.14	10.28	11.54	12.29	12.59	12.67	12.96	12.45
HEXANE	14.23	16.77	14.49	14.48	13.97	15.61	15.28	14.95
ASH	3.450	3.600	3.530	3.530	3.740	3.740	3.860	3.780
PRODUCT DISTILLED FRACTIONS, WT%								
WT% NAPHTHA	4.370	1.980	2.600	1.070	1.230	0.950	1.780	2.020
WT% DISTILLATE	10.5	11.32	11.76	9.840	10.89	10.1	10.01	9.300
WT% VACUUM DISTILLATE	42.62	42.89	34.61	42.63	40.16	42.11	43.51	40.04
WT% RESID+UNCONV COAL	40.55	42.51	50.68	43.54	45.19	45.58	43.79	46.45

TABLE A-11

Black Thunder Coal: NiMo on Hydrous Titanate, Elemental Analyses

	-----.1% NiMo-----			-.1% NiMo-			-.2% NiMo-		
	-----Al2O3-----			---TiO2---			---TiO2---		
SAMPLE PERIOD	2	3	4	5	7	8	10	11	
DIOXANE-FREE DISTILLATE (360-650 F), WT%									
C				86.1		86.9	85.2		
H				10.4		10.4	10.3		
S				0.01		0.01	0.01		
O				2.83		2.79	3.18		
N				0.57		0.58	0.55		
TOTAL				99.9		101	99.2		
DIOXANE.....				8.90		7.80	5.70		
VACUUM DISTILLATE (650-RESID), WT%									
C				88.9		88.8	89.5		
H				9.04		9.16	9.27		
S				0.12		0.15	0.13		
O				1.17		1.10	1.10		
N				0.54		0.54	0.53		
TOTAL				99.8		99.7	101		
RESID + UNCONV COAL, WT%									
C				81.7		81.7	80.3		
H				6.12		6.20	6.10		
S				1.01		1.10	1.14		
O (DIFFERENCE)				1.82		1.55	2.36		
N				1.27		1.26	1.25		
TOTAL				98.2		98.4	97.6		
THF INSOLUBLES.....									
RESID THF INSOLUBLES, WT%									
ASH									
K				11E3		12E3	11E3		
SI				18E4		18E4	18E4		
AL				49E3		81E3	44E3		
CA				6800		34E3	3180		
FE				13E4		13E4	12E4		
MG				3100		4900	750		
MO				830		750	1260		
NA				5500		6000	4600		
NI				279		314	520		
TI				2990		4300	7800		
V				162		159	158		

TABLE A-12

Black Thunder Coal: NiMo on Hydrous Titanate, Product Yields

	-----.1% NiMo-----				-.1% NiMo-		-.2% NiMo-		
	-----Al2O3-----				---TiO2---		---TiO2---		
SAMPLE PERIOD	2	3	4	5	7	8	10	11	
HOURS ON STREAM	46.5	69.2	93	117	140	164	211	225	
NET PRODUCT YIELDS (WT% MAF COAL OR EQUIVALENT)									
OILS.....	58.7	50.7	61.8	63.8	65.4	60.6	62.4	61.1	
ASPHALTENES.....	-6	4.65	-6.4	-8.9	-12	-6.5	-8.5	-7.9	
PREASPHALTENES.....	13.5	11.2	14.6	16.7	17.4	19.1	18.6	16.7	
H2S	.	.	.	2.85	.	2.61	2.64	.	
NH3	.	.	.	0.16	.	0.12	0.23	.	
CO + CO2.....	4.96	5.49	3.89	2.78	2.12	4.37	2.28	2.14	
H2O	.	.	.	6.69	.	6.11	7.30	.	
C1 TO C3	12.4	13.7	8.91	9.38	8.19	8.89	10.1	9.47	
C4 TO 360	7.27	5.92	4.95	3.70	4.34	3.66	7.24	5.48	
360 TO 650	28.2	29.9	32	25.8	29.2	26.9	27.3	24.5	
650 TO 935	25.8	21.3	-5	28.4	19	21.1	23.7	17.2	
935 +	4.93	9.38	38	13.7	18.6	21.4	14.2	22.6	
C4 TO 650	35.5	35.8	37	29.5	33.5	30.6	34.6	29.9	
C4 TO 935	61.3	57.1	32	57.9	52.5	51.7	58.3	47.2	
UNCONVERTED COAL	9.13	7.60	9.11	9.28	8.88	7.49	8.46	9.02	
ASH	-1.3	-1	-.98	-1.1	-.38	-.37	-.33	-.59	
HYDROGEN	.	.	.	-2.8	.	-2.7	-3.6	.	
PRODUCT MATERIAL BALANCES									
% OVERALL BALANCE.....	105	105	102	107	106	97.9	108	106	
% ASH BALANCE	89.9	91.6	92.2	91.6	96.9	97	97.4	95.4	
HETEROATOM REMOVAL (% OF HETEROATOMS IN FEED)									
SULFUR	.	.	.	62.4	.	57	57.8	.	
OXYGEN	.	.	.	.	.	.	.	.	
NITROGEN	.	.	.	4.59	.	3.50	6.58	.	