We have no objection from a patent
standpoint to the publication or
dissemination of this material.

Mark P. Dwyer Feb 20, 1995
Office of Intellectual Date
Property Counsel
DOE Field Office, Chicago

ADVANCED LIQUEFACTION USING COAL SWELLING
AND CATALYST DISPERSION TECHNIQUES

Final Technical Report
for
October 1, 1991-September 30, 1994

Project Manager:
D. C. Cronauer 10/1/91-12/31/93
R. L. Ollendorff 1/1/94-9/30/94

Principal Investigators:
C. W. Curtis, Auburn University
C. Gutterman, FWDC
S. Chander, Pennsylvania State University

Work Performed Under Contract No. DE-AC22-91PC91051

For

U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By

Amoco Oil Company
Research and Development Department
Post Office Box 3011
Naperville, IL 60566

MASTER

DISCLAIMER

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

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	6
SUMMARY OF RESULTS AND ACTIVITY	10
PROJECT DOCUMENTATION	11
TASK 1.0: LABORATORY-SCALE EXPERIMENTATION	11
Subtask 1.1: Laboratory Support	11
TASK 2.0: LABORATORY-SCALE OPERATION	11
Subtask 2.1: Coal Pretreatment	11
Subtask 2.2: Catalyst and Swelling Studies	16
Subtask 2.3: Reactivity of Swelled Coals with Dispersed Catalysts	43
Subtask 2.4: Bench-Scale Studies	82
Subtask 2.5: Solids Separation/Alternative Bottoms Processing	104
TASK 3.0 TECHNICAL ASSESSMENT	125
CONCLUSIONS AND FUTURE WORK	144
ACKNOWLEDGMENTS	147
REFERENCES	148
FIGURES	152
TABLES	263

EXECUTIVE SUMMARY

The overall objective of this project was to develop a new approach for the direct liquefaction of coal to produce an all-distillate product slate at a sizable cost reduction over current technology. The approach integrated coal selection, pretreatment, coal swelling with catalyst impregnation, liquefaction, product recovery with characterization, alternate bottoms processing, and a technical assessment including an economic evaluation. The project was carried out under contract to the United States Department of Energy. The primary contractor was Amoco Oil Company (Amoco Corporation), and the subcontractors were Foster Wheeler Development Company, Auburn University, Pennsylvania State University, and Hazen Research, Inc.

Heterofunctional solvents were the most effective in swelling coals. Also solvent blends such as isopropanol/water were more effective than pure solvents alone. Impregnating slurry catalysts simultaneously during coal swelling showed that better uptake was achieved with nonswelling solvent and higher impregnation temperature.

Some enhancement in initial coal conversion was seen liquefying SO₂-treated Black Thunder coal with slurry catalysts, and also when hydrogen donor liquefaction solvents were used. Noncatalytic reactions showed no benefit from SO₂ treatment. Coupling coal swelling and SO₂ treatment with slurry catalysts was also not beneficial, although high conversion was seen with continuous operation and long residence time, however, similar high conversion was observed with untreated coal. Long term deactivation experiments using SO₂-treated coal and supported AMOCAT™ 1C catalyst indicated higher initial activity but also increased deactivation compared to untreated coal. SO₂ treatment is not economically attractive unless it provides about 17% increase in coal reactivity.

Simultaneous coal swelling and catalyst impregnation was detrimental to both coal and pyrene conversion. Minimal contact between the swelling solvent and the catalyst i.e. direct catalyst addition to the reactor was most beneficial. Swelling or simultaneous impregnation/swelling did not improve the conversion for Illinois NO. 6 coal either.

In most cases, the best results were obtained when the coal was untreated and the slurry catalyst was added directly into the reactor.

Foster Wheeler's ASCOT process had better average liquid yields than either Wilsonville's vacuum tower/ROSE combination or delayed coking process. This liquid product also had good quality.

The economic comparison of delayed coker and ASCOT processes indicated that the calculated crude oil equivalent (COE) cost for delayed coker was \$33.50/bbl, which is \$0.75/bbl above the low rank coal baseline case. COE for ASCOT process was \$32.50/bbl, which is \$0.25/bbl below the baseline case.

PROGRAM OBJECTIVES

The objective of this project was to develop a new approach to the direct liquefaction of coal to generate an all-distillate product slate at a sizable cost reduction over current technology. The approach integrates all aspects of the coal liquefaction process, including coal selection, pretreatment, coal swelling with catalyst impregnation (and parallel runs with dispersed catalyst); coal liquefaction experimentation including solvent evaluation, product recovery with characterization, alternate bottoms processing, and a technical assessment including an economic evaluation. The three tasks of this program were:

1. Task 1: Laboratory-Scale Experimentation--The goals were to obtain samples of coals and Wilsonville-derived solvents and vacuum tower bottoms and to establish experimental procedures.
2. Task 2: Laboratory-Scale Operation--The goals were to (1) reduce the concentration of mineral matter and alkali metals in low rank coals, (2) swell and impregnate coals with dispersed catalysts, (3) characterize the resulting catalyst solids, (4) evaluate the effectiveness of the procedures using liquefaction runs, and (5) study solids separation and alternative bottoms handling, which included observing pumping characteristics, deasphalting, and coking.
3. Task 3: Technical Assessment--The goals were to analyze the data, develop descriptive models, and carry out an economic evaluation.

The research was carried out in cooperation with the following subcontractors: Foster Wheeler Development Corporation (FWDC), Auburn University (AU), Pennsylvania State University (PSU), and Hazen Research Inc. Argonne National Laboratory and the University of Wyoming had small subcontracts.

PROGRAM MILESTONES

The first milestone was to obtain the appropriate feed stocks for the experiments, and the second to prepare the beneficiated bulk samples of coal for subsequent experiments. Both the laboratory-scale coal swelling and catalyst screening program and the bench-scale liquefaction experiments with Black Thunder coal were carried out. The batch deasphalting experiments and delayed coking experiments were completed and the economic analysis was carried out. The program had extensions due to the delay in the approval for start-up; thus the final completion date was September 30, 1994.

SUMMARY OF RESULTS AND ACTIVITY

The objective of this project was to develop a new approach for the direct liquefaction of coal to produce an all-distillate product slate at a sizable cost reduction over current technology. All aspects of the process were included with emphasis upon coal pretreatment, coal swelling with catalyst impregnation, and alternate bottoms processing. Research was carried at Amoco Oil Company, Foster Wheeler Development Company, Auburn University, Pennsylvania State University, Hazen Research, Inc. The University of Wyoming and Argonne National Laboratories carried out small subcontracts.

The overall summary of results is provided in the executive summary.

DISCUSSION OF RESULTS AND ACTIVITIES BY TASK

Project Documentation

The Milestone Schedule and Budget were modified as needed throughout the contract period.

Task 1.0: Laboratory-Scale Experimentation

Subtask 1.1: Laboratory Support

Fresh, bulk samples of Black Thunder subbituminous coal and Martin Lake were received and analyzed by Commercial Testing Laboratories, Inc. These analyses are in Appendix A. Sufficient quantities of coal-derived liquids (atmospheric tower bottoms and solvent) were obtained from Wilsonville. The atmospheric tower bottoms derived from the liquefaction of Black Thunder coal were sent to Foster Wheeler Development Corporation (FWDC) for their experimentation.

Task 2.0: Laboratory-Scale Operation

Subtask 2.1: Coal Pretreatment

Initial Coal Preparation at Hazen Research, Inc.:

Bulk samples of Martin Lake lignite and Black Thunder subbituminous coal (two and three 55-gallon drums, respectively) were pretreated at Hazen Research, Inc.. for subsequent swelling, catalyst impregnation, and liquefaction studies. The treatment included crushing, sizing, SO₂-treatment to remove alkali and alkaline metals, and gravity separation to recover a fraction with low ash content.

The samples were first crushed to pass 8 mesh, and wet screened twice to 65 mesh to recover 8x65 and minus 65 mesh fractions. Bulk samples of the 8x65 mesh material were contacted with concentrated aqueous sulfurous acid up to five hours. The contact time included sparging of gaseous SO_2 into the coal/water mixture and subsequent mixing for one hour. The coal was then screened and immediately flushed with water, followed with a second slurrying in fresh water and another screening. Figure 1 shows a schematic of the SO_2 -treating process.

The SO_2 -treated samples were subjected to heavy media (finely dispersed magnetite) cyclone tests, but it was not possible to isolate an overhead (float) fraction having a coal recovery of 80%. Therefore, the bulk samples of raw and SO_2 -treated were characterized and used as prepared.

Additionally, Hazen Research, Inc., and Standard Laboratories Inc. performed laboratory-scale "washability" experiments with SO_2 -treated coal using heavy chlorinated solvents for gravity separation. Although high recovery (>90%) and low ash content (2.2%) could have been obtained in the separation, the coals swelled in the solvents. While this was interesting, it was not likely to lead to a commercial beneficiation process.

Beneficiation Studies at Pennsylvania State University:

Research at Pennsylvania State University was directed toward beneficiating coal by a combination of chemical treatment and physical separation. SO_2 -treated samples of Black Thunder coal (prepared at Hazen Research, Inc.) and Martin Lake lignite were used.

Flotation/Agglomeration Experiments with Black Thunder coal:

A method was developed for producing a clean low ash (2%) SO₂-treated Black Thunder coal, which involved flotation/agglomeration and is described below:

Grinding: To obtain liberation of the ash-forming minerals, it was necessary to micronize coal. When grinding was done in a laboratory ball mill with steel media, an increase in the ash content of the material was observed due to contamination from the grinding mill and media. In the laboratory tests contamination was decreased by grinding coal in an agate planetary mill and media. The agate mill was relatively inefficient, and it was necessary to use long grinding times. Alternate grinding procedures and mills should be considered for larger scale tests.

Spherical Agglomeration: The recovery of coal was substantially increased when the coal was agglomerated with oil prior to flotation (from 14.7% without agglomeration to 82.0% with agglomeration). The desired amount of oil and the surfactant, when used, were mixed with the coal slurry in a blender. The surfactant used in this series of tests was a block co-polymer, designated as BCl, obtained from BASF Corporation (Pluronic 25R1).

Flotation: The agglomerated slurry from the blender was transferred to a flotation cell, and it was diluted with an equal amount of water. The clean coal was floated for predetermined times. The froth products were filtered, dried, weighed and analyzed.

Effect of Grinding Time: Spherical agglomeration followed by flotation was carried out on three samples of different sizes produced by varying the grinding time (10, 20 and 40 minutes). The amounts of material passing 400 mesh increased with longer grinding time. The results are given in Tables 1-3. The sample ground for 40 minutes had an ash content

of 2.10% and a combustible matter recovery (CMR) of 93.7%. The lack of improvement in the product quality for other two samples suggests poor liberation and a necessity of further grinding.

Effect of Solids Concentration: Four different solids concentrations, namely 1.25%, 2.5%, 5.0% and 10%, were investigated using the sample with 95% passing 400 mesh. The results are given in Tables 4, 3, 5, and 6, respectively. Solid concentrations were based on the amount of solids in a slurry of 500 ml in the blender. Based on 4 minutes of flotation, selectivity for ash removal decreased with increasing concentration of solids. A clean coal product with an ash content of 1.85% ash with a CMR of 84.5% was obtained for a solids concentration of 1.25%.

Effect of Oil and Surfactant Concentration: The amount of oil was varied (1125 μ l, 2250 μ l, 4500 μ l and 9000 μ l), while keeping the surfactant to oil ratio the same at 1 to 10 (Tables 7-10). A solids concentration was 1.25% and the feed size 96% passing 400 mesh for these tests. For 1125 μ l oil amount, both selectivity and the CMR were low, at 2.49% and 75%, respectively. Oil levels of 2250 μ l and higher produced better products with ash contents between 1.96 and 1.99% and with CMR's between about 87 and 91%.

Effect of Addition of Dispersant: A dispersant, sodium hexametaphosphate (calgon), was added in varying amounts during the grinding stage in order to increase selectivity. The amount of calgon was varied from 0, 20, 100, 500 and 2000 mg per 100 grams of coal for these tests. The coal feed size was 96% passing 400 mesh and the solids concentration was 2.5%. The results are given in Tables, 3, 11, 12, 13, and 14 respectively. The addition of calgon resulted in a small increase in selectivity, while CMR was comparable except for 100 mg case.

Effect of Ultrasonic Treatment: The effect of varying the length of ultrasonic treatment on the product quality was investigated. The results

for 0, 4, 10, 30 and 60 minutes are given in Tables 15, 16, 17, 3, and 18. A solids concentration of 2.5% was used. The coal feed size was 96% passing 400 mesh. The results show no significant benefits from the ultrasonic treatment.

Summary and Recommendations from the Flotation/Agglomeration Experiments:

The effect of operating variables such as grinding time, solids concentration, oil and surfactant concentration, chemical and mechanical dispersion was investigated. It was discovered that the sample had to be ground to pass 400 mesh for adequate mineral liberation. At such fine sizes flotation alone did not work satisfactorily, and it was necessary to use selective agglomeration prior to flotation. A solids concentration of 2.5% was found to be optimum from the current studies. It was observed that neither mechanical nor chemical dispersion helped significantly, most probably due to the fact that the strong agitation in the blender helped dispersion of the ash material while agglomerating the coal. A clean coal product with an ash content of about 2.0% with a CMR of about 90% could most likely be produced in commercial equipment.

Advanced Beneficiation Experiments with Martin Lake Lignite:

SO₂-treated Martin Lake lignite was beneficiated using agglomeration and froth flotation techniques. The as-received 8x60 mesh SO₂-treated lignite with 6% ash content was wet-ground in a planetary mill. Three feed size ranges were separated and subjected to flotation with dodecane and methyl-iso-butyl carbinol (MIBC) as the collector and frother, respectively. The combustible matter recovery (CMR) increased with an increase in dodecane concentration. The ash content decreased, except for the very fine coal particles. This decrease in separation quality was not surprising because of the decrease in flotation selectivity at very fine particle sizes. Although pre-emulsification of dodecane appreciably increased CMR, ash rejection was not affected.

The use of a block copolymer of ethylene and propylene oxide, which was effective flotation promoter for the raw lignite, increased CMR and decreased ash content (compared to dodecane alone) also for the SO₂-treated lignite. An advanced flotation technique, where the fine feed particles were mildly agglomerated prior to flotation was also done and resulted in substantial increase in ash rejection. With the advanced beneficiation technique, a clean 60 µm, 4% ash containing coal product with 90% CMR was obtained. Further improvement may be possible by optimizing the amounts of collector and flotation promoter (surfactant). The full report from Pennsylvania State University is in Appendix B.

Subtask 2.2: Catalyst and Swelling Studies

Coal Swelling Background:

The literature concerning coal swelling, both alone and in combination with coal liquefaction was updated and is summarized below. The detailed literature review is in Appendix C.

The proposal of van Krevelen that coals are three-dimensionally cross-linked macromolecular networks is generally being accepted. When brought into contact with most organic solvents, coals absorb the solvent and swell. The amount of swelling depends on both the coal and the solvent. The two factors which control the amount of swelling are the magnitude of the solvent-coal interactions and the cross-link density of the coal. Expressions have been derived to describe these terms. In addition, coals can behave as either a glass or rubber with a transition zone. In a glassy state, the macromolecular chains are constrained and diffusion through the coal matrix is quite slow. For reference, as-mined coals exhibit glass-like properties. In the rubbery state, the macromolecular chains can move relatively freely, and diffusion rates in the solid approach those in liquids. Some solvents can cause a glass-to-rubber transition to occur in coals.

Coal swelling solvents can be divided into two classes: non-hydrogen bonding and hydrogen bonding. The swelling ratios of the coal samples in non-hydrogen bonding solvents are significantly less than those in hydrogen bonding solvents. The most effective solvents are those containing a nitrogen or oxygen atom possessing an unshared pair of electrons.

The swelling data are consistent with a covalent cross-linked structure of coal. This is supported by the high swelling observed in hydrogen bonding solvents. The strong hydrogen bonding solvents replace the coal-coal hydrogen bonds with new coal-solvent hydrogen bonds. If the coal-coal hydrogen bonds are active cross-links, the replacement would result in a lower cross-link density which would cause swelling to increase. The weak hydrogen bonding solvents result in less swelling since more coal-coal hydrogen bonds remain intact. The decrease in swelling in high carbon content coals could be attributed to possible physical stacking interactions between polynuclear aromatics (PNA's) in the coal structure, although there is no supporting evidence in the literature. These interactions will not be easily altered by materials which are liquids.

The best correlation between the extent of swelling and coal rank is that derived from experimentation with pyridine. A relatively constant swelling ratio was observed in pyridine for coal samples with carbon contents of 65% to 85%. A dramatic decrease in the swelling ratio was observed above 86% carbon content.

It appears that swelling coal in suitable solvents prior to liquefaction could improve conversion and product quality. This has been demonstrated, and the application of this technique in combination with catalyst impregnation in coal liquefaction should decrease the costs of commercial liquefaction.

Coal Swelling Experimental Procedure:

Swelling experiments were made using the following three coal samples that were prepared in a previous DOE project: (1) Martin Lake lignite, (2) Black Thunder subbituminous, raw and SO₂-treated, and (3) Illinois No. 6 bituminous coals. The coals were handled in nitrogen whenever possible. These samples were sieved and ground to -325 mesh under nitrogen and dried overnight in a vacuum oven. Following these runs, experiments were carried out using coarse (8 x 60 mesh) samples of raw and SO₂-treated Black Thunder coal that had only been partially dried to about 8 wt% moisture content at ambient temperature in nitrogen.

The experimental swelling procedure for the first set of samples consisted of placing samples of dry coal in a 1 mm. o.d. tube followed by centrifuging for 60 minutes. The height of the coal was measured as h_1 . After breaking up the column of packed coal, solvent in excess was introduced and the tube was vigorously shaken to ensure thorough mixing. The slurry was centrifuged after specified times and the height was measured as h_2 . The swelling ratio was defined as the ratio of the resulting heights of swelled and raw coal ($Q = h_2/h_1$). In the experiments with the coarse coal samples, 10 ml conical centrifuge tubes were used.

Coal Swelling Results:

First Experiments: Initial experiments were made with ten swelling solvents ranging from hydrocarbon solvents to polar liquids. The results in Figure 2 show that hydrocarbon solvents such as hexane do not generally swell coals. Acetone and alcohols cause some swelling but tetrahydrofuran (THF) and tetrabutylammonium hydroxide (TBAH) are effective for swelling. As seen in Figures 2 and 3, TBAH is the best swelling solvent for all three coals; however, for TBAH, swelling decreases with increasing coal rank.

Reproducibility: During the series of swelling experiments, runs were made to determine reproducibility; in addition, two laboratory technicians ran parallel tests. The results are given in Tables 19 and 20. In summary, reproducibility was good. At low swelling ratios, such as those of the methanol runs (average Q of 1.28), the standard deviation averaged about ± 0.06 . At high swelling ratios (tetrabutyl ammonium hydroxide, Q averaging about 2.5), the standard deviation averaged about ± 0.14 .

Effect of Solvent Type: The swelling ratios were determined with a wide variety of solvents using the finely pulverized (through 325 mesh) samples of Black Thunder subbituminous, Illinois No. 6 bituminous, and Martin Lake lignite. The results are given in Table 21. Subsequent experiments were carried out using 8X60 mesh size fractions of raw and SO_2 -treated Black Thunder coal (Table 22).

Overall, results obtained in these experiments were comparable to the initial ones. Only marginal levels of coal swelling were observed for the hydrocarbon solvents. This included hexane, cyclohexane, single-ring aromatics, and tetralin, which is a hydroaromatic hydrogen-donor solvent often used in coal liquefaction experiments.

As shown in Table 21, swelling increased with the introduction of hetero-functionality. Equilibrium (96 hour contact) swelling ratios of the three coals with alcohols and ketones fell in the range of 1.15 to 1.4. There appeared to be no consistent effect of the type (molecular weight) of alcohol or ketone, but the Black Thunder coal swelled to a greater extent than the other coals. Cresol was a more effective swelling agent than the above oxygenates in the case of Illinois No. 6 coal, but it was the same for the other coals. The results with methyl acetate were the same as those of the above oxygenates. Tetrahydrofuran (THF) was a more effective coal swelling solvent than the other oxygenates. The Q ratios ranged from 1.38 to 1.63.

The nitrogen-containing compounds varied greatly in their effectiveness to swell these coals. The highly polar compound TBAH, was very effective with a range of Q ratios of 2.18 to 2.66. Aniline was quite effective for Illinois No. 6 and Black Thunder coals (1.94 and 1.64, respectively), but it was essentially ineffective (1.19) for Martin Lake lignite. Nitrobenzene was poor for all three coals (1.11 to 1.19).

Dimethylsulfoxide was tested due to its unusual solvent properties in other systems. It was found to be particularly effective for the Black Thunder and Illinois No. 6 coals and moderately effective for Martin Lake lignite (2.39, 2.15, and 1.63, respectively).

The results of coal swelling experiments carried out with 8X60 mesh size fractions of both raw and SO₂-treated Black Thunder coal are given in Table IV. There appeared to be little or no effect of coal particle size upon the swelling ratio. However, the SO₂-treated coal swelling was significantly greater than that of the raw coal. As anticipated, the removal of alkali and alkaline earth ions from the subbituminous coal reduced the interaction of coal species with each other (particularly in the case of divalent metal ions).

Summary: The above differences in swelling are attributed to the interaction of the solvent with the various bonds present in coal. The low rank coals contain significant amounts of ionic and hydrogen bonds due to the presence of a relatively large number of polar functional groups, while the high rank coals contain more charge transfer complexes because of their higher aromatic content. TBAH, which is a highly basic solvent, interacts with the ionic and hydrogen bonds readily, thus swelling the Martin Lake lignite to the greatest extent. This is followed by Black Thunder coal and Illinois No. 6. On the other hand, THF disrupts charge transfer complexes, which are predominant in Illinois No. 6, a higher rank coal, thus resulting in a swelling trend opposite to that of TBAH. The increase of swelling ratio in the case of SO₂ treatment is an obvious

extension of this theory, especially with the removal of divalent metal ions, such as calcium.

As shown in Figure 4, an attempt was made to correlate coal swelling with solvent dipole moment (polarity). While coal swelling generally increased with increasing solvent dipole moment, the correlation was poor.

Effect of Solvent Blends: The results of the initial coal swelling experiments made with 325 mesh coal samples and blends of tetralin (TET) and isopropanol (IPA) are shown in Table 21 and Figure 5. There was a high level of synergism with an advantage of using these blends over the pure solvents. In all cases, the swelling ratios were much greater than those derived from a linear correlation between the pure solvents. The largest effects were observed for the experiments made with Black Thunder and Illinois No. 6 coals.

As shown in Figures 6 through 8, the synergism of coal swelling solvents also was demonstrated for the following systems: tetrahydrofuran/water, methanol/water, dimethyl sulfoxide/tetralin, methanol/tetralin, and isopropanol/water.

Experimentation was also carried out with the 8X60 mesh fractions of raw and SO₂-treated Black Thunder coal, as given in Table 22. Again, there were high levels of synergism of solvent blends with both samples of coal.

In summary, there is a distinct advantage of using solvent blends to swell coal. This is of particular importance, because relatively low levels of swelling agent would be needed to be effective in treating coal feed slurries for the liquefaction plant.

Rate of Coal Swelling: As shown in Figure 9, finely pulverized (through 325 mesh) Black Thunder coal quickly reaches its equilibrium level of swelling within about 4 hours.

Literature and Patent Literature Review of the Use of Dispersed Catalysts in Coal Liquefaction:

Review was done covering a literature and patent survey on the use of dispersed or unsupported catalysts in coal liquefaction. It updates previous reviews, such as those of Derbyshire (1988),⁽¹⁾ Charcosset and Genard (1987),⁽²⁾ and Narain et al. (1987),⁽³⁾ with recent developments in process and fundamental studies, particularly in catalyst dispersion methods and characterization of catalyst activity. It was conducted to provide leads on effective dispersion techniques and catalytic components and to identify an effective dispersed catalyst process for subbituminous coal and lignite. The complete review, including the above cited references, is included in the Appendix D, and the Summary, Conclusions, and Recommendations are given below.

Summary:

Sulfides of Mo, Co, W, and Fe have been identified as active catalysts since the pre-World War II development of coal liquefaction, and investigations, particularly of Fe and Mo catalysts, continue. In spite of recent progress in analytical techniques that have allowed better characterization, much remains to be understood of the basis and origin of catalyst activity. The degree of dispersion and catalyst active form largely affect catalyst activity; these factors are, in turn, determined by the nature of the catalyst precursor, the mode of catalyst addition or impregnation, and the catalyst activation conditions for a given set of liquefaction conditions.

The catalyst active form has generally been deduced from characterization of the catalyst after liquefaction. In general, when sufficient sulfur is present (either as added sulfur compounds or as coal sulfur), the catalyst is largely present in the sulfide form. When insufficient or no sulfur is present, the catalyst is in a reduced form (such as the metal or carbide)

of the precursor. The general consensus appears to be that the non-stoichiometric sulfide pyrrhotite (Fe_{1-x}S) is the active form for Fe; recent studies suggest that a similar non-stoichiometric sulfide may be the active form for Mo. In addition to acting as sulfiding agents for the formation of the active sulfide form of the catalyst precursor, added sulfur compounds can enhance liquefaction performance by any of all of the following: (1) they may act as free radical initiators, (2) they may alleviate catalyst poisoning (e.g., by nitrogen), and (3) they help maintain the catalyst in the active form by preventing reoxidation of the catalyst, particularly with high-moisture coals.

The degree of catalyst dispersion has generally been inferred from liquefaction performance. Catalyst powders enhance coal conversion over thermal liquefaction, provided the catalyst is activated and is finely dispersed. Soluble precursors give better liquefaction performance (in terms of coal conversion and oil yield) than thermal liquefaction, and their effectiveness depends on the quality of the donor solvent, the coal type, and the catalyst activation conditions. With an effective catalyst, donor solvent may not be necessary. The dependence on coal type relates to surface properties that affect wettability and dispersability. For example, iron precursors may be better dispersed on low rank coals which contain surface functional groups with which the iron may interact. In general, catalyst powders are less effective than soluble or impregnated precursors. An exception may be very fine (nanometer-sized) catalysts generated from microemulsion-based techniques or aerosol precursors produced from laser pyrolysis or flame processes.

Recent research efforts have focused on catalysis by Fe and Mo. Oil-soluble Molyvan additives, organometallic precursors (such as naphthenates, carbonyls, and molybdic acid), and various molybdates have been demonstrated as effective Mo catalyst precursors, for low and high rank coals. Compared with Fe, Mo has better hydrogenation activity; however, the higher cost of Mo has motivated development of low-Mo

catalysts, such as disposable Fe catalysts promoted by low amounts of Mo. The low activity of Fe catalysts can also be improved by increasing surface area and by sulfation; the latter can also inhibit sintering or agglomeration, thus leading to better catalyst activity maintenance. These enhancements may make Fe catalysts attractive for liquefaction of low rank coals onto which they may be more easily and better dispersed, compared with higher rank coals.

Recommended areas for further research on the development of improved catalysts include (1) dispersion methods combining coal pretreatment with soluble catalysts, such as simultaneous coal swelling and catalyst introduction, (2) Molyvan additives as dispersed catalysts, particularly determination of catalyst active form, activation conditions, and catalyst mechanism, including the role of the phosphorus in the additive, (3) multicomponent catalysts, particularly on fundamentals of catalysis mechanism and metal interaction(s) and on combinations other than Fe + Mo, (4) treatment of dispersed catalysts, such as sulfation, to produce catalysts with higher activity and better activity maintenance, and (5) methods of catalyst recovery.

Conclusions and Recommendations:

(References cited are from Appendix D)

1. On factors affecting dispersed catalyst activity:

- The degree of dispersion and catalyst active form largely affects catalyst activity. These factors are in turn determined by the nature of the catalyst precursor, the mode of catalyst addition or impregnation, and the catalyst activation conditions for a given set of liquefaction conditions. For example, at temperatures $> 275^{\circ}\text{C}$, Mo-based catalysts from soluble precursors⁽³⁴⁾ and from FeOOH ^(34a) appear to be activated, whereas

activation of MoS_2 fine powder occurs at temperatures above 325°C .

- The active form of the catalyst has generally been deduced from characterization of the catalyst after liquefaction. This assumes that the catalyst form remains unchanged between liquefaction and the characterization. In general, when sufficient sulfur is present (either as added sulfur compounds or as coal sulfur), the catalyst is in the sulfide form. When insufficient or no sulfur is present, the catalyst is largely present as a reduced form of the precursor (e.g., metal, carbide).
- The addition of sulfur compounds during liquefaction has generally resulted in enhanced liquefaction performance. This has been attributed to various reasons: (1) they act as sulfiding agents for the formation of the active sulfide form of the catalyst precursor, (2) they may act as free radical initiators, (3) they may alleviate nitrogen poisoning of the catalyst, and (4) they help maintain the catalyst in the active form by preventing reoxidation of the catalyst (particularly with high-moisture coals).
- Better dispersed catalyst activity maintenance has been achieved in the following research areas: (1) sulfation, which can inhibit sintering or agglomeration of dispersed catalysts, which are generally less stable than supported catalysts with respect to sintering, (2) use of oil-soluble Molyvan additives which can reduce coke formation, and (3) use of phosphorus promotion with Mo-based catalysts. In the latter area, in addition to possibly preventing agglomeration of the catalyst particles, P promotion can change the acidic properties of the support (increase or

decrease, depending on the P loading and the structure of the surface phosphates).

2. On the relative performance of dispersed catalysts:

- Catalyst powders enhance coal conversion over thermal liquefaction if the catalyst is fine enough to achieve good dispersion and if the catalyst is activated at the liquefaction conditions used.
- Soluble precursors give better liquefaction performance (in terms of coal conversion and oil yield) than thermal liquefaction.
- The effectiveness of soluble precursors depends on the quality of the donor solvent (if there is any), the coal type, and the catalyst activation conditions. In general, donor solvent may be unnecessary with an effective catalyst. The dependence on coal type relates to surface properties that affect wettability and dispersability. For example, water-soluble precursors may be more effective with high-moisture coal. Iron precursors may be more dispersed on low rank coals which contain surface functional groups with which the iron may interact.
- In general, catalyst powders are less effective than soluble or impregnated precursors. An exception may be very fine (nanoscale) catalysts generated from microemulsion-based techniques or aerosol precursors produced with flame processes.

3. On catalysis by Mo and Fe:

- Mo-based catalysts have been regarded as providing a source of H atoms which induce cleavage and stabilize radicals.

- Oil-soluble additives (such as Molyvan additives), organometallic precursors (such as naphthenates and carbonyls of Mo), and various molybdates have been demonstrated as effective Mo catalyst precursors, for low and high rank coals.
 - The mechanism for Fe catalysis appears to depend on residence time. At short residence time, Fe catalysts reduce coal conversion due to the slowing of coal radical propagation. However, at longer residence times, Fe catalysts can accelerate both direct hydrogenation and reactions involving H-transfer from the donor solvent.
 - The low activity of Fe catalysts can be improved by increasing surface area, sulfation, and/or promotion with low concentrations of other metals (such as Mo). These enhancements may make Fe catalysts attractive for liquefaction of low rank coal whose higher concentration (compared with high rank coals) of surface functional groups may provide greater interaction with the Fe, thereby leading to more facile and greater dispersion.
 - Compared with Fe, Mo has better hydrogenation activity; however, the higher cost of Mo has motivated development of low-Mo catalysts, such as Fe-based disposable catalysts promoted by low amounts of Mo.
4. Recommended areas of research for the development of improved catalysts:
- Combination of coal pretreatment with soluble precursor for catalyst dispersion: In particular, the impregnation of the catalyst precursor onto the coal with swelling solvents appears promising, based on the limited information in the open

literature and preliminary results obtained to date in this DOE contract. The use of blends of swelling solvents to simultaneously swell the coal and introduce the catalyst precursor into the (swollen) coal may prove to be effective. Investigations with both oil- and water-soluble precursors in compatible swelling solvents are recommended with coals of varying moisture contents.

- Oil-soluble Molyvan additives as dispersed catalysts: Process conditions for liquefaction with these additives, which have been demonstrated to be effective for both bituminous (Illinois No. 6) and subbituminous (Black Thunder) coals, need to be optimized. Other recommended areas of research are catalyst active form, activation conditions, and catalysis mechanism, including the role (if any) of the phosphorus in the additive.
- Multicomponent catalysts, particularly on fundamentals of catalysis mechanism and metal interaction(s): Since Derbyshire's 1988 review,⁽¹⁾ where further work with multicomponent catalysts was recommended, numerous investigations have been conducted, primarily with Fe + Mo catalysts. Promotional or synergistic benefits (with respect to coal conversion, oil yield, or sulfur removal, for example) have been reported with Fe + Mo. The combination of hydrocracking and hydrogenation functionalities in one catalyst using combinations other than Fe + Mo can provide opportunities to tailor other catalysts with enhanced liquefaction performance. Although numerous other metal combinations have been claimed in the patent literature, very little is known about the catalyst mechanism or the metal interaction(s).
- Treatment (such as sulfation) of multicomponent catalysts to produce catalysts with higher activity and better activity

maintenance: Although one attraction of a dispersed catalyst is that it can be disposable, one with good activity maintenance can be recycled. This can potentially reduce catalyst recovery and/or disposal requirements. Further research on the combination of high-activity multicomponent catalysts with sulfation, such as the sulfated Fe-Mo oxides catalyst systems developed at the University of Pittsburgh, is recommended. One possible area of research is the use of Molyvan additives, whose phosphorus promoters may enhance stability with respect to sintering, in these catalysts.

- Methods of catalyst recovery: There are numerous patent claims and investigations on catalyst recovery, particularly of Mo; all of the recovery methods are based on solvent extraction. However, there has been limited investigations on optimization.

Catalyst Precursor Impregnation:

Experimental:

Simultaneous swelling and catalyst impregnation experiments with SO₂-treated Black Thunder coal were performed using Molyvan L and Mo octoate as catalyst precursors. Table 23 shows the properties of the coal. Swelling solvents used were THF, DMSO, and isopropyl alcohol (IPA). Swelling solvent (500 g) was added to coal (100 g) in a 5:1 by weight solvent:coal ratio. The swelling solvent was a blend of the swelling solvent with a non-swelling one, such as toluene. The catalyst precursor was then added in the required amount to obtain the desired Mo concentration in the solution (e.g., 100 ppm Mo). The slurry mixture was blended in a 1-L baffled flask which was stirred (with or without heating) in a Brinkman R110 rotavapor unit for the desired time. After this time, a 25-ml liquid aliquot portion was withdrawn, allowed to stand for at least five minutes to settle the coal solids, then pressure-filtered

(<2 psig) with nitrogen. For most of the experiments, liquid samples were withdrawn at given times (i.e., 0.5, 1, 2, 4, 6, 24, and 48 hours) from the same starting coal-solvent slurry.

It was necessary to establish an effective technique to quantify the level of organo-molybdenum compounds present in the solvents being used for the coal swelling/penetration experiments. The first proposed technique was UV-visible spectroscopy, and while it originally held promise for detection, the sensitivity of the features due to Molybdenum were insufficient to overcome the signals arising from extracted coal liquids. Next, inductively coupled plasma spectroscopy (ICP) was tried. ICP is capable of simultaneously determining up to 30 elements including Mo, Ni, Fe and Cr. However, it is necessary to prepare a calibration curve with each solvent system. A series of laboratory experiments was carried using the current solvent systems including alcohols, THF, and V-1074 Wilsonville coal-derived liquids. The reproducibility was within 1% for samples within the calibration limits. X-ray fluorescence (XRF) was yet another viable technique. Thus, either ICP or XRF was used to determine the amount of Mo-compounds. A summary of experimental conditions and results is in Appendix E.

Results:

Sampling Corrections and Experimental Error: The extent of Mo uptake by coal at a given time may be estimated from the fraction of Mo remaining in the solution withdrawn at that given time (Mo_i/Mo_o). The extent of catalyst uptake is then proportional to $1-Mo_i/Mo_o$.

For the experiments where liquid samples were continuously withdrawn from the same starting coal-solvent slurry at various times, corrections were made for the dilution effect due to the catalyst withdrawal. Appendix F describes the corrections, which were generally within experimental error.

Table 24 and Figure 10 give indications of the magnitudes of the corrections and the experimental error.

Table 24 compares the results obtained from a swelling and impregnation experiment with single sampling after 24 hours with those obtained from an experiment with multiple samplings prior to the 24-hour sampling. The results are for treatment with 30/70 (by weight) THF/toluene and 100 ppm Mo as Molyvan L. Uncorrected and corrected uptake values are shown for the experiment with multiple sampling to illustrate the magnitude of the correction. Figure 10 shows the results for two sets of repeat experiments: one at moderate uptake and the other at high uptake. In general, relative error was within 10%.

Possibility of Catalyst Stripping: The possibility of stripping or re-extracting the catalyst precursor from the coal particle during the swelling and impregnation, particularly at the longer times, was investigated. An examination of some of the preliminary uptake data with simple diffusion and immobilization models which utilize Langmuir adsorption isotherms indicated that initial uptake rates may be described by the limiting case of strong sorption.⁽⁴⁾ The adsorption appeared to be irreversible.

Three samples of SO₂-treated coal that had been simultaneously swollen and impregnated in 30/70 THF/toluene with Molyvan L were subsequently contacted with fresh 30/70 THF/toluene for 48 hours or up to 14 days. Table 25 shows the analyses of the solution and the solids. As confirmed by both liquid and coal ICP analyses, very little Mo, if any, was removed from the coal by the THF. Moreover, the measured Mo concentration on the coal after the stripping agreed well with the calculated value (after the dilution corrections) for the coal prior to the stripping.

Effect of Swelling Solvent: If swelling alone determines diffusion rates of the catalyst precursor into the coal particle, then the rate of metal

catalyst uptake should follow the order DMSO > THF >= IPA >> toluene. This general trend is seen in Figures 11a and 11b which show the extent of catalyst uptake for some of the Molyvan L impregnation experiments with these solvent blends. Molyvan L uptake by the toluene-swollen coal was small while the uptake by the coals swollen by the polar solvents THF and IPA was greater (Figure 11a). Catalyst uptake by coal swollen by the more polar DMSO was greater than that achieved with either the IPA- or THF-swollen coal (Figure 11b).

In the previous investigations on coal swelling, blends of swelling solvent with a non-swelling solvent (such as toluene) were equally or more effective in swelling coal than the pure swelling solvent. For most of the solvents, a concentration of 30% swelling solvent appeared to be optimal, which was the reason for its use in this study. Swelling and impregnation experiments were conducted with a lower swelling solvent concentration to determine the effect on catalyst uptake. Figure 11c shows catalyst uptake for coal particles swollen and impregnated in 20% and 30% THF in toluene. The lower swelling solvent concentration did result in 10-20% (absolute) less uptake at ambient impregnation. However, it is interesting to note that the use of a higher impregnation temperature with 20% solution can result in catalyst uptake similar to or better than that obtained with the 30% solution with ambient impregnation.

Effect of Impregnation Temperature: Figure 12 shows catalyst uptake for impregnation using Molyvan L with toluene (-70 mesh coal), THF or DMSO (8x60 mesh coal) as swelling solvents. As shown in the figure, a higher impregnation temperature promoted catalyst uptake, even for the non-swelling toluene. However, the catalyst uptake attained with toluene at the higher temperature was still less than that achieved with a swelling solvent at ambient impregnation. Further, the combination of a good swelling solvent (like DMSO) and the 150°F impregnation temperature resulted in 90% penetration after 30 minutes. At room temperature, this same penetration could be achieved after about 2 hours.

Effect of Coal Particle Size: Figures 13a and 13b show catalyst uptake for coals of various particle sizes impregnated with Molyvan L using IPA and THF, respectively. The results demonstrate that penetration was better with finer coal particles, particularly at short times and ambient impregnation. For THF-swollen coal, the difference between the results for ambient impregnation of the -70 mesh and -200 mesh particles were within experimental error (Figure 13b). At increased impregnation temperature, however, the difference in uptake between the coarse 8x60 mesh and the fine -70 mesh particles was insignificant. This implies that fine grinding of coal may not be necessary at feed slurry tank temperatures.

Effect of Catalyst: Figure 14, which shows catalyst uptake for 8x60 mesh coal treated with IPA and Molyvan L, indicates that catalyst uptake at higher initial concentration was not as extensive as that obtained with a lower initial concentration. This difference could be an effect of saturation of deposition sites.

All results so far have been with Molyvan L as catalyst precursor. Figure 15a compares catalyst uptake for 8x60 mesh IPA-swollen coal for ambient impregnation with Molyvan L and Mo octoate. Penetration was similar at short times (<6 hr) but became better for Molyvan L as time increased. The uptake of Mo octoate at 150°F is also shown.

Similar uptake experiments were conducted with Mo octoate as precursor for DMSO and THF as swelling solvents (Figures 15b and 15c, respectively). As with IPA-swollen coal, the uptake of Molyvan L was greater than that of Mo octoate for DMSO-swollen coal (Figure 15b). The results also suggested that the use of high impregnation temperatures decreased the difference in uptakes between Molyvan L and Mo octoate. [Note in this figure that the Mo octoate uptake was calculated as $(1-Mo_i/Mo_o)$ instead of using the sampling corrections. This was because of the large scatter in the Mo content data, particularly at the early impregnation times; the sampling

corrections require that molybdenum content monotonically decrease with time. (Appendix F explains how the corrections were handled when the Mo content did not decrease with time.)]

Figure 15c suggests that Mo octoate penetrated more effectively than Molyvan L in the THF-swollen coal. This was contradictory to the findings for coal swollen by IPA and THF. This apparent superiority of Mo octoate may be an artifact due to an instability observed with Mo octoate in THF/toluene. With storage, the formation of an immiscible film was observed followed by the formation of a precipitate. The solutions from the Mo octoate impregnation with THF and DMSO were analyzed by X-ray fluorescence. If the precipitate contained molybdenum, its settling during the XRF analysis would deplete the molybdenum in the solution, resulting in the inferred better impregnation with Mo octoate.

Although this instability of Mo octoate was also observed with DMSO/toluene, the results for the DMSO-swollen coal suggested Molyvan L uptake was higher than that for Mo octoate. This indicates that the precipitate formed with DMSO may not contain Mo. No instability was observed for Mo octoate with IPA/toluene and for Molyvan L with all four solvents (THF, IPA, DMSO, and toluene) at the 100 ppm Mo concentration.

A similar instability was observed with swelling solvent in tetralin solutions containing high concentrations (1000-5000 ppm) of Molyvan L. The instability was observed either as a change in the color of the solution or the formation of a precipitate. For example, the color of a 33/67 IPA/tetralin solution changed from almost clear/slight yellow tint at 50 ppm Mo (as Molyvan L) to blue-green at >1000 ppm Mo. With DMSO, a precipitate formed at the high concentrations.

Conclusions of the Coal Swelling/Catalyst Impregnation Experiments:

1. Simultaneous swelling and catalyst impregnation experiments conducted with SO₂-treated Black Thunder coal resulted in greater catalyst uptake compared with impregnation using a non-swelling solvent, such as toluene. The rate and extent of catalyst penetration into coal particles correlates with the ability of the solvent to swell coal, i.e., DMSO >> THF ~ IPA >> toluene.
2. Higher impregnation temperature enhances catalyst uptake, with the larger improvement obtained with less effective swelling solvents. Moreover, the effect of lower concentration of the swelling solvent can be offset by increasing the impregnation temperature.
3. Although uptake is better with smaller coal particles, particularly at short impregnation times and ambient temperature, the enhancement is lost at increased temperatures. Therefore, fine grinding of coal should not be necessary at feed slurry tank temperatures.
4. Catalyst uptake with Molyvan L as precursor is more extensive than that with Mo octoate. However, the instability of Mo octoate (at typical Mo loadings) with some swelling solvents could result in an inactive catalyst form.

Catalyst Impregnation and Characterization via Analytical Electron Microscopy:

The results of the analytical electron microscopy analysis (AEM) of coal solids subjected to simultaneous swelling and impregnation with soluble catalysts showed that catalyst uptake with Molyvan L was greater than that with Mo octoate because of better dispersion. The Mo species from Molyvan-L was finely-dispersed throughout the coal particle whereas that from Mo octoate resulted in surface impregnation. Some degree of Mo

surface impregnation was observed with Molyvan L impregnated onto coal that had been pretreated with SO_2 to remove mineral matter.

The characterization of AEM results for catalyst metal dispersion in coal particles that had been simultaneously swollen and impregnated with soluble precursors is described here.

Experimental:

Swelling and Impregnation Procedure: Simultaneous swelling and catalyst impregnation experiments with raw and SO_2 -treated 8 x 60 mesh Black Thunder coal were performed using Molyvan L and Mo octoate as catalyst precursors. Table 23 shows the properties of the coal. The swelling solvent used was either a 30/70 (by weight) blend of IPA/toluene or 100% IPA. The swelling solvent was added to coal in a 5:1 by weight solvent:coal ratio. The catalyst precursor (Molyvan L or Mo octoate) was then added in the required amount to obtain the desired Mo concentration in the solution. The slurry mixture was blended in a 1-L baffled flask which was stirred at ambient temperature in a Brinkman R110 rotavapor unit for the desired treatment time. The treated coal was passed through a Millipore filter, dried over N_2 , then submitted for electron microscopy analysis. Some samples were analyzed by ICP to determine the actual Mo concentration on the coal.

The initial experiment was done using swelling with the 30/70 IPA/toluene solvent and impregnation with a catalyst concentration of 0.5 wt% Mo nominal (based on coal) as Molyvan L for 24 hours. Mo uptake was estimated to be about 65%. Preliminary microscopy analysis with these coal solids indicated that Mo was present in levels less than the detection limit of the instrument.

Subsequent experiments were done using 100% IPA as swelling solvent, catalyst concentration of 1 wt% Mo nominal on coal, and swelling/impregnation time of 48 hours.

Heat Treatment Procedure: Portions of these simultaneously swollen and impregnated coal solids were subjected to heating in temperatures just below liquefaction temperature but hopefully above the activation temperature of the catalyst precursor. The coal was placed in an autoclave with 1-methylnaphthalene (1-MN) then heated to either 315°C (600°F) or 400°C (750°F). For the 315°C experiments, 5 g coal were charged with 50 g 1-MN while for the 400°C runs, 2.0-2.5 g coal were charged with 1-MN. When the setpoint temperature was reached (after about 22-27 minutes), the batch autoclave was quenched rapidly back to room temperature. The reactor contents were washed with toluene and the toluene-insolubles were recovered by Soxhlet extraction.

Electron Microscopy Analysis: The analysis was done on three sets of particles: swollen/impregnated (S/W) coal solids, S/W coal solids that had been heat-treated to 315°C, and S/W coal solids that had been heat-treated to 400°C. For each set of particles, four samples were prepared: (1) raw coal impregnated with Molyvan L; (2) SO₂-treated coal impregnated with Molyvan L; (3) raw coal impregnated with Mo octoate; and (4) SO₂-treated coal impregnated with Mo octoate.

Samples for the microscopy analysis were prepared by embedding coal particles with diameters of 1-2 mm in a spur low-viscosity epoxy resin and curing these in a vacuum oven. Thin-section samples of ~200 nm thickness, obtained by diamond knife ultramicrotomy, were then examined by scanning transmission electron microscopy (STEM) to determine if there are Mo-enriched phases in the particles. Coal particles from each of the samples were also analyzed by energy dispersive X-ray spectrometry (EDXS) to map the distribution of Mo, S (and P for Molyvan L-impregnated samples) and to identify impurity phases. EDXS line scans for Mo, S, P, Ca, and O were

also collected over areas within the coal particle to the particle surface to obtain concentration profiles for these elements.

In interpreting the EDXS data, one should note that although the Mo-L α and S-K α lines overlap, these overlapping peaks (S+Mo) are labelled as S in the element profiles. If Mo is present as MoS₂, then only if the intensity of S (actually S+Mo) is more than twice that of Mo is the presence of S a certainty. This is because the intensity ratio of (S+Mo)/Mo is about 2 for a pure MoS₂ standard.

Results:

Analysis of Unheated Samples: Table 26 lists the experimental run numbers, analytical run numbers, experimental conditions, and ICP analysis. Figures 16-19 show the element profiles for representative swollen/impregnated coal solids that had not been subjected to any heat treatment. Except for SO₂-treated coal impregnated with molybdenum octoate (Figure 19), most of the coal particles had Mo concentration profiles which suggest that any Mo present is uniformly dispersed throughout the particle. The Mo intensities in these samples, although detectable, were relatively low compared to what would be expected for the Mo concentration levels in these coal particles, as determined by ICP (Table 26). At these levels (0.32-0.52 wt% on coal), Mo is definitely above the instrument detection limit unless it is not present in crystalline form or is present as a fine dispersion. Work done at an initial Mo concentration in the IPA swelling solvent of 500 ppm on coal, Mo uptake by SO₂-treated coal is about 85% for Molyvan L and 65% for the octoate. The lower uptakes (32-52%) obtained with the higher initial Mo concentration of 1 wt% may be due to a saturation of deposition sites on the coal surfaces.

Although localized Mo enrichment (either on the surface or in some spots within the coal) was observed in some particles in both raw coal solids

(impregnated with either Molyvan L or molybdenum octoate) and Molyvan L-impregnated SO₂-treated coal, this was very rare. On the other hand, the SO₂-treated coal impregnated with molybdenum octoate (Figure 19) had an element profile with a definite surface enrichment of Mo. Moreover, the Mo and S concentration profiles appeared to be correlated. On the assumption that the Mo may very likely have remained in the organo-metallic form in these samples that were not heat-treated so that it was not detectable even at the high Mo loading used, heat-treated S/W coal solids were prepared for similar AEM analysis.

Analysis of Heat-treated Samples: Minimal (<1 wt%) coal conversion to toluene-solubles occurred with heat-treatment at 315°C of the S/W coal solids. Preliminary TEM scans of these 315°C-treated coal solids showed no significant difference to the unheated samples. The coal remained about the same size and Mo levels were low, indicating either no substantial conversion to crystalline Mo, or finely-dispersed Mo. For the samples heated to 400°C, conversion to toluene-solubles was 10-20 wt% maf coal; hence, further STEM/EDXS analysis was conducted only with the 400°C-treated samples.

In general, the distribution of Mo and S in the coal particles was inhomogeneous although the degree of inhomogeneity varied from sample to sample (i.e., raw vs. SO₂-treated; impregnation with Molyvan L vs. with Mo octoate). Surface concentrations of Mo and S were observed in many coal particles for both Mo-octoate-impregnated samples. Figure 20 shows the results for raw coal and Figure 21 for the SO₂-treated coal. This surface enrichment was also observed in a few particles for the Molyvan L-impregnated SO₂-treated coal as shown in Figure 22. The Mo-enriched surfaces show up in the TEM pictures as relatively darker regions.

The surface concentration was most pronounced in the Mo-octoate-impregnated samples and was confirmed by the EDXS spectral and elemental line scan analyses. Figure 23 shows the EDXS spectral line scan analyses

for Mo-octoate-impregnated raw coal. Note that the scans for analysis spots PF-1, S-1, S-2, S-4, S-6, and B-6 along the coal particle surface show higher Mo and S concentrations than the interior analysis spots PF-2, S-5, and S-8. Figures 24a and 24b show the elemental line scan for a raw Mo-octoate-impregnated coal particle; in general, the S and Mo profiles track each other. In the SO₂-treated Mo-octoate-impregnated sample, S does not always track Mo; Mo concentrates near the surfaces and crack edges while S remains high throughout the coal particles. Figures 25a and 25b show two elemental line scan analyses that suggest this. The high S concentration throughout the particle may be due to adduction of S from the SO₂ used in the pretreatment.

In the regions with high Mo and S concentrations in the Mo-octoate-impregnated samples, very small solid particles of 10-30 nm size were detected. Attempts to individually analyze these particles with a higher-resolution electron microscope at Northwestern University were unsuccessful due to equipment malfunctions.

For the SO₂-treated Molyvan L-impregnated sample, the surface concentration of Mo was found in only a few particles. Figures 26a and 26b show two elemental line scans for one such particle. S and Mo track each other and while the tracking of P with Mo was not as apparent, higher P content was observed in areas with higher Mo and S concentrations.

For the raw coal impregnated with Molyvan L, most of the Mo appeared to be finely-dispersed and did not form particles greater than 1 nm (the detection limit). In general, S and Mo were associated with P. In one sample area which was quite rare (within a coal particle crack), clusters of small particles with high concentrations of Mo and S were located (Figure 27).

Impurities were observed in all samples. For the raw coals, the major impurities were Ca species (CaO and/or CaSO₄) while for the SO₂-treated

coals, the major ones appeared to be derivatives (Si- and Al-enriched) from the clay. This is consistent with the X-ray diffraction findings of quartz SiO_2 as the major and kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ as the minor crystalline phase. For the non-heat-treated and 315°C -treated samples, traces of molybdenum oxide (Mo_2O_7) or molybdenum oxide hydrate ilsemanite ($\text{Mo}_3\text{O}_8 \cdot \text{H}_2\text{O}$) were detected. For the 400°C -treated samples, traces of Mo_2O_7 were found in the raw Molyvan L-impregnated and in the SO_2 -treated molybdenum-octoate-impregnated coals. If any molybdenum sulfide species were present, they were probably too fine (<10 nm at 1.0 wt% Mo) to be detected by the XRD instrument.

Other impurities observed include coke, Fe-Co (for raw Molyvan L-impregnated), Al_2O_3 , and TiO_2 . Concentrations of impurities appeared to be much higher in both SO_2 -treated coals. Moreover, the Mo-octoate-impregnated samples appeared to be more susceptible to coke formation.

The results of previous bench-scale simultaneous swelling and impregnation experiments indicated that Molyvan L yielded better catalyst uptake by coal than Mo octoate. The STEM/EDXS analysis suggests that the Molyvan L dispersion in the coal is better than the surface impregnation obtained with Mo octoate. Parallel bench-scale liquefaction work at Auburn University being conducted at 410°C suggests that there is no advantage to the simultaneous swelling and impregnation treatment. Direct addition of the soluble catalyst to preswollen coal resulted in better liquefaction performance. This may be related to the effects of swelling solvent and the SO_2 -treatment on the coal surface properties (such as charge density) which may affect the nature (and consequently catalytic activity) of the Mo species formed. Another possibility is the effect of liquefaction temperature. If by swelling coal the active component of the slurry-phase catalyst can be deposited at or near reacting coal sites, catalyst effectiveness is enhanced because of the more intimate contact. In the Auburn work, the 410°C liquefaction temperature may have caused the direct catalyst addition method of catalyst introduction to be more effective

than the simultaneous swelling and impregnation. At 410°C, coal dissolves rapidly and may be totally dissolved prior to the formation of the active catalyst phase.

Summary:

Coal solids produced from simultaneous swelling with IPA and catalyst impregnation with either Molyvan L or Mo octoate were analyzed by STEM/EDXS to determine Mo penetration depth from concentration profiles of Mo. Both raw and SO₂-treated Black Thunder were used; the coal was heated to up to 400°C (750°F) in 1-methylnaphthalene in a autoclave (followed by quick quench) prior to analysis.

1. Although the Mo and S distributions in all the swollen/impregnated coal samples were inhomogeneous, the degree of inhomogeneity varied from sample to sample (raw vs. SO₂-treated; impregnation with Molyvan-L vs. with Mo octoate).
2. High surface concentrations of Mo were most pronounced in the Mo-octoate-impregnated samples (both raw and SO₂-treated).
3. Some degree of Mo surface impregnation was observed in the SO₂-treated coal impregnated with Molyvan L, although most of the particles had Mo finely-dispersed.
4. For the raw Molyvan L-impregnated coal, the Mo was finely-dispersed and did not form particles greater than 1 nm (the STEM detection limit).
5. The analysis confirms the findings from previous laboratory-scale swelling and impregnation experiments that Molyvan L yields better catalyst uptake into the coal than Mo octoate.

6. SO₂-treated coals appeared to have higher concentrations of impurities (including coke), and Mo-octoate-impregnated samples were more susceptible to coke formation.

Task 2.3: Reactivity of Swelled Coals with Dispersed Catalysts

The work done at Auburn University can be divided into three different areas:

1. The effect of coal beneficiation and swelling on liquefaction behavior of Black Thunder subbituminous coal.
2. The effect of simultaneous coal swelling and catalyst impregnation on liquefaction of untreated and SO₂-treated Black Thunder coal at two different reaction temperatures.
3. The effect of swelling and reaction parameters on catalytic activity.

The complete final report is in Appendix G. Some of the conclusions made here differ slightly from those in Appendix G due to a difference in interpretation of the large variabilities in the data.

Introduction:

In the first part of experimentation, the effect of aqueous SO₂ coal beneficiation on the thermal and catalytic liquefaction behavior of Black Thunder subbituminous coal was investigated. Aqueous SO₂ beneficiation has potential for improving coal liquefaction behavior because SO₂ treatment has been shown to reduce the ash content of both bituminous and subbituminous coals as well as lignite.⁽⁵⁻⁹⁾ Aqueous SO₂ beneficiation of bituminous Illinois No. 6 coal resulted in both positive and negative effects on liquefaction behavior. The positive effects came from a reduction in the solids introduced into the reactor and, hence, less

difficulties arose from processing the solids; however, the reduction in the mineral matter resulted in less inherent reactivity of the coal.⁽⁵⁾ A subbituminous coal, Clovis Point, gave equivalent liquefaction results for both untreated and SO₂ treated materials,⁽⁷⁾ while Martin Lake lignite showed improved conversions with SO₂ treatment.^(5,7) SO₂ beneficiation of coal involves first crushing and sizing coal and then contacting the coarse fraction with aqueous SO₂ to remove alkali metals and alkaline earth metals. This deashing treatment is followed by gravity separation to recover the size fraction that contains the lowest ash content.⁽¹⁰⁾ Metals that are typically removed from subbituminous coals using aqueous SO₂ are Ca, Mg, Na, and K.⁽⁷⁻⁹⁾ The iron content is also frequently reduced, which is possibly caused by the solubilization of siderite.⁽⁷⁾ This reduction in iron also probably accounts for the reduction in the inherent catalytic activity of the coal mineral matter.

Swelling of coal by organic solvents has been investigated by a number of researchers⁽¹¹⁻¹⁶⁾ after Van Krevelen first proposed that coal was composed of a three dimensional cross-linked macromolecular network.⁽¹⁷⁾ Organic solvent when contacted with coal becomes incorporated in the structure and swells the coal. The degree of swelling depends on the chemical composition of the solvent. Hydrogen bonding solvents swell coals significantly more than non-hydrogen bonding ones. Liquefaction of solvent-swollen coals by Joseph⁽⁹⁾ showed that bituminous and lower rank coals yielded enhanced conversion and product slates. The improvement in yield was postulated to be caused by the opening of the coal pore structure allowing greater accessibility to hydrogen donor solvents.

In this study, hydrogen bonding solvents were utilized in conjunction with the aqueous SO₂ beneficiation of coal. Possible synergistic effects of the two modes of pretreatment were examined. Thermal and catalytic liquefaction reactions were performed with both untreated and SO₂-treated

Black Thunder coal. In the catalytic reactions, the effect of different slurry-phase catalyst precursors on the liquefaction behavior for both untreated and SO_2 -pretreated coal was examined. The first set of liquefaction experiments used a probe hydrogenation species, pyrene, as the solvent. In the second set of experiments, the amount of pyrene was decreased and an additional solvent was added for the liquefaction reaction. The solvents used ranged from a nondonor solvent, 1-methylnaphthalene (1-MN), to a hydrogen donor solvent, 9,10-dihydroanthracene (DHA), to a coal-derived solvent, V1074. The last set of experiments evaluated combining two types of coal pretreatment, in which SO_2 treated as well as untreated Black Thunder coal was swelled prior to liquefaction reactions. The swelling solvents chosen were methanol, isopropanol, tetrahydrofuran (THF), and dimethylsulfoxide (DMSO) on the basis that these solvents swell coals to different degrees.^(18,19) The alcohols had a swelling index of 1.35 to 1.39 for Black Thunder coal, while THF and DMSO had larger swelling indices of 1.53 and 2.39, respectively.^(18,19) Molybdenum L and Ni octoate were used as the catalysts because of their demonstrated activity in the slurry-phase catalyst screening study. 1-MN was chosen as the reaction solvent for the swelled coals because of its relative inertness under the reaction conditions and apparent lack of interaction with the coal and pyrene during liquefaction. The use of this noninteracting solvent allowed the effect of swelling untreated and SO_2 -treated coals on their liquefaction behaviors to be more clearly demonstrated.

Increases in the liquefaction conversion and production of upgraded product from subbituminous coal are desirable to make the process a feasible option for production of transportation of fuels. In the second part of the research conducted at Auburn, a process concept was tested. This conceptual process involved several steps: (1) coal was pretreated with aqueous SO_2 ; (2) the pretreated coal was then swollen in a hydrogen

bonding solvent in which a slurry catalyst was present; (3) during swelling the slurry phase catalyst was deposited onto the coal; and (4) the impregnated coal was liquefied having the catalyst in intimate contact with the reacting coal molecules.

This conceptual process was tested using both untreated and SO_2 -treated coals. The reason that a substantial number of experiments were performed with the untreated coal was that initial results^(20,21) indicated that swelling coal prior to liquefaction was more beneficial to coal conversions of untreated coal than those of SO_2 -treated coal. Reactions were performed (1) without swelling prior to liquefaction; (2) with swelling prior to liquefaction with the catalyst being added directly to the reactor; and (3) with swelling prior to liquefaction with catalyst being added to the swelling solvent. Three different swelling solvents (THF, isopropanol, and methanol),⁽²²⁾ three different catalysts, Mo naphthenate, Molyvan L and Ni octoate, and three different reaction solvents (inert 1-MN, a coal-derived V1074 solvent, and DHA, a hydrogen donor solvent) were used. The effect of the reaction temperature on the preswollen catalyst impregnated coal was also investigated.

In the third part, various parameters that affected the preswelling and liquefaction reactions were investigated. The parameters included compositions of the reaction and the swelling solvents, catalyst loading, and swelling time. In addition, several different types of experiments were performed evaluating Molyvan L stability. These experiments included examining the effect of contact between the swelling solvent and Molyvan L and evaluating the effect adding phosphorus to Molyvan 822, an additive similar to Molyvan L, but which did not contain phosphorus. The effect of adding a solid support such as carbon black to the slurry catalyst system was also evaluated. The reaction solvent was composed of 80% coal-derived V1074 and 20% DHA, which was chosen to simulate a hydrogenated coal recycle solvent.

Experimental:

Materials: The coals used were untreated and SO₂-treated Wyoming Black Thunder coals. Proximate and ultimate analyses for both coals were given earlier in Table 23. Several swelling solvents were used: methanol, isopropanol, THF, and DMSO, and toluene all of which were obtained from Fisher Scientific and were used as received. Distilled water was also used as a swelling solvent. The liquefaction solvents were 1-MN (98% purity), 9,10-DHA, both from Aldrich, and V1074 coal-derived distillate (650-1000°F), which was obtained from Wilsonville Run No. 258 with Black Thunder coal. Several slurry and powder catalysts were used: Molyvan L and Molyvan 822, both antifriction agents from Vanderbilt Chemical Company; Mo naphthenate, Ni octoate, Ni acetylacetonate and Ni citrate all from Shepherd Chemical Company; Ni, Co, V or Cr naphthenate, molybdic oxide, Mo dioxide bis acetylacetonate, Cr-2-ethylhexanoate and ammonium tetrathiomolybdate from Strem Chemical Company; and V naphthenate from Aldrich. Carbon black, Regal 660, from Cabot Industries was used as a solid support for Mo naphthenate. Triphenylphosphine from Aldrich was utilized as phosphorus additive.

Catalyst Screening Test: The catalytic activity of a number of different slurry-phase catalysts for coal conversion of untreated and SO₂ treated Black Thunder coal to THF solubles and for pyrene hydrogenation was evaluated. The system, was composed of 1.5 g of pyrene, 0.33 g of moisture and ash free (maf) coal and a nominal 600-800 ppm of active metal from the catalyst precursor based on the maf coal feed. These reactions were performed without an additional solvent at 410°C for 30 min using ~20 cm³ stainless steel microtubular reactors which were agitated horizontally at 450 cpm. The pyrene reaction products were analyzed by gas chromatography using a Varian Model 3400, J&W DB-5 column and flame ionization detector. Pyrene conversion and hydrogenation to partially saturated products were determined to evaluate the effect of different catalysts and SO₂-pretreatment on the hydrogenation reactions.

Pyrene hydrogenation was defined as the moles of hydrogen required to form the liquid hydrogenation products from pyrene as a percentage of the moles of hydrogen required to form pyrene's most hydrogenated product, perhydropyrene. The hydrogenation products obtained from pyrene were dihydropyrene (DHP), tetrahydropyrene (THP) and hexahydropyrene (HHP). Coal conversion to THF solubles was also determined and is defined as percent coal conversion = $[1 - ((\text{g of IOM}) / (\text{g of maf coal charged}))]$ where IOM is insoluble organic matter which is ash-free.

Liquefaction Test: Liquefaction reactions were conducted in which an additional solvent was employed. The operating conditions (Table 27) were 385°C or 410°C, 1250 psig H₂ at ambient temperature, 10, 20 or 30 min reaction time, 1.33 g of maf coal, 0.67 g of pyrene, 2.00 g of solvent, and catalyst loading of 600 to 800 ppm of active metal based on maf coal feed. In these reactions, the primary solvent present was either DHA, 1-MN, or V1074 at 2.00 g. Hence, the solvent to pyrene to maf coal ratio was 2.00:0.67:1.33 so that the total solvent (added solvent plus pyrene) to coal ratio was 2:1. The reactors were the same as above; pyrene reaction products and coal conversion were obtained as stated earlier. Recovery of the reaction products was generally 95% or higher.

Coal Swelling Reactivity Test: A Pyrex glass apparatus was fabricated in which the coal was swollen with the solvent and afterwards the solvent was removed (Figure 28). The bottom part of the tube contains the solvent and coal and is connected to a detachable top and sealed with a viton o-ring. The detachable top has a hose fitting which allows removal of the solvent from the coal after the swelling is completed.

Untreated and SO₂-treated Black Thunder coals were swollen prior to reaction by introducing 1.33 g of maf coal to a pyrex swelling tube along with 7 ml of swelling solvent. After 2 hr, the amount of coal swelling that occurred was determined by measuring the height of the coal and

comparing that to the height of the coal prior to swelling. The change in the volume was calculated by

$$\% \Delta V = \frac{h_1}{h_0} \times 100\%$$

where ΔV is the volume change of the coal, h_0 is the initial height of the coal in the tube in an unswollen state, and h_1 is the height of the coal in the tube as swollen. The coal remained in the swelling solvent for a total of 24 hr, after which the nonabsorbed solvent was removed from the coal and the coal was contacted for 7 hr in ambient air, but remained in a swollen state. The weighed coal and any absorbed solvent (0.6-1.0 times the coal mass) was placed in the reactor and liquefied with or without catalyst at various conditions. For simultaneous coal swelling and catalyst impregnation experiments, the same amount of coal and solvent were used, however, slurry catalysts were added into the swelling solvent at 1.05 times 600-800 ppm of active metal. For some experiments lower (100-150 ppm) and higher (1400-1600 ppm) levels of catalysts were also used. Generally, the coal was then allowed to sit unagitated in the swelling solvent for up to 96 hrs, although some experiments were carried by agitating the coal and the swelling solvent using an orbital shaker at 250 rpm during the swelling period. Catalyst uptake into coal during preswelling averaged about 92%. Again, the coal and catalyst were liquefied.

Reaction Using Carbon Black as a Catalyst Support: Experiments were performed in which Cabot Regal 660 carbon black was used as a solid support for Mo naphthenate, a slurry phase catalyst. Four sets of experiments were performed: (1) carbon black and catalyst were placed directly in the reactor; (2) carbon black was placed in the reactor but the catalyst was placed with coal in the swelling solvent; (3) carbon black was placed in the swelling solvent with coal and the catalyst was added to the reactor; and (4) carbon black and catalyst were placed into

the swelling solvent with coal for 96 hr. Baseline experiments without carbon black were also performed. The swelling solvent used was THF and the reaction solvent was 1-MN. Sulfur was added to the reactor at a 3:1 weight ratio of S:Mo. The reaction procedures were the same as previously reported.

Reactions with Added Phosphorus: Molyvan L from Vanderbilt is a sulfurized oxymolybdenum organophosphorodithioate which was designed as an antiwear agent. Molyvan 822 from Vanderbilt is an organo molybdenum dithiocarbamate which was designed to be a nonphosphorus containing antifriction agent. Both compounds are soluble in petroleum oils but are insoluble in water. The effect of adding phosphorus in the form of triphenylphosphine to the thermal and catalytic reactions was investigated. The experimental set that was performed included (1) catalyst and phosphorus being added to the reactor; and (2) the catalyst being added to the swelling solvent and the phosphorus to the reactor. The swelling solvent was THF and the reaction solvent was 1-MN. The phosphorus was added at a level of 1300 to 1550 ppm on the basis of the coal charge. Baseline reactions were also performed in which phosphorus was added into a noncatalytic reactor.

Discussion of Results

Part I: The Effect of Coal Beneficiation and Swelling on Liquefaction Behavior of Black Thunder Coal.

The effect of coal beneficiation with SO₂ treatment was investigated by screening catalysts with no reaction solvent, using various reaction solvents and swelling both untreated and SO₂-treated coals.

Effect of Catalyst Precursor on Coal and Pyrene Conversion: Catalyst screening reactions were performed with untreated and SO₂-treated Black Thunder coals using pyrene as both a probe hydrogenation species and a solvent. The catalysts tested included Molyvan L, Mo-, Fe-, Ni-, V-, Cr-, and Co naphthenates, Ni octoate and Cr-2-ethylhexanoate. When Black Thunder coal was treated with aqueous SO₂, the amount of ash present in the coal was halved, but the amount of sulfur doubled. Residual sulfur from the SO₂-treatment was retained in the coal (Table 23). The THF soluble and pyrene conversions of raw and beneficiated coals using different catalysts are in Table 28. The %HYD, which is a measure of the hydrogenation of pyrene to partially saturated products, is also given in Table 28.

The amount of coal conversion achieved in the liquefaction reactions was dependent upon pretreatment of coal, and presence of catalyst and its type. The thermal coal conversions for untreated and SO₂-treated Black Thunder coals with no additional solvent present were similar although there is unacceptably large variance for the results of SO₂-treated coal. Pyrene conversion was less than 2%. The range of thermal conversions for untreated coal was large (48-74%). The most active catalysts for the untreated coal were Molyvan L and Ni octoate (73% coal conversion) and Ni naphthenate (63%). The other naphthenates (Mo, Fe and V) and Cr-2-ethylhexanoate showed lower activities, some had even lower conversion than that with no catalyst (thermal). Since the liquefaction reactions were performed without the addition of any sulfur, the catalyst precursors which required sulfur for their activity had to rely on sulfur that was either indigenous to themselves as with Molyvan L or was released from coal. Two of these catalyst precursors, Mo naphthenate^(23,24) and Fe naphthenate^(25,26) have shown considerably higher activity in systems that contain excess sulfur.

The activity of most of the catalysts increased in the presence of the SO₂-treated coal. Two factors were probably responsible for the increase: the removal of the alkali and alkaline earth metals such as Ca^(7,9) and the presence of additional S which was residual in the coal from the SO₂ treatment (Table 23). The largest improvement in both coal (from 48.2 ± 1.8% to 85.7 ± 2.0%) and pyrene (from 3.4 ± 1.7% to 26.3 ± 2.5%) conversions was seen with Mo naphthenate, where the increase in sulfur content from the SO₂-treated coal had a positive effect (Figure 29). Sulfur seemed to also increase the coal conversion activity, but not pyrene conversion for Molyvan L (Figure 30) and Ni octoate (Figure 31). The process of removing alkali metals and alkaline earth metals during the SO₂ treatment could have opened up the porous structure of the coal, thereby allowing more contact between the finely dispersed catalyst and the reactive coal particles, while removing Ca and other interfering metal species from the system.^(7,9)

The primary hydrogenation product from pyrene observed with all of the catalyst precursors was dihydropyrene (DHP) while the more active catalysts also yielded tetrahydropyrene (THP) and hexahydropyrene (HHP) as the reaction products. The percent pyrene hydrogenation (% HYD) given in Table 28 gives an indication of the degree of saturation achieved in the reaction products produced. The higher values of % HYD indicate that DHP with small amounts of THP and HHP was formed while the lower values show that DHP was the only product although trace amounts of the other two products may also be present.

Effect of Additional Solvent on Liquefaction Behavior: The effect of introducing an additional solvent to the liquefaction reaction on the thermal and catalytic liquefaction of untreated and SO₂-treated coals was also examined as shown in Table 28. In these reactions, the primary solvent present was either 1-MN, V1074, or DHA. When the liquefaction

behavior of the solvent plus pyrene systems was compared to that of pyrene alone, interactions among the solvent, coal, and catalyst precursor became evident.

The nondonor solvent, 1-MN, used without a catalyst precursor, decreased the amount of coal conversion for untreated coal compared to no solvent (from $59.6 \pm 0.9\%$ to $49.3 \pm 0.8\%$). Pyrene served as a better solvating medium than 1-MN, and it has been shown to be an effective shuttler of hydrogen in some coal liquefaction systems.⁽²⁷⁾ Pyrene also has the propensity, because of its four-ring structure, to be a better solvating agent for coal than the two-ring 1-MN. Hence, both factors may be responsible for the higher conversion in pyrene than for 1-MN. The addition of both Molyvan L and Ni octoate catalysts to the 1-MN system (untreated and SO_2 -treated coal) resulted in substantial increases in both coal and pyrene conversion compared to thermal 1-MN liquefaction. Molyvan L was the more active of the two in terms of both coal and pyrene conversions. Figures 32 and 33 show the coal and pyrene conversions for Molyvan L and Ni octoate, respectively. Cr naphthenate was not active for either untreated or SO_2 -treated coal.

With V1074, a coal-derived reaction solvent from Black Thunder coal, with untreated coal and Molyvan L, the coal conversion (Figure 34) was similar to reactions with 1-MN (Figure 32) but higher than for pyrene alone (Figure 30). There was some increase in coal conversion using V1074 with untreated coal and Ni octoate (from $70.7 \pm 4.1\%$ to $81.5 \pm 0.9\%$; Figure 31 vs. Figure 35). There was no difference in the coal conversions with Molyvan L for SO_2 -treated coal with pyrene alone, or 1-MN and V1074 liquefaction solvents. However, the V1074 solvent was detrimental to pyrene conversion as shown in Table 28. Coal-derived V1074 contains a multiplicity of compounds which could partially poison the finely dispersed catalyst and render the catalyst less active for pyrene

hydrogenation. Although pyrene conversion with Ni octoate is good with no reaction solvent, it reduced drastically when reaction solvent (1-MN or V1074) was used.

The hydrogen donor solvent, DHA, yielded an increased coal conversion for untreated coal and both Molyvan L and Ni octoate compared to the other solvents. The hydrogen donability of DHA promoted also coal conversion using Cr naphthenate. Hence a synergistic interaction occurred between the catalysts and solvent when the untreated coal was used. Synergism was also observed when DHA, Ni octoate and SO₂-treated coal were reacted together compared to these reactions with 1-MN. A previous activity study of Mo naphthenate and excess sulfur compared to presulfided NiMo/Al₂O₃ showed that the presence of a hydrogen donor in the reaction system had the most effect on the catalyst with the lesser activity.⁽²⁸⁾ The same phenomenon was also demonstrated in this study with the reaction of coal in DHA with Cr naphthenate. Coal conversions in DHA using the low activity Cr naphthenate were 73-84% compared to 51-55% in 1-MN for both untreated and SO₂-treated coals. However, DHA had less effect on the more active catalysts such as Ni octoate and Molyvan L: the same result as obtained in the previous study.⁽²⁸⁾ Pyrene conversions using Molyvan L and Ni octoate in DHA were less than those that occurred in 1-MN, but similar to those obtained with V1074.

Of the three solvents used with untreated coal, DHA produced the highest coal conversion, whereas V1074 showed similar (Molyvan L) or higher (Ni octoate) coal conversion than 1-MN. This ranking of solvents appears quite reasonable. DHA is a hydrogen donor solvent, and V1074 is a coal-derived solvent with solvating characteristics that should be effective for converting coal. 1-MN should be least effective since 1-MN is a relatively inert solvent containing a limited amount of partially saturated methylnaphthalenes produced under these reaction conditions. In

contrast, pyrene conversions were the highest with 1-MN as the solvent. The primary hydrogenation products from pyrene in the reactions with the added solvents were DHP; only minor amounts of THP were formed when DHA was added as a solvent while neither THP or HHP was formed with the other two solvents.

Effect of Coal Swelling on Liquefaction: Four swelling solvents, THF, methanol, isopropanol, and DMSO, were used to swell untreated and SO₂-treated Black Thunder coals. The swelling solvents ranked in effectiveness as methanol $\approx$ isopropanol < THF < DMSO. DMSO swelled the untreated coal by 100% so that the volume of the coal doubled as shown in Table 29. The other swelling solvents, methanol, isopropanol and THF, swelled the untreated coal by 16 to 42% with THF being the most effective among the three. Methanol and isopropanol remained in the coal in similar amounts which ranged from 0.9 to 1.3 g for 1.6 to 1.7 g of coal. More THF was absorbed in the coal, leaving between 1.45 to 1.7 g in 1.6 to 1.7 g of coal. Dimethylsulfoxide absorbed the most, giving 3.1 to 4.3 g of DMSO in 1.6 g of untreated coal.

All of the swelling solvents increased the volume of the SO₂-treated coal more than that of the untreated coal. Ca⁺² ions, which may serve to cross-link acid groups in coal, were removed by SO₂-treatment, thereby allowing greater mobility within the coal molecule. Methanol and isopropanol swelled SO₂-treated coal by 31 to 45%, THF by 79 to 98% and DMSO by 170 to 180%. More swelling solvent was retained in the SO₂-treated coal than in the untreated coal. Again DMSO remained strongly absorbed in the coal after removal of the swelling solvent with amounts ranging from 4.0 to 5.7 g for 1.6 to 1.7 g of coal. Substantial amounts of the other solvents were retained in the SO₂-treated coal: nearly 2.0 g of THF and about 1.0 g of either methanol or isopropanol. Liquefaction using swollen, untreated and SO₂-treated coals were performed

noncatalytically and catalytically with Molyvan L and Ni octoate using 1-MN as the solvent (Table 29). Pyrene was added as a probe hydrogenation agent. Molyvan L and Ni octoate were chosen because they demonstrated high activity for coal conversion as shown in the previous set of experiments given in Table 28.

The effect of swelling coal prior to liquefaction was demonstrated by comparing the coal conversion in the noncatalytic reactions with and without preswelling. Untreated coal swollen by THF, methanol or isopropanol showed increased coal conversion. The absorbed DMSO present in untreated coal was detrimental to noncatalytic coal conversion, decreasing the amount of coal conversion by almost half. When either Molyvan L or Ni octoate was used as the catalyst precursor, all of the swelling solvents except for DMSO increased the amount of coal conversion (49% with no solvent) achieved for untreated coal (Figures 36 and 37). The swelling solvent affected liquefaction behavior positively by the opening of the coal structure and allowing accessibility to the finely dispersed catalyst during the liquefaction reaction. But retention of aprotic DMSO diminished the reactivity of the coal.

Swelling of SO_2 -treated coal with THF and isopropanol improved noncatalytic coal conversion compared to no swelling, while methanol and DMSO did not. However, there was no difference in coal conversions with Molyvan L (89-91%) with SO_2 -treated coal swollen with THF, methanol and isopropanol (Figure 38) compared to swollen untreated coal (Figure 36). Again DMSO was detrimental to coal conversion. The coal conversion for Ni octoate was similar to THF or isopropanol-swollen untreated (Figure 37) or SO_2 -treated coals (Figure 39). However, methanol swollen untreated coal with Ni octoate as a catalyst showed higher coal conversion (86%). Ni octoate gave higher conversion only with SO_2 -treated coal. For most liquefaction reactions, pyrene conversion was decreased when the coal was

swollen compared to nonswollen coal. The pyrene conversion was highest when Molyvan L catalyst was used. As expected, no hydrogenation (<2%) occurred with noncatalytic reaction.

Summary: Aqueous SO₂ beneficiation of Black Thunder coal removed alkali metals and alkaline earth metals from subbituminous Black Thunder coal; the sulfur content of the coal also increased. Both factors enhanced coal conversion of SO₂-treated Black Thunder coal when slurry-phase catalysts were present, especially when no reaction solvent was present. The reduced ash content decreased the amount of potential catalyst poisons, and linked carboxylic acid groups while the available sulfur helped to sulfide the slurry-phase catalysts. Noncatalytic reactions did not show any benefit from SO₂ treatment. The addition of a hydrogen donor solvent, DHA enhanced coal conversion for most of the catalysts. A coal-derived reaction solvent also had a positive effect on coal conversion compared to no solvent.

Coupling aqueous SO₂ beneficiation with coal swelling did not have any improvement for coal conversion with Molyvan or Ni octoate. Swelling of the untreated coal prior to liquefaction with THF, methanol or isopropanol showed some benefit for untreated coal. The swelling of coal could have opened the structure and increased reactivity sufficiently to improve both thermal and catalytic coal conversion.

Part II: Liquefaction Behavior of Coal Impregnated with Catalyst during Preswelling

The liquefaction reactions were performed at two temperatures, 385°C and 410°C. The basic premise for performing these reactions at 385°C was to achieve a greater sensitivity for evaluating catalytic activity. Since

the effect of the noncatalytic reactions would be less at the lower temperature, the effect of the catalyst and its method of introduction should be more apparent at 385°C than at 410 °C. The reactions performed at the higher temperature of 410°C were more representative of the reaction temperatures that are used in commercial processing.

Liquefaction Reactions at 385°C:

Liquefaction reactions were performed in nondonor solvent 1-MN at 385°C with untreated Black Thunder coal (none were done with SO₂-treated coal) to examine the liquefaction behavior of coal impregnated with catalyst during preswelling as compared to a slurry catalyst being added directly to the reactor. The three slurry phase catalysts used were Mo naphthenate with sulfur, Molyvan L and Ni octoate. Isopropanol and THF were used as the swelling solvents. The data in Table 30 and Figures 40-43 represent these two types of reactions.

THF as Swelling Solvent: For the reactions with THF as the swelling solvent, the amount of coal conversion with the three slurry phase catalysts added directly to the reactor were similar, ranging from 72-75% for Mo naphthenate + S, 69-76% for Molyvan L, and 62-77% (large variance) for Ni octoate. When the three catalysts were added to the swelling solvent, substantial differences in the catalytic activity for coal conversion were observed. Comparing simultaneous swelling/impregnation to direct catalyst addition, Mo naphthenate + S had similar activity at 77%. Both Molyvan L and Ni octoate were negatively affected by contact with THF swelling solvent and the coal prior to reaction. Molyvan L yielded much lower coal conversion of 47-54%, and Ni octoate had slightly lower activity of 56-58%.

Likewise, in the reactions in which the coal was preswollen in THF and the catalyst added directly to the reactor, pyrene conversion and hydrogenation were fairly high for Mo naphthenate + S and Molyvan L. For Ni octoate, the results had a large variance: 5-27%. The primary hydrogenation product was DHP with only minor amounts of THP and HHP being formed. The catalyst impregnation process had the same effect on pyrene conversion as it did on coal conversion. Pyrene conversion with Mo naphthenate + S added to the THF swelling solvent remained high at 35.4% while pyrene conversion for Molyvan L decreased substantially (25.7 to 45%).

The results suggest that Molyvan L is sensitive to the addition method. Direct addition to the reactor containing coal is the best method. Contacting Molyvan L with the THF swelling solvent for a long period of time (96 hr) is detrimental to catalyst activity (both coal and pyrene conversion). It is likely that chemistry with Molyvan L changes in THF, so that the catalytically active form is no longer present. The same is not true for Mo naphthenate + S, where the method of addition makes no difference. The results with Ni octoate had a large variance, and the coal conversion could have been slightly lower for the impregnation case.

Isopropanol as Swelling Solvent: With isopropanol as the swelling solvent and adding catalyst directly to the reactor, coal conversion ranged from 72-88% for Mo naphthenate + S, 76-77% for Molyvan L and 64-66% for Ni octoate. When the catalyst was added to the swelling solvent the coal conversion results were 76-83% for Mo naphthenate + S, 56% for Molyvan L (Figure 42) and 60-65% for Ni octoate (Figure 43). Both Mo naphthenate + S and Ni octoate retained their activity when impregnated into the coal during preswelling, whereas Molyvan L had a decrease when it was preswollen in isopropanol. Pyrene conversion was high and remained so

during swelling and impregnation for Mo naphthenate + S, but it decreased for Molyvan L. Ni octoate had poor pyrene conversion in both cases.

Again, it did not make any difference for coal conversion with Ni octoate or Mo naphthenate + S, whether the catalysts were added directly to the reactor with coal preswollen by isopropanol or simultaneously impregnated/swollen onto coal using isopropanol.

Liquefaction reactions at 410°C:

Untreated Coal with 1-MN as Reaction Solvent: The results from liquefaction reactions performed in the nondonor solvent 1-MN using untreated and SO₂-treated, unswollen or swollen (in THF, methanol or isopropanol) Black Thunder coal, with Molyvan L or Ni octoate are in Tables 31 and 32, respectively. For untreated, unswollen Black Thunder coal, Molyvan L catalyst was more active for both coal ($82.4 \pm 3.0\%$) and pyrene ($30.0 \pm 5.4\%$) conversions than Ni octoate ($70.7 \pm 4.1\%$; $6.8 \pm 0.3\%$).

THF as Swelling Solvent: Using THF as a swelling solvent for Black Thunder coal, the highest coal ($87.3 \pm 1.6\%$) and pyrene ($18.6 \pm 1.3\%$) conversions were obtained for Molyvan L, when the catalyst was added directly to the reactor (Figure 44). When the reaction time was shortened from 30 min to 20 and 10 min, the coal and pyrene conversions decreased (Table 31). Agitation of the swelling solvent with coal and catalyst present did not increase coal conversion. Doubling Molyvan L catalyst loading and the amount of catalyst impregnated into the coal did not improve coal conversion but there was some enhancement in pyrene conversion.

Ni octoate results showed no significant difference whether THF was used or not, and whether the catalyst was impregnated onto the coal or added directly into the reactor. Pyrene conversion was again poor. Ni is a good hydrogenation metal, but it works best as reduced Ni metal and gets easily poisoned by sulfur. Also the hydrogenation/dehydrogenation equilibrium for Ni shifts easily at higher temperatures, which could have caused the poor pyrene hydrogenation.

Methanol as Swelling Solvent: Using methanol as a swelling solvent, the coal and pyrene conversions were good for Molyvan L with both direct catalyst addition ($88.0 \pm 0.9\%$; $24.3 \pm 1.8\%$) and surprisingly also with impregnation ($88.0 \pm 0.5\%$; $25.7 \pm 2.7\%$). For Ni octoate, the coal conversion results were higher with direct addition ($85.5 \pm 0.1\%$) than with simultaneous swelling and impregnation ($70.1 \pm 1.1\%$). It is obvious that the nature of the swelling solvent has a large effect on the reactivity of the catalyst and coal.

Isopropanol as Swelling Solvent: The results with isopropanol as a swelling solvent are shown in Table 31 and Figures 45 (Molyvan L) and 46 (Ni octoate). Molyvan L activity decreased when simultaneously impregnated onto coal, whereas it made no difference how Ni octoate was added to the reaction. Reduced reaction time lowered coal and pyrene conversion.

SO₂-treated Coal with 1-MN as Reaction Solvent:

Reactions with SO₂-treated coal showed that swelling of the pretreated coal had less effect on liquefaction behavior than swelling of the untreated coal.^(20,21) Impregnation of Molyvan L with any of the three swelling solvents resulted slightly less coal conversion (Table 32; Figure 47) than adding the catalyst directly to the reactor (Table 32;

Figure 48). The differences were less pronounced at this higher temperature. Pyrene conversion remained high with Molyvan L (between 19-34%). With Ni octoate as a catalyst, the coal conversions were similar with THF, whether direct addition ($72.5 \pm 5.8\%$; Figure 49) or simultaneous swelling/impregnation ($71.4 \pm 4.1\%$; Figure 50) was used. This was also the case for Ni octoate and methanol swelling solvent ($78.7 \pm 1.1\%$ vs. $78.4 \pm 0.2\%$), and isopropanol ($73.9 \pm 5.1\%$ vs. $67.9 \pm 2.3\%$). As seen previously with untreated coal, pyrene conversion was poor with Ni octoate in all cases.

Untreated Coal with V1074 as reaction Solvent: A series of reactions was also performed with coal-derived V1074 as the reaction solvent and THF as a swelling solvent with untreated Black Thunder coal (Table 33). Comparison of the reaction solvent V1074 to 1-MN for liquefaction showed similar coal conversion ($84.7 \pm 1.0\%$ and $82.4 \pm 3.0\%$ respectively) with Molyvan L when no swelling prior to liquefaction was used. However, a slight advantage was seen for V1074 when the coal was swelled prior to reaction and reacted without catalyst ($70-74\%$ vs. $51-67\%$). When coal was swelled prior to liquefaction and Molyvan L was added directly to the reactor, the coal conversion was $82.8 \pm 2.0\%$. The simultaneous swelling and impregnation had a large variance in coal conversion with V1074 as a reaction solvent ($76.0 \pm 8.1\%$), and this could be comparable to that of direct addition ($81.9 \pm 1.6\%$; Figure 51). Again, Molyvan L catalyst had a good hydrogenation activity with the direct addition method (28% pyrene conversion). The amount of coal conversion achieved with Ni octoate was similar regardless of the introduction method, but its hydrogenation activity was poor (Figure 52).

Untreated Coal with Dihydroanthracene (DHA) as Reaction Solvent: Very high coal conversion ($89.7 \pm 0.2\%$) of untreated Black Thunder coal occurred in hydrogen donor solvent DHA and Molyvan L when no swelling

solvent was used compared with the other two reaction solvents (Table 34). The hydrogen donor solvent promoted noncatalytic conversion of Black Thunder coal, yielding $82.4 \pm 2.1\%$ coal conversion after swelling in THF while $72.0 \pm 1.7\%$ was achieved in V1074 and $59.7 \pm 8.9\%$ in 1-MN. The coal conversion of $87.3 \pm 2.8\%$ occurred with swelling in THF and Molyvan L catalyst added directly to the reactor and it was similar when the catalyst was added to the swelling solvent ($84.5 \pm 0.4\%$; Figure 53). Pyrene conversion was high in DHA when Molyvan L was added directly to the reactor with or without preswelling the coal in THF. The addition of the catalyst to the THF swelling solvent was detrimental to pyrene conversion reducing the amount from $23.5 \pm 4.7\%$ when the catalyst was added directly to the reactor to $8.9 \pm 2.3\%$ when preswelled with THF.

Summary: The improvement in coal conversion expected by impregnating slurry phase catalysts onto the coal during swelling prior to liquefaction was not achieved. Swelling of untreated Black Thunder coal increased the accessibility of the interstices of the coal structure to the catalyst and increased coal reactivity under liquefaction conditions. However, absorbing the catalyst into coal, prior to liquefaction, thereby making the catalyst more accessible to the dissolving coal molecule, did not necessarily achieve increased coal conversion. In some cases, Mo naphthenate with sulfur and Ni octoate showed comparable coal conversions with swelling/impregnation and direct addition. Catalyst impregnation with the swelling solvent was detrimental to Molyvan L. Liquefactions at lower temperature (385°C) showed lower coal conversion as expected. Pyrene conversion and hydrogenation provided a sensitive measure of catalyst activity.

Part III: Effect of Swelling and Reaction Parameters on Catalytic Activity

The research in Part III evaluated a number of different reaction parameters and their effect on conversion of untreated Black Thunder. Among the parameters examined were the reaction solvent composition, swelling solvent composition, swelling time, catalyst loading and catalyst type.

Composition of Reaction Solvent: The effect of the reaction solvent on the conversions of untreated Black Thunder coal and pyrene (Table 35) was dependent upon the reaction system and the catalyst introduction method.

Direct catalyst addition to a reactor containing THF preswollen coal resulted in equivalent coal conversion with Molyvan L in 1-MN ($87.3 \pm 1.6\%$) and DHA ($87.3 \pm 2.8\%$) as reaction solvents; only V1074 showed a lower conversion of $82.8 \pm 2.0\%$ (Figure 54). Pyrene conversion was high (17-28%) for all three reactions. When Molyvan L was simultaneously impregnated in THF swelling solvent (Figure 55), the coal and pyrene conversions were slightly lower for 1-MN and DHA reactions compared to those of direct addition. The coal conversion with V1074 had a large variability but it would also be expected to be decreased. Ni octoate gave equivalent coal conversions and similar pyrene conversions when added directly to either 1-MN or V1074, or even when simultaneously impregnated with THF swelling solvent. As already seen previously, Ni octoate is not a good hydrogenation catalyst and provided poor pyrene conversion for all cases.

In these reaction systems, contact of Molyvan L with THF and coal prior to liquefaction had a deleterious effect on both coal and pyrene conversion. Since the Molyvan L catalyst seemed to be rendered less effective by preswelling in THF, the reaction solvents had a greater influence on the

reactivity of the system. Under these less favorable conditions, hydrogen donor solvent, such as DHA, affected the conversion slightly more positively than the other swelling solvents. The Ni octoate was not affected by THF in preswelling conditions.

Three catalysts were used with isopropanol as the swelling solvent: Molyvan L, Molyvan 822, and Ni octoate. Two different reaction solvents were used, the relatively inert 1-MN and a solvent mixture of 20% DHA and 80% V1074, which modeled a coal-derived solvent with hydrogen donor capability. Molyvan L, which was directly added to the reactor containing 1-MN as the reaction solvent, yielded higher coal conversion ($88.1 \pm 0.4\%$; Figure 56) than when impregnated into coal with IPA swelling ($79.9 \pm 0.8\%$; Figure 57). Using the reaction solvent mixture of 20% DHA/80% V1074 gave similar coal conversion results ($81.2 \pm 1.1\%$; Figure 57) for simultaneous swelling/impregnation of Molyvan L catalyst. Molyvan 822 (Figure 58) had a high coal conversion of $88.0 \pm 0.1\%$ when impregnated into coal and reacted in the 20% DHA and 80% V1074 solvent, which was also higher than that of 1-MN used as a reaction solvent ($83.3 \pm 0.8\%$). Pyrene conversions were also high ($>20\%$). Molyvan 822 was not tested with the direct addition method. The impregnated Ni octoate catalytic systems were insensitive to the reaction solvent (Figure 59) and were also much less sensitive than Molyvan L to the method of catalyst introduction.

Composition of Swelling Solvent: The effect of the chemical composition of the swelling solvent on conversion of untreated Black Thunder coal that had been swollen with a catalyst as well as pyrene conversion results are in Table 36. In the first set of reactions, the reaction solvent used was 1-MN. The swelling solvents ranged in their ability to swell the untreated coal. THF was very effective in swelling coal with Molyvan L present. The %AV ranged from 40% for the typical addition of Molyvan L to 7 ml of solvent followed by 96 hr of swelling to 55.8% where Molyvan L

was added to the coal by treating the coal with 1.5 ml of THF containing Molyvan L followed by 96 hr of swelling in 7 ml of THF. A mixture of 40% THF and 60% H₂O swelling solvent with Molyvan L yielded the greatest percent change in volume (%ΔV) of 62.4%; while the same swelling solvent with Molyvan 822 gave a %ΔV of 44.2%. The methanol and isopropanol systems increased the coal volume the least, giving %ΔV's of 25% or less.

No correlation was apparent between the %ΔV and the amount of coal conversion achieved with Molyvan L reacted in 1-MN. The coal and pyrene conversions for Molyvan L catalyst, when coal was swollen with various swelling solvents are graphed in Figure 60. The highest coal conversion of 89.6% occurred with the highly polar swelling solvent mixture of 20% isopropanol and 80% water, but the %ΔV for the system was only 25%. However, when the same 20% isopropanol was mixed with nonpolar toluene, the coal conversion was much lower ($60.7 \pm 1.2\%$). Coal preswollen with isopropanol, THF, and the mixture of 40% THF and 60% water which had %ΔV's which ranged from 18.2% to 62.4% gave similar coal conversion of 80 to 82%, although 40% THF/60% water experiments had large variability in the results: $81.3 \pm 7.1\%$. Methanol was ineffective as a swelling solvent for Molyvan L yielding only 68.4% coal conversion. Although water caused hardly any swelling (3.7-9.7%), the coal conversion was $80.1 \pm 3.1\%$, and pyrene conversion was high ($25.0 \pm 2.2\%$). When 1-MN was used as a swelling solvent the results were poor ($50.8 \pm 0.2\%$).

Pyrene conversion in the reactions with Molyvan L also reflected the effect of the swelling solvent. The highest pyrene conversion of $34.7\% \pm 2.9\%$ was obtained after coal had been swelled with 20% isopropanol and 80% water (Figure 60). Other effective solvents were water and 40% THF/ 60% water, both gave about 25% pyrene conversion. These swelling solvent mixtures evidently opened the coal structure sufficiently to allow Molyvan L to penetrate but were not detrimental to its catalytic activity.

Both THF and isopropanol gave similar pyrene conversion of 15 to 17%; although these swelling solvents opened the coal pore structure allowing catalyst access as evidenced by the coal conversion achieved, both swelling solvents were worse for Molyvan L catalytic activity as measured by pyrene conversion and hydrogenation.

Molyvan 822 was sensitive to the type of swelling solvent used when liquefied in 1-MN. The swelling solvents, isopropanol, 20% isopropanol and 80% water, and 40% THF and 60% water, increased the coal volume by ~24, 34, and 44%, respectively. Swelling in isopropanol yielded a coal conversion of 83.3% (Figure 61), while the water-containing swelling solvents were detrimental to the activity of Molyvan 822, giving lower coal conversions (from 61 to 77%). In these two swelling solvent systems the increase in the organic fraction of the swelling solvent and the consequent decrease in the percentage of water improved both coal and pyrene conversion, which indicates that Molyvan 822 catalytic activity was negatively affected by water.

Ni octoate catalyst was not very sensitive to the swelling solvent (Figure 62). This was also seen previously. Pyrene conversion was again low.

The performances of the three catalysts (Molyvan L, Molyvan 822 and Ni octoate) are compared in Figure 63. Both Mo-containing slurry catalysts are more active for coal and pyrene conversion than Ni octoate.

When the reaction solvent was the coal-derived V1074 to which the hydrogen donor DHA had been added, the type of swelling solvent used still affected the amount of coal conversion achieved. When reacted under the same liquefaction conditions, both Molyvan L and Molyvan 822 were affected by the composition of the swelling solvent. Molyvan L gave higher coal and

pyrene conversions when preswollen in 20% isopropanol/80% water compared to isopropanol alone (Figure 64). As seen previously with 1-MN reactions, Molyvan 822 was again negatively affected by the water present in the 20% isopropanol/80% water swelling solvent mixture: $83.2 \pm 2.8\%$ vs. $88.0 \pm 0.1\%$ for 100% isopropanol (Figure 65). When Ni naphthenate was used, the polarity of the swelling solvent had no effect on the amount of coal or pyrene conversion.

Catalyst Loading: The effect of Molyvan L catalyst loading on coal and pyrene conversion as a function of the three swelling solvents is demonstrated in Table 37. The amount of Molyvan L introduced into THF was 600-800 ppm of Mo on maf coal basis as a standard loading and the amount was then doubled to 1200-1600 ppm. Reactions were also performed at a low loading level of 100-150 ppm of Mo on maf coal basis. Doubling of catalyst loading when Molyvan L was swollen with coal in THF did not increase coal conversion but doubled pyrene conversion (Figure 66). The effect of doubling the Molyvan L loading when methanol was used as a swelling solvent, was more substantial (Figure 67). Coal conversion increased from 68% at the standard loading level to 89% while the pyrene conversion increased from 3 to 26%. The methanol swelling solvent system evidently depressed Molyvan L activity or access of Molyvan L into the coal structure. Doubling the amount of Molyvan L overcame these barriers and substantially increased the activity of the system.

The effect of Molyvan L loading on coal and pyrene conversions was also examined using isopropanol as the swelling solvent (Figure 68). Four different methods of catalyst introduction were evaluated. The initial loading level of Molyvan L was 600 to 800 ppm yielding $79.9 \pm 0.8\%$ conversion. Doubling the catalyst gave comparable coal conversion, although pyrene conversion increased from 17 to 28%. Introducing Molyvan L at the low of 100-150 ppm resulted in low coal conversions in

the range of 50% for isopropanol as well as for the other two swelling solvents. Pyrene conversions were also low at about 2%. These coal conversions are in the range of thermal reactions. The next two experiments evaluated combining impregnated catalyst with catalyst added directly to the reactor. When half the normal loading, 300-400 ppm, was added to the swelling solvent and the other half to the reactor, hardly any difference was seen compared to when Molyvan L was impregnated into coal ($83.0 \pm 1.8\%$ vs. $79.9 \pm 0.8\%$). However, when the doubled loading amount was split between the swelling solvent and reactor, the coal conversion increased from $81.9 \pm 1.8\%$ (impregnated) to $87.3\% \pm 1.3\%$ (split). Pyrene conversion for both of these reactions was high at 25-29%. Direct access of the liquefying coal to slurry phase Molyvan L was also shown to be beneficial in the earlier experiments. Several factors may have caused this effect: (1) contact of isopropanol with Molyvan L may have limited its catalytic activity, and/or (2) the impregnated catalyst may not have been available to all of the reacting coal sites. Therefore, when the catalyst was in the slurry phase, it may have had access to more of the reacting sites than when it was impregnated into the coal.

Swelling Time: Liquefaction reactions were performed at 410 °C with untreated Black Thunder coal that had been preswelled in THF or isopropanol with Molyvan L for 12, 24, 48 and 96 hours. These data are given in Table 38. The initial time of no contact between the catalyst and the swelling solvent is where the catalyst is added directly to the reactor. The reaction systems preswollen in THF were reacted in V1074 and 1-MN while the system preswollen in isopropanol was reacted in 1-MN.

For the THF swelling solvent and V1074 reaction solvent system, coal conversion was comparable for short swelling times to direct addition (Figure 69) and although there is a large variability in the longer 96 hr

swelling results ($76.0 \pm 8.1\%$), the trend is decreased coal conversion for 48- and 96-hr swelling systems, which has also been observed in earlier results. Pyrene conversions were between 20 and 30% for direct addition and short swelling times (12, 24 hr) but decreased after 24 hours of swelling. Swelling with THF was effective in opening the coal structure and allowing access of Molyvan L as evidenced by good coal and pyrene conversion at short swelling times. However, longer contact between THF and Molyvan L was detrimental to the activity of Molyvan L.

When Molyvan L was preswollen in THF and liquefied in 1-MN, the coal conversion achieved was highest at $87.3 \pm 1.6\%$ when Molyvan L was not contacted with THF (Figure 70). Coal conversion after 6, 16, and 28 hours of preswelling with THF was less, ranging between 73 to 83%. Variability in coal and pyrene conversions was fairly high at the shorter swelling times, indicating that the impregnation process was not complete at short swelling times. After 96 hours the amount of coal conversion was $81.9 \pm 1.6\%$ and less variable than the shorter swelling time. Since ~92% of the catalyst was absorbed by the coal after 96 hours of preswelling and the amount of catalyst present in the reactor when added directly or preswollen was essentially the same, the difference in catalytic activity after swelling solvent contact and impregnation could have been caused by Molyvan L and THF somehow complexing and thus inactivating the catalytic compound. Further experiments to study the effect are described below.

The effect of swelling time on the isopropanol system was somewhat different. In the case of isopropanol, the increase in coal volume was less than that of THF. Again, Figure 71 shows that adding the catalyst directly into the reactor was most beneficial for coal conversion ($88.1 \pm 0.4\%$). Contact of 96 hours had a lower coal conversion of $79.9 \pm 0.8\%$, but comparable pyrene conversion ($16.9 \pm 2.3\%$) to that of direct catalyst addition ($18.7 \pm 0.8\%$). Shorter swelling times (12, 24 hrs have a large

variability in the results. Only 48 hr swelling time shows a definite decrease in coal conversion ($70.2 \pm 0.5\%$) and pyrene conversion ($9.5 \pm 0.3\%$).

Effect of THF Contact Time on Molyvan L Activity: To further test the effect of the THF swelling solvent on Molyvan L activity in liquefaction reactions, two additional experiments were performed. First, Molyvan L was contacted with THF for 15 min, then separated from the THF and added to the liquefaction reactor. The amount of coal and pyrene conversions were comparable to those of direct addition (Table 39). The second experiment evaluated the stability of Molyvan L in THF by placing Molyvan L in THF at an equivalent concentration level as used in liquefaction experiments. After 96 hours of contact, the THF was removed by rotary evaporation. No liquid Molyvan L was left in the flask but a solid mass of black residue was stuck to the bottom of the flask. The residue could not be removed from the flask and, therefore, its liquefaction activity could not be tested. However, this residue probably was an inactive form of Molyvan L.

Spectroscopic Analysis of Catalyst in Swelling Solvents: The effect of the swelling solvent on stability of three different slurry phase catalysts was examined by UV-visible spectroscopy. Three catalysts, Molyvan L, Mo naphthenate and Ni octoate were evaluated in two swelling solvents, isopropanol and THF. The analysis wavelengths were 710 nm for Molyvan L, 495 nm for Mo naphthenate and 400 nm for Ni octoate. All of the catalysts dissolved readily and completely in THF; however, Mo naphthenate and Ni octoate dissolved very slowly in isopropanol, giving an error for the initial reading.

Each catalyst showed different spectroscopic effects for the two swelling solvents. Mo naphthenate, which converted coal equally well with or

without contact with the swelling solvent, showed decreased absorbance in THF with time as presented in Table 40. In isopropanol, Mo naphthenate dissolved slowly showing increased absorbance during the first 24 hours. After Mo naphthenate achieved solubility, its absorbance and apparent concentration decreased with time.

Molyvan L behaved differently from Mo naphthenate. Molyvan L showed decreased absorbance for the first 48 hours in THF and then increased. The final apparent concentration of Molyvan L in THF was quite high, giving a concentration value of three times its original concentration. These results suggest that Molyvan L formed a complex with THF which not only affected its spectroscopic properties, but also its liquefaction and hydrogenation activity. Molyvan L acted differently in isopropanol showing decreased absorbance and decreased apparent concentration of the complex with time. This complexing with THF and Molyvan L would explain the poor coal conversion whenever Molyvan L was simultaneously impregnated with THF swelling solvent.

Ni octoate behaved differently in the two swelling solvents compared to the other two catalysts. The values of the visible absorbance fluctuated over the 96 hours. The general trend was a lowering in the absorbance so that the final concentrations in both THF and isopropanol were somewhat lower than the original concentration. The effect of the swelling solvent on the behavior of Ni octoate in liquefaction reactions was a decrease in its overall performance.

Reactions with Carbon Black: Slurry phase catalysts were used throughout this work because of their solubility in the reaction medium as well as their ability to diffuse and deposit on the coal surface or perhaps into swollen porous structure. Although slurry phase catalyst present a number of benefits such as high activity and accessibility, a test was conducted

to see if providing a support for these catalysts would improve their overall performance in liquefaction. Therefore, Regal 660 carbon black, with some surface oxygen, was added to the reaction system to evaluate if a surface for deposition would improve the overall activity of Mo naphthenate in the system.

The reaction system that was tested evaluated the liquefaction of untreated Black Thunder coal with 600 to 800 ppm of Mo as Mo naphthenate on maf coal basis and sulfur added at three times the Mo loading. The swelling solvent used was THF and the reaction solvent was 1-MN. Experiments were performed as shown in Table 41: (1) Mo naphthenate + S was added to the reactor and one of three conditions existed for carbon black: no carbon black was added; carbon black was added directly to the reactor; and carbon black was added to the swelling solvent; and (2) Mo naphthenate was added to the swelling solvent THF, sulfur was added to the reactor and carbon black was added in the same three ways as described in (1).

When Mo naphthenate + S was added directly to the reactor, the highest coal conversion of $9.9 \pm 1.2\%$ was achieved without carbon black (Figure 72). When carbon black was added either directly to the reactor or to the swelling solvent, lower coal conversion was seen ($78.2 \pm 0.9\%$ and $80.0 \pm 2.8\%$, respectively). Pyrene conversion was similar with or without carbon black. When Mo naphthenate + S was added to the swelling solvent, the same phenomenon occurred (Figure 73). The highest coal and pyrene conversions were achieved without carbon black, yielding $89.9 \pm 0.1\%$ coal conversion and $26.0 \pm 0.5\%$ pyrene conversion. When carbon black was added, the amount of coal conversion decreased to 78-79% and pyrene conversion to 21-22%. The carbon black probably deposited Mo naphthenate on its surface thus effectively removing the catalyst from the system.

Carbon black may have also served as a diluent. Thus, a support for a slurry catalyst only reduces its activity.

V1074 as a Swelling and Reaction Solvent: In one set of experiments, V1074 was used as both a swelling and reaction solvent. The swelling solvent V1074 with coal present was so dark that the amount of coal swelling that occurred could not be measured. The data are in Table 42 and they are graphed in Figure 74. In the first experiment, coal was preswollen but no catalyst was used. The second experiment involved no preswelling of coal and the catalyst was added directly to the reaction solvent. The coal was swollen simultaneously with catalyst impregnation in the third experiment.

V1074 solvent converted 70.7% of untreated Black Thunder coal without a catalyst present; this high conversion indicated that V1074 was a good swelling solvent. When Molyvan L catalyst was added directly to the reactor, or into the V1074 swelling solvent, the coal conversion increased to $76.8 \pm 2.3\%$ and $77.9 \pm 0.4\%$, respectively. Generally, coal conversion decreases when simultaneous swelling/impregnation is used compared to direct catalyst addition, however, here the conversions were comparable. The reason could be because of the chemical nature of V1074: the swelling solvent could not readily be removed from coal and was introduced directly into the reactor with possibly some slurry catalyst remaining in the solvent. This could have caused the good conversion that was seen with the impregnated/swollen coal experiment.

Addition of Phosphorus to Catalytic and Thermal Reactions: Molyvan L and Molyvan 822 are similar materials, both being composed of a oxythiomolybdenum compound. The primary difference is that Molyvan L contains phosphorus while Molyvan 822 does not. The reactions were performed where phosphorus was added in the form of triphenylphosphine to

the thermal reaction and to the Molyvan 822, which was added directly to the reactor. Corresponding reactions without phosphorus were also performed. Further reactions were also conducted where the phosphorus was added to the reactor when Molyvan 822 and Molyvan L were simultaneously impregnated with the swelling solvent. Again, corresponding reactions without phosphorus were performed. The swelling solvent was THF and the reaction solvent was 1-MN. The results are in Table 43.

The addition of phosphorus to the thermal reactions showed no difference in coal conversion (large variability in the results: $59.7 \pm 8.9\%$ and $54.3 \pm 5.7\%$) or pyrene conversion. The addition of phosphorus to Molyvan 822, when it was added directly to the reactor, increased coal conversion from $73.4 \pm 0.8\%$ to $83.6 \pm 1.8\%$; pyrene conversion also increased substantially from $8.8 \pm 3.7\%$ to $26.6 \pm 1.6\%$. Molyvan L introduced directly to the reactor (no added phosphorus) yielded the highest coal conversion of $87.3 \pm 1.6\%$ and pyrene conversion of $18.6 \pm 1.3\%$.

When Molyvan 822 was added to the swelling solvent, the amount of coal conversion was $64.7 \pm 9.5\%$ (large variability), which could be similar or lower than that of direct addition. Pyrene conversion was similar. The addition of phosphorus to the reactor decreased coal conversion ($58.5 \pm 0.8\%$). Addition of Molyvan L to THF with or without additional phosphorus reduced coal conversion compared to direct addition, however, the results were similar whether phosphorus was added or not. Pyrene conversion was not affected and was similar whether Molyvan L was added directly to the reactor or into the swelling solvent.

Only in the reaction where Molyvan 822 and phosphorus added directly to the reactor did the activity of Molyvan 822 increase with phosphorus in the system, although Molyvan L still had the best coal conversion. All other additions of phosphorus did not affect coal conversion.

Effect of Catalyst Type: The effect of catalyst type on coal and pyrene conversions was evaluated for reaction systems in which the catalyst was preswollen with coal (Table 44). The swelling solvent used for most of the systems was 100% isopropanol; 20% isopropanol /80% water was also used. After catalyst impregnation, the coal was liquefied in a reaction solvent composed of 20% DHA and 80% V1074. The catalysts were divided into two groups: the slurry phase catalysts were Molyvan L, Molyvan 822, Ni octoate, Ni naphthenate, Mo naphthenate and Co naphthenate; and the powdered catalysts were Ni acetylacetonate, Ni citrate, MoO_3 , MoO_2AcAc , and $(\text{NH}_4)_2\text{MoS}_4$. All of the catalysts were introduced at a nominal 600 to 800 ppm of active metal based on maf coal. Some of these catalyst conversions are graphed in Figure 75. Liquefaction of Molyvan L-impregnated coal gave a coal conversion of $81.2 \pm 1.1\%$. This reaction was chosen to serve as a benchmark with which to compare the activities of the other catalysts. The coal conversion activities of other slurry catalysts, Mo naphthenate plus sulfur, Molyvan 822 and Molyvan 822 plus sulfur, and Ni naphthenate were higher than Molyvan L, yielding between 84 and 88% coal conversion. The reaction with the powdered catalysts Ni acetylacetonate, MoO_2AcAc , and MoO yielded similar coal conversion to Molyvan L. The three catalysts, which had lower conversion than Molyvan L under equivalent conditions were Ni octoate, Ni citrate, and Co naphthenate. Co naphthenate gave the lowest conversion of $73.4 \pm 0.6\%$. When more polar swelling solvent, 20% isopropanol/80% water was used, Molyvan L converted more coal than after preswelling in less polar isopropanol. Molyvan 822 showed the opposite effect while Ni naphthenate was not affected by the composition of the swelling solvent (Figure 76).

The pyrene hydrogenation reactions that occurred simultaneously in these liquefaction reactions differed among the catalysts. For the catalysts preswelled in isopropanol, Mo naphthenate plus sulfur and Molyvan 822 with and without sulfur yielded pyrene conversions above 20% while all of the

other catalysts, including Ni naphthenate and Molyvan L, yielded much lower pyrene conversions of ~11% or less. By contrast, Molyvan L and $(\text{NH}_4)_2\text{MoS}_4$ produced pyrene conversions of ~28 to 29%, and Molyvan 822 yielded 11.5% pyrene conversion after being preswollen in the isopropanol-water mixture. The only difference in the activities of these catalysts for pyrene conversion was the effect of the contact with different swelling solvents, since all other reaction conditions were the same. Contact of Molyvan L with isopropanol was detrimental for pyrene conversion while contact with 20% isopropanol and 80% water mixture was beneficial. The opposite effect was observed for Molyvan 822. The activity of Ni naphthenate for pyrene conversion was not affected by the swelling solvent.

These samples of solids generated from reactions with isopropanol swollen coal and Molyvan L, Mo naphthenate + S, or Molyvan 822 catalysts were analyzed by X-ray diffraction. The presence of MoS_2 was among other mineral solids (α -quartz, CaCO_3 , pyrrhotite, etc.). MoS_2 crystallite size was the largest with Molyvan L solids (650 Å). Both Mo naphthenate + S and Molyvan 822 solids had MoS_2 size at 440 Å. These results are in Appendix H.

Summary: A number of parameters affected the activity of a given catalyst in the preswelling and liquefaction reaction process. The most influential of these parameters was the swelling solvent. The swelling solvent both affected the ability of the catalyst to impregnate Black Thunder coal and the inherent activity of the catalyst itself. Length of swelling time also affected the activity of the catalyst; the effect was directly dependent upon the type of swelling solvent used. As in any coal liquefaction system, the reaction solvent in the liquefaction reaction itself affected the overall reactivity of the system. Addition of a relatively inert solid that could serve as a catalyst support was

detrimental to the overall reactivity of the system. Addition of phosphorus to a non-phosphorus-containing Molyvan 822 was only positive when added directly to the reactor; however, Molyvan L was still the most active. The use of catalyst-impregnated coal with phosphorus was detrimental to coal conversion. Different catalysts composed of Mo, Ni, and Co displayed inherently different activities under the same swelling and liquefaction conditions. The Mo-containing catalysts were the most active and were followed in activity by Ni-containing catalysts. The Co-containing catalyst had the least activity. Pyrene conversion and hydrogenation were more sensitive measures of catalytic activity than coal conversion.

Argonne Catalyst Impregnated Coal Samples:

Argonne SO₂-treated Black Thunder and Wyodak coals used in the liquefaction reactions were impregnated by ion-exchange or adsorption with Mo, Ni, Co and Fe individually and with Mo and Fe or Fe and Ni in combination as shown in Table 45. Two batches of impregnated Black Thunder coal were used (labelled "1" and "2"). The first batch ("1") was drier and more free flowing than either the second batch or the batch of Wyodak (-20+200 mesh) coal. The samples were labelled accordingly Mo 1, Mo 2, Fe 1, Fe 2, Ni 1, Ni 2, Co 1 and Co 2. Black Thunder coal was also treated with two metals simultaneously: Fe and either Mo or Ni. The loadings were calculated by knowing the input metal solution concentration and measuring the metal content of the coal rinse solution. The liquefaction conditions were: reaction temperature 410°C, reaction time 10 minutes, pressure 1250 psig H₂ at ambient temperature, agitation 450 cpm. The reactor charge was 2 g 1-MN, 0.67 g pyrene, and 1.33 g maf coal.

Black Thunder Coal: The results from liquefaction reactions of Black Thunder coal impregnated with Mo, Fe, Ni and Co are presented in Tables 46 and 47. The reaction solvent was 1-MN.

The amount of metal impregnated on SO₂-treated Black Thunder coal varied according to the batch of Black Thunder coal and the metal type (Table 45). For batch 1, Mo was impregnated at 800 ppm while Fe was in the 500 ppm range and both Co and Ni were in the 200 ppm range. Regardless of the metal type, metal loading or coal batch, the coal conversion was very similar and ranged from 59% for Fe batch 1 to 70% for Ni batch 2. The variance in the coal conversion data was considerable as can be seen from Table 46. Although no firm conclusions can be made from the data due to the variance in the liquefaction results, it looks like Co is active even at low levels (<100 ppm) and doubling Mo or Ni does not increase coal conversion. There is no substantial difference when the coal was impregnated with the combination of metals, such as Fe-Mo. Pyrene conversions were very low for all these experiments, ranging from 2.5 to 5.5%. Catalyst dispersion, which provides catalytic activity, depends on the extent of the accessibility to the coal structure. Most coal reactions are inhibited by mass transfer effects and this might have been the reason for the poor activity for these coal samples. These catalysts were not presulfided, nor did they contain sulfur in their structure (like Molyvan L), which could have also contributed to the poor activity. The pyrene product distributions are in Table 47.

Wyodak Coal: This coal was pretreated with H₂SO₄ and impregnated with different levels of Mo, Fe, Co, and Ni as shown in Table 45. The levels of both Ni and Mo were in the 800 ppm range while Co was in the 600 ppm, and Fe was lower in the 500 ppm range. The coal and pyrene conversions achieved for the impregnated Wyodak coals are given in Table 48. The coal conversions for Ni, Mo, and Fe were similar and ranged from 73 to 76%,

while the coal conversion with Co was lower at 50-57%. The coal conversions achieved with Wyodak and Mo, Fe, and Ni were higher than those achieved with Black Thunder coal, which would indicate that the catalyst was slightly better dispersed in the Wyodak coal matrix. In comparison, noncatalytic testing of Wyodak coal⁽¹⁰⁾ in similar conditions (400°C, 1200 psig hydrogen pressure) showed 67% coal conversion. In the same study, preswelling Wyodak coal in THF increased the conversion to 74%. The pyrene product distribution is in Table 49.

This method of impregnating the catalytic metals onto coal could have dispersed them poorly, thus reducing the activity for coal conversion, especially for Black Thunder coal reactions.

Conclusions:

Aqueous SO₂ beneficiation of Black Thunder coal removed alkali metals and alkaline earth metals, increased the sulfur content and improved catalytic liquefaction conversion to THF solubles compared to untreated Black Thunder coal, especially when no reaction solvent was present. The liquefaction solvent had varying effects on coal conversion, depending upon the type of solvent added. The hydrogen donor solvent, dihydroanthracene, was most effective, while a coal-derived Wilsonville solvent promoted more coal conversion than did relatively inert 1-methylnaphthalene. Swelling of coal with hydrogen bonding solvents tetrahydrofuran (THF), isopropanol, and methanol, prior to reaction resulted in increased noncatalytic conversion of both untreated and SO₂-treated Black Thunder coals, while dimethylsulfoxide (DMSO), which was absorbed more into the coal than any other swelling solvent, was detrimental to coal conversion. Coupling swelling of SO₂-treated coal before liquefaction did not have much effect with Molyvan L or Ni octoate. Some benefit was seen with swelling untreated coal with THF, isopropanol

or methanol, however, the aprotic solvent DMSO was detrimental to coal conversion.

The effect of impregnating coal with slurry phase catalysts such as Molyvan L during solvent preswelling was detrimental to coal and pyrene conversion. Mo naphthenate and Ni octoate catalysts showed comparable conversion for both methods of catalyst introduction i.e. direct addition or simultaneous swelling/impregnation.

The results from the swelling and reaction parameter study indicated that swelling solvent type and length of swelling influenced the conversion activity for catalysts. Mo catalysts showed the most activity followed by the Ni catalysts with Co catalyst showing the least activity.

Impregnating the catalytic metals onto nonswollen SO_2 -treated Black Thunder or Wyodak coals via ion-exchange or adsorption does not increase the coal conversion activity. Dispersion of the catalytic metals in the coal structure could have been poor.

Subtask 2.4: Bench-Scale Studies

The objectives of this subtask were (1) to evaluate the effectiveness of the coal swelling and catalyst impregnation procedures using a continuous flow liquefaction unit, (2) to generate products for solids separation trials, and (3) to provide leads for subsequent experimentation.

Experiments comparing long-term stability and deactivation of untreated and SO₂-treated Black Thunder coal samples using AMOCAT™ 1C supported catalyst were conducted at University of Wyoming.

Several sets of runs were made with Black Thunder and Illinois No. 6 coals runs using both single-stage (AU-44L) and two-stage (AU-51L) pilot plant units.

The following sets of runs were made:

1. Black Thunder coal raw and SO₂-treated, swollen and unswollen with dispersed catalysts, which were either added directly to the reactor or were impregnated during swelling: at 775°F (AU-44L), 800°F (AU-51L), and 825°F (AU-44L, AU-51L) temperature.
2. Illinois No. 6 coal raw, swollen or unswollen with dispersed catalysts either added directly to the reactor or impregnated during swelling: at 825°F (AU-44L).

The initial series of runs were made with SO₂-treated Black Thunder subbituminous coal in the continuous feed AU-51L unit at relatively mild conditions (800°F and 80 min. nominal space time) to bring out the effectiveness of the catalyst and pretreatment conditions. However, these conditions were too mild to achieve good coal conversion and provide a

representative product to be subjected to the solids separation procedures of FWDC. Attempts were made to distill and recover an atmospheric bottoms product, but the solids level was high, thereby leading to poor transfer properties. Further runs with SO₂-treated Black Thunder were made at 825°F and 2.0-hr residence time in AU-51L. At these severe conditions, coal conversions were generally high so that it was difficult to determine the individual effects of swelling and catalyst. However, the results conclusively demonstrated that simultaneous swelling and catalyst impregnation pretreatment was detrimental to conversion of SO₂-treated Black Thunder. In order to compare with some of the batch-scale results from Auburn University, continuous unit runs on raw (non-SO₂-treated) Black Thunder were performed at lower severity conditions (770°F, 30 min) on AU-44L to confirm the effects of SO₂ treatment and swelling that were seen at Auburn studies. Unlike the differences seen in the batch studies, the effects of swelling and catalyst (Molyvan L) were minimal during continuous operation at these low-severity conditions.

The last two continuous runs with Black Thunder coal (AU-51L pilot plant) were done to serve as reference for some of the earlier pilot plant runs. High coal conversion was seen using preswollen SO₂-treated coal with long residence time (3 hr) and Molyvan L added directly into the reactor. Using untreated, preswollen coal with shorter residence time (1.5 hr) and Molyvan L direct addition, the oil yields were much better than with SO₂-treated coals, although coal conversion was similar.

Illinois No. 6 bituminous coal was also liquefied in the continuous feed AU-44L unit at 825°F and 0.5 hr space time to reevaluate the combined use of coal swelling and catalyst impregnation. The results indicated no significant enhancement in liquefaction performance with coal swelling and catalyst impregnation.

Experimental

The liquefaction experiments were carried out in two different pilot plants, single-stage AU-44L, and two-stage AU-51L units, both of which operate in a once-through continuous mode in regard to hydrogen and feed slurry. A schematic of AU-44L is in Figure 77 and AU-51L is in Figure 78.

The AU-44L single-stage unit is divided into feed, reaction, product separation, and product recovery sections. The slurry feed is prepared by blending screened/pulverized coal (<100 mesh), preheated solvent(s), and catalyst precursor (if desired). The blend is then charged to the feed tank having both an internal stirrer and recirculation loop. A slipstream flows from the recirculation loop through a positive displacement, high pressure Milton Roy pump. The slurry is then combined with hydrogen and fed to the bottom inlet of a 300 cc stirred Autoclave Engineer's reactor. The working liquid volume of the reactor is 273 cc. The product flows through a series of three dump valves with intermediate volumes to allow for gas expansion and pressure decrease. The product stream flows to one of two vapor/liquid separators. A small amount of light ends is carried with the gas stream to knock-out traps, after which the product gases are metered and analyzed. The product slurry is periodically withdrawn from one of the receivers.

AU-51 two-stage unit is also divided into feed, reaction, product separation, and product recovery sections. The slurry feed is prepared the same way as for AU-44L. The blend is then charged to the feed tank having both an internal stirrer and recirculation loop. A slipstream flows from the recirculation loop through a positive displacement, high pressure Bran-Lubbe pump. The slurry is then combined with hydrogen and fed to the inlet of the first of two 1-liter stirred reactors. The liquid volume of the two reactors are 271 and 270 cc, respectively. The first

stage product flows to the second through an overflow line. The second stage product flows to one of two vapor/liquid separators. Pressure is controlled by regulators in the vent gas stream. The product gases are metered and analyzed. The product slurry is periodically sampled by cycling the two slurry receivers.

Product analyses from the runs consisted of GC analyses of the gas, distillation (Oldershaw or high-temperature simulated distillation) of the product slurry, and Soxhlet extraction of the slurry using toluene, THF, and hexane as solvents. The extraction cuts are defined as follows:

- (1) Unconverted coal -- THF-insoluble
- (2) Preasphaltenes -- THF-soluble, toluene-insoluble
- (3) Asphaltenes -- Toluene-soluble, hexane-insoluble
- (4) Oils -- Hexane-soluble.

The amount of hexane-solubles (wt% of slurry) is defined as 100% minus hexane-insolubles (=asphaltenes + preasphaltenes + THF-insolubles). The latter definition is used to take into account any light ends that may be lost during hexane stripping from the hexane-solubles.

Two approaches were used in calculating material balances and yields. As-recorded data and flows were used in the first case and in the second one, the product slurry rate was adjusted for an overall material balance of 100.0%. It was assumed that the feed rates were accurate and the recovery of the product slurry rate was adjusted. This assumption appears valid, because of the difficulty of collecting all the material out of the product receivers. The material balances were calculated using a program written using Lotus 1-2-3 spreadsheet.

Results and Discussion

Black Thunder Coal Experiments at 800°F:

The run periods were made in the continuous feed AU-51L unit at relatively mild conditions (800°F and 80 min. nominal space time) to bring out the effectiveness of the catalyst and pretreatment conditions.

Five continuous flow unit liquefaction runs were completed using the following operating periods:

- (1) SO₂-treated coal and Wilsonville solvent (V1074); Run No. 93.
- (2) SO₂-treated coal with Molyvan L catalyst (100 ppm Mo based on feed coal) and Wilsonville V1074 solvent; Runs 95 and 102.
- (3) SO₂-treated coal that was swollen with 30/70 THF/toluene and then liquefied with Wilsonville V1074 solvent containing 20% resid (the run was non-catalytic); Run 113.
- (4) SO₂-treated coal that was mixed with THF, Wilsonville V1074 solvent, resid, and Molyvan L (100 ppm Mo based on feed coal), Run 115, Periods 1 and 2.
- (5) The same system as 4, but without sufficient time for catalyst penetration prior to being used; Run 115, Period 3.

The analyses of Black Thunder coal (raw and SO₂-treated) were given earlier in Table 23. The liquefaction solvents consisted of either Wilsonville V1074 distillate (650-1000°F), or a blend of V1074 with 20 wt% Wilsonville resid. The analyses are given in Table 50.

The swollen coal for Run 113 was prepared by blending a mixture of one part pulverized, SO₂-treated coal with two parts of 20 wt% THF with 80 wt% toluene. The slurry was mildly agitated for two days, and then filtered. The solids underwent limited drying. A liquefaction feed slurry was blended for a concentration of approximately 30 wt% (dry) coal with V-1074. The resulting feed slurry was too thin to establish a uniform feed through the Bran-Lubbe piston pump; therefore, resid was added to the feed. The resulting feed blend consisted of 27.4% coal (dry), 17.0% swelling solvent, 44.4% V-1074, and 11.2% resid.

The first two periods of Run 115 were carried out using a feed blend of THF, V-1074, resid, SO₂-treated coal, and Molyvan L in the following percentages: 11.7%, 47.1%, 11.8%, 29.4%, and 100 ppm Mo (based on coal). This blend was mixed for two days at about 110°F prior to the run. The third period of Run 115 was carried out using the same slurry concentrations, but with only three hours of blending before the run period.

Reference Run: The reference run (93) was carried out using a 2/1 slurry blend of V1074 solvent with SO₂-treated Black Thunder coal at reaction conditions of 800°F and 2000 psig pressure. The nominal space time of the feed slurry (calculated at ambient conditions) was 80 minutes. The normalized results are given in Table 51 and the product analyses are given in Tables 52 and 53.

The level of coal conversion to THF solubles was low at 79.2%. The yield of pre-asphaltenes was high at about 10.3% on MAF feed coal. Of particular significance, the yield of asphaltenes was in excess of 70%, indicating that little upgrading of coal-derived material was occurring. In fact, a portion of the V-1074 solvent, which contains only 1.3% hexane insolubles, reacted with the coal-derived material to form additional

insolubles. The yield of C_1^+ gases was reasonable at 8.1% on MAF feed coal, as was that of carbon oxides at 4.4%.

Run with Molyvan L Catalyst: As shown in Table 52, the addition of 100 ppm Mo (as Molyvan L) in Run 102 resulted in a nominal increase in conversion of coal to THF solubles (81 vs. 79%). However, there was a sizeable increase in the yields of pre-asphaltenes and asphaltenes. Considering past Wilsonville results and those of our previous DOE-sponsored study, these results are suspect. It is also noted that the yield of hydrocarbon gases was high at 12.7%.

Run with Swollen Coal: Run 113 was carried out using SO_2 -treated coal that had been swollen with a 20/80 mixture of THF in toluene. In addition, resid from Wilsonville was added to the feed to make the slurry more pumpable (thin coal slurries result in plugging of the pump checks).

The resulting level of coal conversion to THF solubles was slightly better than the reference run (82 vs. 79%). The yield of pre-asphaltenes was reasonable at about 10% after provision was made for the additional level in the feed resid. The yield of asphaltenes was again very high, even after subtracting the amount in the feed resid. Although the reaction temperature was not excessive ($800^\circ F$), some retrogressive reactions could have occurred.

Runs with Swollen and Impregnated Coal: Due to difficulties in preparing for the above run (113), the initial coal slurry (first two periods of Run 115) was prepared by charging in succession coal, THF, V-1074, and resid to the feed tank. The percentages were 11.7%, 29.4%, 47.1%, and 11.8%, respectively. The slurry was blended for about one hour and Molyvan L was added at a level of 98 ppm Mo based on coal. This feed slurry was then mixed for two days at about $80^\circ F$ prior to the start of the

run. The third period of Run 115 was carried out using a feed blend of material remaining in the feed tank with added slurry that was freshly prepared. The ratio of fresh to remaining slurry was 3.4/1, so the feed slurry can be considered only partially catalyst impregnated.

The level of coal conversion to THF solubles for the three periods of Run 115 was low at 72%. A total of eight extractions were done, and there were no differences between the results from periods with feed slurries blended for two days and that with fresh slurry. There were also high yields of pre-asphaltenes, asphaltenes, and gases.

Product Analyses: The analyses of the individual product fractions of the above runs are given in Table 53.

The analyses followed expected trends. Hydrogen contents increased in the following order: THF insolubles < pre-asphaltenes < asphaltenes < oils. The nitrogen and oxygen contents of the pre-asphaltenes were equal to or greater than those of the THF insolubles. The levels of nitrogen and, in most cases, oxygen in the asphaltenes were high. It appeared that there was insufficient hydrogenation severity for both effective liquefaction and hydrocracking. Typical of most coal liquefaction, the level of desulfurization was reasonable for all fractions.

Observations/Conclusions on AU-51 Unit Runs: The above results indicate that the liquefaction runs were not carried out with sufficient reaction severity. These products could not be sent to FWDC for further solids separation procedures, and more severe conditions were needed. In addition, the swelling of coal in combination with the use of low levels of catalyst precursor was not effective.

Black Thunder Coal Experiments at 825°F:

Previous runs with 800°F could not provide a suitable material for FWDC's solids separation studies; thus experiments were conducted with higher severity (825°F). The following runs were carried out with SO₂-treated Black Thunder coal and a liquefaction solvent consisting of 40% hydrogenated V1074 with 60% untreated (raw) V1074 in AU-51L pilot plant:

- (1) Unswollen coal, no slurry catalyst, no AMOCAT™ 1C, and no red mud (Runs 27A and 27B).
- (2) Coal preswollen in 20% isopropanol and 80% toluene, no slurry catalyst, no AMOCAT™ 1C, and no red mud (Run 27C).
- (3) Coal simultaneously swollen and impregnated with 100 ppm Mo on coal basis (as Molyvan L), AMOCAT™ 1C and red mud also used (Run 44AB).
- (4) Same as (3) but with an additional 100 ppm Mo on coal basis (as Molyvan L) added directly to the feed tank (Run 44C).

The system was started up with the V1074 blend solvent with Mo naphthenate at 130 ppm Mo on solvent basis (Run 66A). Then the following set of runs was carried out:

- (5) Same as (3) but with Mo naphthenate, instead of Molyvan L (Run 66B).
- (6) Same as (4) but with Mo naphthenate, instead of Molyvan L (Run 66C).

Run 66C was terminated because the second reactor containing the AMOCAT™ 1C catalyst started to coke. Fresh catalyst was charged and the third set of runs was conducted:

(7) Unswollen coal with 100 ppm Mo on coal basis (as Mo naphthenate) and red mud added to feed tank (Run 66E).

(8) Same as (7) but with 200 ppm Mo (Run 66F).

Sulfiding agent (TPS-32) was added whenever red mud was used (see Table 54 for concentrations). The coal-derived V1074 distillate (650-1000°F) was generated from Wilsonville Run 258, which was made using Black Thunder coal as feedstock.

Tables 54 and 55a summarize the operating data and Soxhlet extraction data, respectively. The conversion to THF-solubles (coal conversion) and to toluene-solubles that are shown in Table 55a were calculated from the extraction data after forcing the material balance to 100%. In this approach, the slurry weight is adjusted to close the balance. The assumption is that the unaccounted slurry weight is of the same composition as that of the collected slurry. Table 55b shows the actual product recovery, product yields, distillation results, and performance data. Extraction yields and performance data were calculated using the actual mass balances for these runs, which ranged from 78% to 99%. Exceptions were Runs 66E and 66F, where there were errors in weighing the product slurry. For these runs, the material balances were forced to 100%. In the discussion that follows, the yields and conversions calculated using the actual mass balances will be used. Table 56 shows a summary of the extraction data for the feed slurries and the elemental analyses of the various extraction fractions are in Table 57.

Runs with Unswollen Coal: The two noncatalytic runs with unswollen coal were made at different feed rates, 1.3 (Run 27A) and 1.0 lb/hr (Run 27B),

and yielded similar coal conversions of 88.0% and 86.1%, respectively. Coal conversion is expected to increase with decrease in feed rate. It is possible that the effect of feed rate at this high severity operation may not be large. Another possibility is the effect of retrogressive reactions at the longer space time, as seen by the decrease in the yield of oils (hexane-solubles): from 40.6 wt% maf coal at 1.3 lb/hr to 19.5% at 1.0 lb/hr.

Runs with Swollen Coal: Preswelling the coal with 20/80 IPA/toluene (Run 27C) resulted in 79.2% coal conversion, which is lower than the 88.0% value obtained when liquefying unswollen coal at similar conditions. Batch liquefaction runs (825°F, 30 minutes) at Auburn have shown that preswelling in isopropanol increases thermal conversion of SO₂-treated coal. This difference in results may be due to the longer (2.0 hr) space time in the continuous runs during which retrogressive reactions may have occurred to a greater extent in the presence of the swelling solvent.

Simultaneous swelling and catalyst impregnation of coal with Molyvan L using 20/80 IPA/toluene swelling solvent (Run 44AB) yielded a coal conversion of 68.1%, the lowest coal conversion achieved. However, if 100 ppm Mo (as Molyvan L) is added directly to the feed tank, in addition to the 100 ppm Mo added to the isopropanol during preswelling of the coal, the resulting coal conversion is 84.5% (Run 44C). This performance was similar to or slightly less than that achieved during thermal liquefaction (86.1 or 88.0% coal conversion for the base case runs). At the high severity used, the conversions were high so that significant changes in conversion with catalyst addition were not demonstrated. This result also raises the possible complication of interaction between the swelling solvent and the catalyst precursor during the simultaneous swelling/impregnation pretreatment. If this interaction results in the

deactivation of the catalyst, then the decrease in coal conversion with increased contact between swelling solvent and catalyst may be expected.

Molyvan L vs. Mo Naphthenate: When simultaneous swelling (with isopropanol/toluene) and catalyst impregnation of coal were done with Mo naphthenate, coal conversion was 87.7% (Run 66B), much higher than the 68.1% obtained with Molyvan L (Run 44AB). An additional 100 ppm Mo to the feed tank did not change coal conversion (89.5% for Run 66C); however, the yield of hexane-solubles from coal increased significantly (from 13.5 to 37.2 wt% maf coal). The 89.5% coal conversion is slightly lower than the 93.1% coal conversion attained during the liquefaction of unswollen coal with 100 ppm Mo (as Mo naphthenate) directly added to the feed tank (Run 66E). Increasing the catalyst concentration to 200 ppm Mo did not change coal conversion (92.2% for Run 66F), although it doubled the oil yield from coal. The distillation data (in Table 58) show a reduction in 900°F+ and increase in oil yield (IBP-900°F). This suggests that the optimum catalyst concentration for coal conversion seen here is about 100 ppm Mo; increasing the concentration beyond this could result in saturation of catalyst deposition sites on the coal.

The higher coal conversions achieved with Mo naphthenate compared with those obtained with Molyvan L under similar reaction conditions and catalyst loadings are consistent with the batch liquefaction results reported in Subtask 2.3. Mo naphthenate plus sulfur resulted in higher conversion than that of Molyvan L.

Heteroatom Removal and Product Quality: The extent of heteroatom removal was estimated and is shown in Table 55b. Hydrodenitrogenation (HDN) was essentially zero in these runs (except for Run 27B, which may be due to errors in the nitrogen measurements). Oxygen removal (HDO) generally ranged from 70-90%. Hydrogen consumptions for the highest conversion

runs, Runs 66E and 66F with direct addition of Mo naphthenate to the feed rank with unswollen coal, were higher than those with Molyvan L (except for Run 44C, where the high 11.6% H₂ consumption may be due to the low 78% product recovery). This is consistent with the higher conversions and oil yields attained with Mo naphthenate, although oil quality, as seen from its elemental composition in Table 57, is similar to that obtained with Molyvan L. Hydrodesulfurization values for this series of runs were suspect because of unusually high sulfur concentrations in the product slurry. Estimates of the gross product quality from the distillation yields indicate that the runs with Mo naphthenate generally gave higher yields of naphtha and distillate.

Summary: At the high severity conditions used in this series of runs, coal conversions were generally high (>84 wt% maf coal) so that it is difficult to determine the effects of swelling alone and catalyst alone on liquefaction of SO₂-treated Black Thunder coal. However, the results conclusively demonstrate that simultaneous swelling and catalyst impregnation pretreatment are detrimental to coal conversion. The possibility of a deactivating interaction between swelling solvent and the catalyst was indicated by the decrease in liquefaction performance with increased contact between solvent and catalyst. This deactivation was more severe with Molyvan L than with Mo naphthenate. These products were sent to FWDC for their experimentation. These results are described in Subtask 2.5.

Black Thunder Coal Reference Runs:

AU-44L Runs:

The following set of Black Thunder coal baseline runs were completed using AU-44L pilot plant:

- (1) Untreated, unswollen coal with no catalyst: Run No. 171.
- (2) Untreated, swollen coal, no catalyst: Run No. 188.
- (3) Untreated, unswollen coal, Molyvan L, direct addition: Run No. 174.
- (4) Untreated, swollen coal, Molyvan L, direct addition: Run No. 190.
- (5) Untreated, swollen coal, Molyvan L, direct addition, high temperature (825°F): Run No. 191.

Tables 59 and 60a summarize the operating and Soxhlet extraction data, respectively. The extraction yields in Table 60a are wt% of total MAF feed and were calculated after forcing the material balance to 100%. In this approach, the slurry weight is adjusted to close the balance. The assumption is that the unaccounted slurry weight is of the same composition as that of the recovered slurry. Table 60b shows the actual product recovery, product yields, simulated distillation results, and performance data. Extraction yields and performance data were calculated using the actual mass balances for these runs, which were >95% (except for Run 174, where it was 82%). In the discussion that follows, the yields and conversions calculated using these actual mass balances will be used. Table 61 shows the elemental analyses of the various extraction fractions from the feed and product slurries.

Effect of Swelling: Figure 79 shows the yield structures (wt% of total MAF feed, as shown in Table 60a) from the thermal liquefaction at 770°F of non-swollen vs. swollen raw Black Thunder coal. Swelling alone appeared to have an insignificant effect on the thermal yields and conversions of the total MAF feed; oil yield is slightly increased. Looking at the yields based on MAF coal in Table 60b, the yield of hexane solubles from coal is increased (from 14.4 to 28.5%) with swelling, although coal conversion (THF-solubles yield) remains constant. Figure 80 shows the corresponding yield structures (wt% of total MAF feed) from the catalytic liquefaction at 770°F with 100 ppm Mo as Molyvan L. As in the thermal

case, swelling alone did not cause significant enhancement of the yields and conversions of the total MAF feed; oil yield is again slightly increased. Based on MAF coal feed, the yield of THF-solubles actually decreased from 73.2% to 65.8% with swelling. Swelling did not change the product quality as estimated from the simulated distillation yields (Table 60b).

Effect of Molyvan L: For unswollen raw Black Thunder coal, the addition of Molyvan L resulted in no significant change in conversion of MAF coal (70.9% to 73.2%, Table 60b); however, there was an increase in oil yield (14.4% to 28.5% MAF coal). Product qualities, as estimated from simulated distillation (Table 60b), were comparable. For the swollen coal, addition of Molyvan L during liquefaction at 770°F actually reduced both coal conversion (71.1% to 65.8% MAF coal) and oil yield (26.7% to 17.9% MAF coal). This is an unexpected result. It is possible that the lower 1.1 lb/hr feed rate during the swollen + Molyvan L run (Run 190) may have increased the probability of retrogressive reactions. As in the unswollen case, the product qualities of the products from the thermal and catalytic runs with the swollen coals were similar (Table 60b).

Effect of Temperature: The effect of temperature on the catalytic liquefaction of swollen raw Black Thunder coal is shown in Figure 81. Although conversion to THF solubles of the total MAF feed is unchanged by increasing the temperature from 770 to 825°F, oil yield is substantially reduced from 79.3% to 62.9%. From Table 60b, it is seen that this corresponds to a negative yield of hexane-soluble oils from MAF coal, indicating the occurrence of retrogressive reactions at the higher temperature. The feed rate at 825°F was lower at 1.0 lb/hr (longer residence time) than the 1.3 lb/hr feed rate at 770°F. This may also explain the occurrence of retrogressive reactions. Although coal conversion was unchanged with increase in temperature, the yield of

lighter boiling fractions naphtha and distillate increased slightly from 20.5 wt% to 26.1% (Table 60b).

At the low severity conditions, hydrodenitrogenation (HDN) was low (<10%) and oxygen removal (HDO) was in the range 40-70%, which is lower than the 70-90% HDO levels attained when liquefying at 825°F. Hydrogen consumption was in the range 4-6%.

Summary: There was no effect on coal conversion with swelling alone on both the thermal and catalytic liquefaction of raw Black Thunder coal observed at low severity liquefaction at 770°F. Moreover, the addition of Molyvan L to either non-swollen or swollen coal did not result in any enhancements with respect to coal conversion under these low-severity conditions. At 825°F, retrogressive reactions may have occurred, causing a decrease (5 wt% absolute) in coal conversion and dramatic decrease in hexane-solubles yield from coal.

AU-51L Runs:

The last two continuous runs with Black Thunder coal were designed to serve as a reference for the earlier studies, and were conducted in AU-51L:

- (1) SO₂-treated coal, 180 min total space time (Run 58).
- (2) Untreated coal, 87 min total space time (Run 60).

Table 62 summarizes the operating data, actual product recovery, product yields, and performance data. Extraction yields and performance data were calculated using the actual mass balances for these runs, which were 65.0 and 92.7%, respectively. The low material balance for Run 58 may be due to the difficulties during run start-up to achieve the target feed rate

for a nominal space time of 80 min; hence, the resulting 180-minute space time for the run. Table 63 shows the same results, but the calculations are done by forcing the material balance to 100%.

Batch studies at Auburn indicated that enhancements in coal conversion were achieved with SO_2 treatment and coal swelling during catalytic liquefaction where Molyvan L was added directly to the feed tank. Earlier continuous runs were either of too low (770°F , 30 min) or too high (825°F , 30 min or 2.0 hr) severity to demonstrate any enhancement compared with liquefaction of raw (nonswollen, untreated) coal. In the previous DOE-contract (No. DE-AC22-88PC88819),⁽⁸⁾ Black Thunder coal was also tested in two-stage pilot plant AU-51 with Molyvan L (96 ppm Mo level) at 800°F , 3 hr contact time but 2500 psig pressure (instead of 2000 psig). The results showed 89.9% coal conversion (maf coal) with 58% distillate yield (C_4 - 935°F). From the Run 58 data with swollen SO_2 -treated coal and Molyvan L at 100 ppm Mo level (Table 58), similar results were obtained: high coal conversion (92.4% maf coal) and high oil yield (44.2% maf coal). No retrogressive reactions appear to have occurred, and heteroatom removal and hydrogen consumption were high (85.2% oxygen removal and 6.9% hydrogen consumption).

Run 60 with untreated coal was conducted to provide a reference run for previous AU-51L runs which have been conducted with SO_2 -treated coal. The results for these previous runs are also shown in Tables 62 and 63 for comparison. For this reference run at 800°F and 87 min with direct addition of Molyvan L to the feed tank, conversions of coal and toluene insolubles were 80.0 and 74.4% maf coal (Table 63), respectively. Moreover, oil yield was positive (4.4% maf coal), compared with the negative oil yields from previous AU-51L runs (93, 102, 113) with SO_2 -treated coal (thermal/catalytic, nonswollen/swollen), although conversions of coal and toluene-insolubles were not significantly affected by SO_2 -

treatment. The simultaneous swelling and catalyst impregnation (Run 115) resulted in the lowest conversions and oil yields.

Summary: High conversions of coal and toluene-insolubles (92% maf coal) and high oil yield (44% maf coal) were demonstrated when SO₂-treated Black Thunder coal preswollen in 20/80 IPA/toluene was liquefied at 800°F for a long contact time of 3 hr with V1074 as liquefaction solvent and 100 ppm Mo (as Molyvan L) added directly to the feed tank. At a shorter contact time of 1.5 hrs, untreated IPA/toluene swollen coal gave better oil yield than any of the SO₂-treated (thermal/catalytic, nonswollen/ swollen) coals, although coal conversions were similar.

Illinois No. 6 Coal Experiments:

The following runs were completed with Illinois No. 6 in order to evaluate the effect of swelling and low levels of Molyvan L addition (100 ppm Molyvan; 600-800 ppm Mo on MAF coal basis):

- 1) Raw Illinois No. 6 coal.
- 2) Raw Ill. No. 6 coal with 100 ppm Molyvan L added to the feed tank.
- 3) Same as No. 2, but at 1/2 space velocity.
- 4) Ill. No. 6 coal preswelled with IPA and toluene (non-catalytic).
- 5) Ill. No. 6 coal preswelled with IPA, toluene, and 100 ppm Molyvan L.
- 6) Same as No. 5 with an additional 100 ppm Molyvan L added to the feed tank.

The operating conditions, results, and stream analyses are reported in Tables 64 through 66.

At a reasonable temperature of about 825°F but with a short space time of 22 min, the conversion levels of as-received/raw Illinois No. 6 coal to THF and toluene solubles were 83 and 68%, respectively. With the addition of 100 ppm MoS_2 as Molyvan L, both levels of coal conversion increased 2 to 3% (absolute). These are nominally above the levels of reproducibility of about 1-2%. There was also a nominal increase in the level of hydrogenation (3.7 to 4.5%). The levels of denitrogenation and deoxygenation were unchanged at about 3 and 48%, respectively. There is a question of sulfur analyses, so the levels of desulfurization are not reported. The levels of sulfur remaining in the preasphaltenes and asphaltenes remained relatively high at about 1%.

When the space time was increased to about 36 min for the run with added 100 ppm Molyvan L, coal conversions increased to 91 and 81% (THF and toluene solubles, respectively). The extents of hydrogenation and deoxygenation also increased (7.7% and 62.5%). The level of denitrogenation increased to 11%, but this is still relatively low and it is consistent with observations that a supported catalyst is needed to achieve a high level of denitrogenation.

Run 18119-01 was made with preswollen Illinois No. 6 coal to serve as a non-catalytic reference for subsequent Molyvan L runs. Considering the differences of space times, the levels of conversion of Run 01 were about those projected from the non-swelled coal runs: namely, the swelling step offered no increase of yields over that of swollen coal.

As observed in Table 65, the addition of 100 ppm MoS_2 as Molyvan L during the swelling step resulted in the same, or perhaps lower, levels of coal

conversions to THF and toluene solubles. Run 18119-04 had conversion levels of 85 and 72%, respectively, while those of Run 18119-01 were 87 and 77%, respectively. When the space times are taken into account (29 vs. 36 min), these levels are equivalent. It is interesting that the further addition of Molyvan L (100 ppm MoS_2) to the feed tank (Run 18119-05) resulted in no additional conversion. In addition, there were no changes in the levels of hydrogenation, denitrogenation, and deoxygenation.

Summary: There was a nominal increase of coal conversion and hydrogenation with the addition of a low level of Molyvan L (100 ppm MoS_2) to the feed tank for the liquefaction of Illinois No. 6 coal. However, there appeared to be no increase of conversion or hydrogenation when the coal was either swelled or Molyvan L was introduced during the swelling step.

Catalyst Deactivation Experiments

University of Wyoming conducted a series of catalyst deactivation runs with untreated (used as a reference) and SO_2 -treated Black Thunder coal to further explore the effects of demineralization the coal with aqueous SO_2 . The catalyst selected for this study is AMOCAT™ 1C, a NiMo-alumina catalyst, and a comparison was made with a CoMo-alumina, AMOCAT™ 1A, which has been employed in their previous work. The switch to a different catalyst necessitated the establishment of a new baseline run with the untreated Black Thunder coal. Upon establishment of the baseline, the coal was treated with aqueous SO_2 and then subjected to coal liquefaction in an ebullated microreactor unit to explore the effects of the pretreatment on catalyst activity maintenance. The reaction conditions were 800°F, 2000 psig, 4000 scf/bbl hydrogen, weight hourly space velocity of 2, and solvent/coal ratio of 3. A thermal run was also performed in

order to determine the thermal level for Black Thunder subbituminous coal. A detailed description of the experimentation is in Appendix I.

Results:

AMOCATTM 1C baseline with Untreated Black Thunder Coal: The conversion results for baseline run, ZHQ08, are graphed in Figure 82. A steady deactivation of the AMOCATTM 1C catalyst is observed over the duration of the run. The initial deactivation is less rapid for AMOCATTM 1C compared with AMOCATTM 1A under identical operating conditions. This is shown in Figures 83-85.

From the information thus far available, it is not possible to identify the reason for this improvement. However, one can speculate based on the pore size distributions for the two catalysts, Figure 86. It is evident that the pore size distributions for these two catalysts are very different in the macropore range. The much smaller macropore sizes for the AMOCATTM 1C catalyst might serve to slow penetration of the large coke deposition precursors to the interior of the catalyst, and thereby maintain a higher level of activity for this catalyst. Interestingly, at the end of the run both catalysts are comparable. In analyzing the effects of macroporosity on activity and activity maintenance, Leung and Haynes⁽²⁹⁾ concluded that an optimum macroporosity generally exists with regard to activity maintenance. Of course it is also plausible that the improvement observed for the AMOCATTM 1C catalyst is due to the difference in active metals NiMo vs. CoMo. Cobalt sintering has been observed in used CoMo catalysts taken from coal liquefaction pilot plants.^(30,31)

The product analyses show decrease in both hydrogenation and denitrogenation functions as the catalyst deactivates (Figure 87).

A comparison of BET surface areas of fresh and used catalysts show that slightly less than 20% of the surface area was lost for both AMOCAT™ catalysts (Table 67). It is interesting to note that after 21 days on coal, the two used catalysts contain approximately the same amount of deposits (about 86 wt% of the original catalyst). Less metals but much more carbon were deposited on the AMOCAT™ 1C catalyst as compared with 1A. Again, the difference in pore size distributions may be responsible for this.

Thermal Run with Untreated Black Thunder Coal: The thermal run for the untreated Black Thunder coal, identified as Run ZHQ07, was conducted in the CCLM unit under identical nominal operating conditions as Run ZHQ08. The catalyst, however, was replaced with an equal volume of 3 mm diameter glass beads. Figures 83-85 show that thermal conversions are lower than catalytic, as expected.

AMOCAT™ 1C Catalyst Run With SO₂-treated Black Thunder Coal: The conversion results of the AMOCAT™ 1C catalyst deactivation run, ZHQ10, show high initial values; however, the catalyst deactivated quickly during the early stages of the run. The comparison of conversions between Runs ZHQ08 and ZHQ10 and the corresponding thermal conversions are Figures 88 through 90. Also, solvent C/H ratios are compared in Figure 91. The results show that the initial activity is slightly higher for the acid washed coal, but the corresponding thermal conversions are also higher by comparison with those obtained for the as-received coal. The catalyst for the acid washed coal run deactivated quickly and assumed a lower level of activity as compared with that for the original coal. There were some operational difficulties with this run such as plugging, which might be partly responsible for the deactivation due to a large loss in surface area and high coke buildup (Table 68). Also, in some cases high initial activity encourages rapid coking. All in all, no improvement

in catalyst activity maintenance was observed for the acid treated coal run.

The product properties again show the hydrogenation and denitrogenation functions of the catalyst suffered as the run progressed (Figure 92). The H/C ratio is poorer for this run than that of the baseline, which is consistent with the more rapid catalyst deactivation during this run. The used catalyst properties in Table 68 indicate about 60% loss in BET surface area and 40% increase in coke deposit.

Thermal Run with SO₂-treated Black Thunder Coal: Run ZHQ09 is the thermal run for the sulfurous acid treated coal. The thermal conversion results are shown in Figures 88-90.

Summary:

A new base line was established for processing Black Thunder coal with AMOCAT™ 1C catalyst. This catalyst had higher conversion activity than AMOCAT™ 1A catalyst. The cause cannot be stated with certainty, but significant differences in pore structure may have been a factor. Decreased liquefaction yields are accompanied by decrease in H/C ratio and increase in nitrogen content in the product. Pretreatment with aqueous SO₂ removes most of the calcium from the Black Thunder coal. This acid washed coal is initially slightly more reactive, but longer term catalyst activity maintenance is poorer than that of the untreated coal.

Subtask 2.5: Solids Separation/Alternative Bottoms Processing

The overall objective of this project was to develop a new approach for the direct liquefaction of coal, producing an all-distillate product slate at a sizable cost reduction over current technology. The approach taken

was to investigate and integrate all aspects of the coal liquefaction process including coal selection, pretreatment, catalyst and solvent evaluation, and alternate bottoms processing. The advanced process that developed would then be subjected to a technical and economic assessment. These results were then integrated into the overall improved coal liquefaction concept.

FWDC investigated alternative bottoms processing and solids separation through its ASCOTsm (Asphalt Coking Technology) process and direct delayed coking. The ASCOTsm process couples solvent deasphalting with delayed coking to maximize the production of coal-derived liquids while rejecting troublesome solids within the coke drum. A portion of the final liquid product is recovered by an appropriate solvent through solvent deasphalting. The asphalt product from this process is then coked to produce additional liquid product and coke. The coke will contain any solids and nearly all the metals that were present in the original feedstock.

FWDC's primary bottoms feedstock was the atmospheric residue generated at DOE's Wilsonville facility from Run 262 with Black Thunder coal. Amoco, as part of their coal liquefaction study, also produced an atmospheric bottoms product which was directly coked (without first being subjected to solvent deasphalting).

A preliminary economic assessment of the battery limits for the ASCOTsm process and direct delayed coking was completed by Foster Wheeler USA Corporation (FW USA), the commercial offerer of these processes.

The complete report is in Appendix J.

FWDC's program investigating the ASCOTSM process and direct delayed coking for producing liquid product and rejecting solids included the following:

Feedstock Characterization:

Two different feedstocks were used during the test program. The primary feedstock, used to investigate the ASCOTSM process and compared with direct delayed coking, was an atmospheric residue produced during Run 262 with Black Thunder subbituminous coal at DOE's Wilsonville facility (FW #22777). Amoco produced a small quantity of atmospheric residue for a direct delayed coking test in a series of dispersed catalyst runs (FW #22779A).

Tables 69-72 show there are significant differences between the Amoco and Wilsonville materials, such as the percentages of ash, sulfur, and sodium, the quinoline insolubles, Conradson carbon residue, softening point, and boiling range--all significantly lower for the Amoco material. Total carbon, as must follow from the low ash in the Amoco feedstock, is notably higher (89.5% compared with Wilsonville's 77.6%). The oil content is about the same in both feedstocks, while the mix of the other constituents defined in Tables 70 and 72 (asphaltenes, preasphaltenes, insoluble organic matter, and ash) are quite different. Based on these feedstock characterizations, the Amoco material was considered as superior.

Batch Solvent Deasphalting Tests (Wilsonville Feed)

These tests determined the relationship between deasphalting conditions, yield, and product quality. Three different asphalt yields were selected to study their transport properties.

A series of sixteen batch deasphalting screening tests (summarized in Table 73) were needed to select the solvents and extraction conditions that would provide the necessary control and product yield range for producing asphalt from the Wilsonville feedstock.

The screening tests were begun using one paraffin (heptane) and one aromatic (xylene) solvent. Figure 93 indicates the effect of temperature on the deasphalted oil (DAO) yield for the solvents that were deemed "too effective" (i.e., extraction temperature could not be used to effectively control the yield)--pentane, hexane, heptane, and xylene. Here, it is evident that the controlling variable was solvent type (i.e., paraffin or aromatic), not temperature. The DAO yield was essentially independent of temperature and solvent/feed ratio. The yield was near constant and averaged 61.3 wt% for the paraffin solvents and was 80.6 wt% for the single test with xylene. These values were consistent with the feedstock characterization (Tables 69 and 70) of 65.9 wt% oil (paraffin-soluble material) and 76.8 wt% soluble in toluene (an aromatic solvent). None of these solvents provide the means for readily achieving lower yields (40 to 60 weight percent DAO yield range).

Figure 94 shows the effect of temperature on the DAO yield when using n-butane as the solvent. This was the first solvent that readily permitted the use of temperature as a controlling variable. Butane's solvent power, however, limits the maximum yield to about 50 wt% DAO. It must also be used over an undesirable temperature range, as is evident by its yield vs. temperature curve. As the temperature is lowered from near the critical temperature (306°F), the DAO yield increases as it should, peaks, and then falls off precipitously. This occurs in solvent deasphalting when the extraction temperature is reduced to the degree that the asphalt phase becomes too viscous for effective extraction. Potentially extractable material is then trapped in the asphalt.

In order to produce the needed yield range, pentane (more effective paraffin solvent) was chosen to be blended with butane (Figure 95). Temperature was fixed at 290°F, near the critical temperature of butane.

Above 50 vol% pentane, the yield peaks and tends to drop off. This is the same phenomenon noted with 100 percent n-butane as the extraction temperature was lowered. In this case it was suspected that as more and more oil was extracted, with successively higher concentrations of pentane in the blend, the asphalt phase became too viscous for effective extraction at the test temperature (290°F). The data indicated that the oil yield at 290°F for n-butane/pentane will not exceed about 55 wt%. However, 100% pentane at 380°F does provide an oil yield (63.6 wt%) that will satisfy the need for a higher level of extraction. A dashed line is drawn on Figure 95 to show that a 60+ wt% oil yield is achievable if low temperature is eliminated as the controlling variable.

ASTM D-1160 distillation can be used to approximate the amount by defining deashed resid as "the volume percent of deasphalted oil (DAO) corresponding to the 900°F + fraction from its ASTM-D-1160 distillation." Figure 96 shows the relationship of DAO yield to deashed resid yield, showing the linear regression line and equation. The correlation coefficient, r , is 0.77.

Transport Tests (Wilsonville Feed)

The scope of the program required the use of an existing delayed coking pilot plant. The transport tests were needed to determine the practical transport characteristics of the asphalt as it pertained to the plant design.

Three transport tests were completed to determine the practical transport characteristics of asphalt corresponding to oil yields of approximately 40, 50, and 60 wt%.

The batch deasphalting data shown in Figure 95 was initially used to select the solvent and predict the oil yield for these tests. While the 40 wt% oil yield was produced as the curve predicted, the higher yields were off target. There is a relative insensitivity to blend composition expressed by a segment of the data--the curve flattens and then falls off, which may account in part for the discrepancy. The flatness and fall-off was theorized as due to the high viscosity of the asphalt phase at a 290°F extraction temperature. A rising viscosity, corresponding to increasing the pentane portion of the blend, may have been the culprit.

Nonetheless, the remaining screening data provided enough information to allow the quick determination of effective extraction parameters. Straight pentane was used to produce a near 50 wt% yield, and hexane was selected as the solvent for a 60 wt% yield because pentane produced a somewhat lower yield than indicated by the screening tests. Therefore, moving up to a better solvent would more readily achieve the desired yield.

The results from the asphalt production runs are shown in Table 74. The asphalt from the butane/pentane blend, containing 21.03 wt% ash, was selected for the first transport test. The test was successful and represented a milestone in the program. This was the first demonstration that a coal-derived asphalt with a high solids loading could be handled with our pilot plant equipment.

Two follow-up transport tests, one on asphalt containing 24.14 wt% ash and the other containing 27.23 wt% ash, were less successful. Neither test

was able to demonstrate an ability to properly transport these materials. The visual evidence suggested the asphalt never reached a stage of fluidity where the solvent could effectively aid in its transport through the system. Even a higher temperature operation, in the range of 350-400°F, did not help to properly transport these materials.

The asphalt containing approximately 21 wt% ash, which was transported successfully with the pilot plant equipment, was therefore selected as the candidate for delayed coking.

Delayed Coking Asphalt From Solvent Deasphalting (Wilsonville Feed)

The batch deasphalting and transport tests were used to select a practical and promising asphalt feedstock for the delayed coking portion of the ASCOTsm process.

An extended series of batch extractions were needed to produce the required amount of asphalt coker feed corresponding to a targeted 40 wt% DAO yield. The solvent blend had to be adjusted, increasing the percentage of pentane to 40 vol%, to consistently achieve this yield.

The asphalt chosen for delayed coking was produced in sequential production Runs 3039 and 3040, which were blended for the needed quantity. The asphalts from reported Runs 3034 and 3035 were rejected candidates for coking after evaluating the transport tests (Table 75).

Two asphalt coking tests were completed with the material produced in blended Runs 3039 and 3040. The first, Run 3047 reported in Tables 76 and 77, produced a normalized liquid product yield of 38.6 wt% (on asphalt feed). The overall ASCOTsm yield of liquid product was 63.3 wt% (on the

atmospheric residue feed): 40.2 wt% from solvent deasphalting and 23.1 wt% from coking.

This run demonstrated that liquid products from the ASCOTSM process are essentially free of ash (< 0.02 wt%) and metals (< 1 ppm Ni and V, ≤ 4 ppm Cu and Na, ≤ 61 ppm Fe). Specific values for the metals in the deasphalted oil and distillate oil from delayed coking are given in Table 75 (Run 3039/3040) and Table 77 (Run 3047) respectively.

A second test with the same asphalt/solvent feedstock blend served to confirm the liquid yield data and improve upon the material balance of the first run. The results from this test (run 3048) are reported in Tables 78 and 79.

The normalized liquid product yield of distillate oil, from coking the asphalt, was 35.7%. The overall ASCOTSM process yield of liquid product was 61.5 wt% (on the atmospheric residue feed): 40.2 wt% from solvent deasphalting and 21.3% wt% from coking. The overall liquid yield from this run was a little lower than from Run 3047 (63.3 wt%). The material balance at 98.2% was a significant improvement over that of Run 3047 (93.7%), lending confidence to our conclusion that ASCOTSM liquid yields greater than 60 wt% are readily attainable from Black Thunder subbituminous coal.

Run 3048 was conducted at a higher coke drum temperature, higher steam rate, and longer steamout period to try and increase the yield of distillate oil. This proved ineffective, as the liquid yield was lost to gas and coke formation, when compared with Run 3047 results. The higher drum temperatures and longer steamout period did reduce the coke's volatile manner; however, the overall distillate yield suffered. The metals content of the distillate, although low, was greater than in Run 3047. This may be due to the higher drum temperature and extended

steamout schedule driving over some heavier material with higher associated metals. The API gravity of the liquid product also indicates a heavier average material than in Run 3047.

Direct Delayed Coking Wilsonville Bottoms Product

The atmospheric bottoms product produced at Wilsonville was directly coked to compare with the ASCOTsm process. The residue feedstock from the liquefaction of Black Thunder coal at Wilsonville had a high concentration of quinoline insolubles (22.2%) and ash (11.5%). These characteristics set a limit as to the amount of liquid product that can be expected from the feedstock. Direct delayed coking proved less capable of getting the potential liquid product available from this feedstock than the ASCOTsm process did. This is generally the case, as the ASCOTsm process removes a significant amount of liquid through a nondegrading extraction mechanism before delayed coking's thermal treatment can convert a portion of it to gas and coke products.

Data are reported in Tables 80 and 81. The yield was calculated "as measured," normalized and on a solids-free basis, solids being defined as the quinoline insolubles. This helps in comparing results with Amoco's feedstock, which had a lower solids loading even though the same Black Thunder coal was used.

The liquid yield from direct delayed coking was 50.0 wt%, significantly lower than the >60 wt% from the ASCOT process. On a solids free basis the liquid yield was 64.3 wt%; ASCOTsm produced solids-free yields of 81.4 and 79.0 wt%. Comparing liquid quality criteria, i.e., ash, metals, and sulfur, shows low levels of these impurities, indicating direct delayed coking and ASCOTsm produce good quality product.

The gas yield was desirably low, though higher than ASCOTSM produced, and was comprised mainly of hydrogen and methane with some ethane and propane present. Other hydrocarbons were present in relatively small concentrations. This is consistent with the ASCOTSM data and past results when processing other liquefaction feedstocks.

Direct Delayed Coking Amoco Bottoms Product

The atmospheric bottoms product produced at Amoco from dispersed catalyst liquefaction of Black Thunder coal was directly coked to compare with the results from the Wilsonville feedstock. Tables 82 and 83 summarize the test's operating conditions, material balance, and product characterization.

The Amoco feedstock had characteristics (Tables 71 and 72) that were superior to the feedstock produced at Wilsonville, as most evident by its significantly lower quinoline insoluble (QI) matter. QI material will essentially all end up as solid product in the coke drum. The quinoline soluble portion of a feed will produce liquid product to greater or lesser degree depending on its specific composition. The material balance results bear this out, indicating a 66.5 wt% liquid yield from the Amoco material compared with a 50.0 wt% yield from the Wilsonville feedstock (Table 80). Comparing liquid yields on a solids-free feed basis, although closer, still shows the Amoco feedstock to be superior to Wilsonville's for delayed coking application (71.3% vs. 64.3% liquid yield).

The benefit of the ASCOTSM process in producing liquid product is also apparent from the program's cumulative data. When solvent deasphalting was combined with delayed coking to process the Wilsonville feed, the liquid yield, on a solids-free basis, averaged 80.2 wt% (Tables 76 and 78), a greater yield than was achieved with the superior Amoco feedstock

(Table 83). Even when the high solids loading of the Wilsonville feed is ignored, the liquid yields are fairly close: 62.4 wt% on average, with ASCOTsm vs. 66.5 wt% when directly coking the Amoco feed.

The low metals and ash contents of the oil product from the Amoco feed are consistent with the general quality of liquid product from delayed coking. These impurities are concentrated and found in the solid coke product. The coke, which has a much lower ash content (4.7 wt%) than that produced from the Wilsonville-derived feedstock (averaged 29.9 wt%), could serve as a supplemental solid fuel in an integrated process.

Process Comparisons

Solvent deasphalting of the Wilsonville atmospheric residue in tandem with delayed coking of the resultant asphalt product (ASCOTsm process) can be considered in direct competition with a vacuum distillation in tandem with the ROSEsm process, which was used in Wilsonville.

Wilsonville's Run 262 data on Black Thunder coal was analyzed to determine the combined liquid yield from the vacuum tower and ROSEsm process. This was then compared with the ASCOTsm process and direct delayed coking of the representative atmospheric residue supplied for this program.

The combined liquid yield from the vacuum tower/ROSEsm process was 58.6 wt% (27.2% from vacuum distillation and 31.4% from the ROSEsm process). To compete, this is the yield the ASCOTsm process should meet or exceed. It is felt (by FWDC) that the ASCOTsm process has the advantage of providing greater flexibility to reach a high liquid yield than the ROSEsm process in tandem with a vacuum tower because solvent deasphalting can cut more deeply into a feedstock than a vacuum distillation to better optimize the process.

The two ASCOTsm tests produced overall liquid yields (63.3 wt% and 61.5 wt%) that exceeded the combined liquid yields from the vacuum tower and ROSEsm process. Direct delayed coking of the atmospheric residue fell short, generating a 50.0 wt% yield. Table 84 summarizes the comparison of yields from the atmospheric residue. To look at the results from another perspective, the ROSEsm process at Wilsonville (Run 262) produced 41.4 wt% of undesirable solid product. The two ASCOTsm runs produced 35.3% and 36.1 wt%; direct delayed coking produced 47.2 wt%.

Both elements of the ASCOTsm process, solvent deasphalting and delayed coking, produce a distillate fraction and a smaller resid fraction. Examining the ASTM distillations in Table 75 (deasphalted oil) and Tables 77 and 79 (coker distillate) shows a high temperature tail (>850°F) that can be considered as the practical resid fraction (essentially the bottoms from a vacuum distillation). This fraction was about 40 vol% in both cases and roughly corresponds to ASCOTsm producing about three-quarters and direct delayed coking two-thirds the amount of resid as the ROSEsm process. The theoretical resid fraction defined in the Wilsonville program (the non-distillable fraction at 600°F and 0.1 mm Hg in the laboratory) would be significantly less than actually obtained for all three processes.

Comparing the three processes has shown that the primary technical objective set for the ASCOTsm process was met. Its liquid yield exceeded the combined liquid yield from the vacuum tower and ROSEsm process.

Economic Assessment

A preliminary economic assessment was done by Foster Wheeler USA (FW USA) for the battery limits for two case studies--the ASCOTsm process, employing proprietary technology which integrates Foster Wheeler's solvent

deasphalting and delayed coking technologies and their proprietary SYDEC (Selective Yield Delayed Coking) delayed coking process standing alone, as might be incorporated into an integrated direct coal liquefaction processing scheme.

Each case study includes the following:

- Schematic Process Flow Diagram
- Process Description
- Overall Material Balance
- Summary of Operating Utilities
- Estimated Capital Cost

The objective of the study was to determine how cost competitive the ASCOTSM process is compared with direct delayed coking at and around the projected product yields developed from the test data. The investment cost can also be used for comparisons with other processes which are competing to maximize the production of liquid product.

The actual yields of liquid product achieved during the test program are summarized in Table 85. The economic study covers three levels of liquid product from solvent deasphalting (25, 40, and 50 wt% deasphalted oil) and direct delayed coking (standing alone) producing 50 wt% liquid product, the yield reached through testing.

FW USA calibrated their solvent deasphalting (SDA) and delayed coking models based on the test run data to facilitate the development of a basis for evaluating the economics of providing new battery limits for these services.

The ASCOTsm process was designated as Case 1 and direct delayed coking as Case 2 for the study. Case 1 was further subdivided as follows:

Case 1: 50 wt% DAO yield

Case 1A: 25 wt% DAO yield

Case 1B: 40 wt% DAO yield

Basis of Study

Capacity of the new units, as set in the study basis package, is 713,334 lb/hr of atmospheric residue from liquefied coal feedstock. Assuming 330 operating days/year (on-stream factor of 0.904), the unit feed capacity is 789,086 lb/hr (45,604 BPSD). This capacity is the same for both cases.

As the liquefied coal residue feedstock is very heavy (-12.29°API, 38.1 wt% Conradson carbon), a minimum coke yield operation was selected for the delayed coking sections. A minimum coke yield operation is typified by a low pressure, low recycle type operation.

Physical characteristics for the atmospheric residue derived from liquefied Wilsonville Black Thunder Subbituminous Coal are listed in Table 86. This is the feedstock for the SDA section of the ASCOTsm unit for Case 1, and the SYDEC delayed coking unit for Case 2. For Case 1, the feedstock for the delayed coking section is the asphalt product from the SDA section. The Case 1 asphalt yield is specified in the study as 50 wt%, and the estimated (by SDA model) properties of this asphalt feedstock are listed in Table 87.

Overall theoretical material balances and estimated product characteristics for Case 1 and Case 2 and are given in Tables 88 and 89,

respectively. An on-stream factor of 0.904 was used for a typical run length of 330 days. Additionally, 48 hour coking cycles (24 hours coking and 24 hours decoking) were assumed for all cases. The test run data was used to calibrate the models.

Process Description

The following schematic process flow diagrams are included in Appendix H:

	Figure	Drawing No.
Case 1: ASCOT sm Unit	8	37294-1-50-101
Case 2: Delayed Coker Unit	8	37294-1-50-102

Case 1: ASCOTsm unit is an integration of solvent deasphalting (SDA) and delayed coking technologies. This integration takes advantage of the excess heat generated by the delayed coking section, to supply heat to the SDA solvent recovery section. The ASCOTsm unit described in this study does not include a gas plant for light ends processing.

The liquefied coal residue feed enters the unit and is mixed with the recycle material from the fractionator. The feed and recycle mixture is preheated and fed to a liquid-liquid multistage extraction column. In the extractor, the feed mixture is contacted counter-currently against a solvent (typically a light hydrocarbon). The extract exiting from the top of the extractor is a solution of deasphalted oil (DAO) and solvent. The bottoms product is a mixture asphalt and entrained solvent. The DAO mix is fed to the heater and the solvent recovery unit where the solvent is separated from the DAO. The recovered solvent is recirculated to the extractor. The DAO is combined with coker gas oil, stripped, cooled, and sent to battery limits. The asphalt is fed to the coker section.

In the coker section of the ASCOTSM unit, the asphalt mix is fed to the coker heater where it is partially vaporized. The heater effluent is delivered to the coke drums, where due to a combination of pressure, temperature, and residence time, coke is formed. When the coke drum is filled with coke, the heater effluent is switched to an empty drum and the full drum is decoked. The overhead vapors from the coke drum are sent to the fractionator.

The fractionator typically has three liquid products: unstabilized naphtha, light coker gas oil (LCGO), and heavy coker gas oil (HCGO). A coker off-gas, suitable for fuel gas use after H₂S removal, is also produced. The unstabilized naphtha is typically sent to a gas plant for further processing. The LCGO and HCGO are combined with the DAO and stripped, cooled, and delivered to battery limits. The LCGO, HCGO, and DAO are suitable cracker feedstocks.

Case 2: A typical delayed coker unit is very similar in operation to the delayed coker section of an ASCOTSM unit. The primary differences involve the mixing of the feed and recycle, as well as the increased steam generation. Again, no gas plant has been provided.

The feed to the coker unit is preheated against the pumparound and hot product streams before entering the bottom of the coker fractionator. In the bottom of the tower, the feed mixes with the recycle liquid condensing in the tower. The feed and recycle mixture is fed to the coker heater and then to the coke drums. Coke is produced in the coke drums, and the overhead vapors flow to the coker fractionator.

Again, there are typically three liquid products in the coker fractionator: unstabilized naphtha, LCGO, and HCGO. A coker off-gas is also produced. The pumparound and product rundown circuits are used for steam

generation rather than integration with the SDA section as in the ASCOT unit. The unstabilized naphtha is typically sent to a gas plant, and the LCGO and HCGO are sent to a cracking unit for further processing.

Utility Summary: The estimated utility requirements, based on existing units whenever possible, for both cases are in Table 90. Actual utility requirements will depend upon finalized heat and material balances as well as downstream processing requirements.

Economic Evaluation:

From the material balances and unit descriptions, curve type total installed cost estimates were developed for both cases. FW USA's Estimating Department prepared cost estimates for the units involved in this study, and the results are summarized as follows:

Case 1 ASCOTsm Process (50 wt% DAO)

ASCOTsm Unit: SDA section processing 45,604 BPSD of atmospheric residue and delayed coker section processing 18,793 BPSD asphalt and producing 3,508 STPD coke.

Installed Cost: \$220 Million

Case 2 Direct Delayed Coking

Delayed Coker Unit: Processing 45,604 BPSD feed and producing 4,761 STPD coke.

Installed Cost: \$212 Million

The estimates include an open type coke collection system, which is a concrete pit with an overhead crane; no further coke handling or storage is included. The estimates do not include a gas plant or coker gas compressor.

Additionally, two other ASCOTsm cases, Alternate A and Alternate B, were developed:

Case 1: Alternate A was an ASCOTsm unit with the SDA section operating at 25 wt% DAO yield. Case 1, Alternate B was an ASCOTsm unit with the SDA section operating at 40 wt% DAO yield. The cost estimates for these units are as follows:

Case 1, Alternate A: ASCOTsm Process (25 wt% DAO)

ASCOTsm Unit: SDA section processing 45,604 BPSD of atmospheric residue and delayed coker section processing 32,345 BPSD asphalt and 3,862 STPD coke.

Installed Cost: \$230 Million

Case 1, Alternate B: ASCOTsm Process (40 wt% DAO)

ASCOTsm Unit: SDA section processing 45,604 BPSD of atmospheric residue and solvent, delayed coker section processing 23,887 BPSD asphalt and producing 3,697 STPD coke.

Installed Cost: \$225 Million

These costs were used as points to develop a graph (Figure 97) of DAO yield vs. installed cost for ASCOTsm units operating on this feedstock. A

reference line showing the cost of the direct delayed coking unit is also included.

These are conceptual estimates of $\pm 30\%$ accuracy, battery limits process units, based on U.S. Gulf Coast, second quarter 1994, instant execution philosophy, through mechanical completion only, and assumes that land is free of above and underground obstructions. Excluded are cost of land, process licensor fees, taxes, royalties, permits, duties, warehouse spare parts, catalysts, forward escalation, support facilities, and all client costs.

The typical percentage breakdown for the bottom-line estimates is as follows:

Process Equipment	28%
Bulk Commodities (steel, concrete, etc.)	22%
Labor	32%
Engineering	<u>18%</u>
Total	100%

Conclusions:

The conclusions drawn from FWDC's alternative bottoms processing test program are:

- The primary technical objective was met. The average liquid yield from Foster Wheeler's ASCOTsm process (62.4 wt%) exceeded the combined liquid yield from the vacuum tower (vacuum distillate) and ROSE-SRsm (Residuum Oil Supercritical Extraction--Solids Rejection) process (58.6 wt%) as operated at DOE's Wilsonville facility. The basis for comparison was the atmospheric residue

from liquefying Black Thunder subbituminous coal as feedstock for both scenarios.

- The ASCOTsm process produces a high quality liquid product. There are very low levels of metals, sulfur and ash present. High levels of sulfur and metals indicate a need for additional steps or potential problems in downstream processing of petroleum substitutes. Corrosion and catalyst deactivation can occur in their presence, leading to operating problems, and lower yield and quality products.
- Direct delayed coking of the Wilsonville feedstock (atmospheric residue) cannot produce as much liquid product as vacuum distillation in tandem with the ROSE-SRsm process or the ASCOTsm process.
- The coal liquefaction bottoms product (atmospheric residue) generated by Amoco in the course of this program was superior to the Wilsonville atmospheric bottoms used as feedstock during the program. The levels of ash, sulfur, quinoline insolubles, and Conradson carbon residue were all significantly lower in the Amoco material.
- The Amoco bottoms used by FWDC as feedstock, as follows from the above conclusion, better met the program objective to produce more liquid product from bottoms processing. However, it was generated in small quantity at Amoco's research facility and may not be representative of what would come from more extensive operation of an advanced, integrated process.

- The practical feeding limitations associated with the pilot plant set the maximum level of solids loading and associated softening point of the asphalt that could be test coked during the ASCOTsm process study. Solvent deasphalting can produce more concentrated asphalt products (lower yields) which make the ASCOTsm process more economical and would most likely improve upon the liquid yield attained in this program.

Recommendations:

- Investigate and modify the delayed coking pilot plant's front-end feeding system to handle asphalts with higher solids loadings and softening points.
- Evaluate the ASCOTsm process at higher deasphalted oil yields and associated heavier asphalts for coking than in the present program.
- Evaluate the ASCOT process with feedstocks other than the bottoms product generated at Wilsonville from Black Thunder subbituminous coal.
- Complete a technical and economic assessment based on the test program's findings and integration into an advanced liquefaction concept. The coking cycle, which incorporates a continuous feeding period, a steam-out period, cooldown, and decoking, would have to be addressed and the proper number of trains determined for a defined integration scheme.

Task 3.0: Technical Assessment

In this task economic evaluation was done on both bottoms processing options (ASCOT and delayed coker) and on SO₂-treatment of Black Thunder coal.

I. Economic Evaluation of the Alternative Bottoms Processing Options

Background:

The delayed coker and ASCOT alternative bottoms processing options were evaluated based on the low rank coal base case.⁽³²⁾ This study developed a conceptual design for a mine mouth, direct coal liquefaction plant that processes 24,951 tons/day (dry basis) of Wyoming Black Thunder sub-bituminous coal. Figure 98 shows a simplified block flow diagram of the base case plant.

The original Baseline Design and System Analysis contract developed a baseline case for the direct liquefaction of Illinois No. 6 coal and for seven optional processing schemes.⁽³³⁾ In the fifth optional processing scheme, Plant 8-1, the ROSE-SR solids/liquid extraction plant, was replaced with a fluid coking plant as shown in Figure 99. In this design, no material is recycled to the coal liquefaction plant for further upgrading. All materials leaving Plan 8-2, the fluid coking plant, are sent downstream for product recovery, further processing, or to the hydrogen production by coal gasification plant, Plant 9.

In developing this option, the following assumptions were made.

- The gas oil fraction from the vacuum tower is recycled to the coal liquefaction reactors to maintain the same solvent to maf coal ratio as the base case.

- The coker liquid is fractionated and mixed with the respective coal liquefaction plant products for hydrotreating purposes. However, since the percentages of these additions are small, no changes were considered for the operating conditions of the naphtha and gas oil hydrotreaters.

- The naphtha and gas oil hydrotreater yields are unaffected by the addition of the coker products and are the same as they were in the base case.

Figure 99 shows not only the process flow scheme for the fluid coking case, but it also shows the flow rates of the major streams for the Illinois No. 6 coal design.

In addition, ASPEN process simulation models of all the baseline and low rank coal cases were developed.^(33,34) These process simulation models generate material balances for the entire coal liquefactions complex, calculate the utilities requirements and number of operators, and estimate the total installed cost of the complex. The original process simulation models were developed on the ASPEN/SP process simulation program and later converted to the ASPEN PLUS process simulation program. The low rank coal simulation models were developed on the ASPEN PLUS process simulation program from the converted original models.

Although these ASPEN process simulation models do not exactly match the process designs from which they were developed, they do provide a more than adequate representation of them. Differences between the design and model predictions generally are less than 0.1% for the flow rates of the major streams, and the capital cost predictions are within 1%. These differences are well within the uncertainties of the process design. For consistency in this evaluation, all comparisons are based on model predictions for the low rank coal case rather than the design values.

Economics studies were performed for the above cases using a LOTUS spreadsheet economics model.^(34,35) This spreadsheet model does a detailed cash flow analysis for a 29 year project consisting of 4 years of construction followed by 25 years of operation. It was developed to analyze the economics of various coal liquefaction processes under various economic scenarios using results generated by the process simulation models. The primary results from this spreadsheet model are the crude oil equivalent (COE) price, which will generate a 15% return on investment for the entire project, and the net present value of the project at a 15% rate of return on equity for a given product selling price.

Bechtel's linear programming tool, PIMS (Process Industry Modeling System), was used to develop a relationship between the value of the coal liquid products and that of crude oil.⁽³⁶⁾ This was done by simulating a typical PADD II (Midwestern) refinery and allowing the coal liquids to be brought in as alternate feeds to the naphtha reforming or fluid catalytic cracking units, or as blendstocks.

Process Modeling:

Because the delayed coking bottoms processing option is similar in structure to the fluid coking option of the original baseline design study for Illinois No. 6 coal, it was decided to use this methodology to evaluate these two alternate bottoms processing options. Thus, there will be no recycle of material from either the delayed coker or the ASCOT unit to the coal liquefaction plant. All material entering these units will go either to fuel gas, to the gasification plant for hydrogen production, or to product recovery, purification, or further upgrading.

Implicit in this assumption is that an internal gas oil stream is produced within the coal liquefaction plant that is recycled to the coal liquefaction reactors to maintain the same solvent to maf coal ratio as the base case. Also, it was assumed that the material withdrawn which

goes either to the delayed coker or to the ASCOT unit does not alter the net yields from the coal liquefaction plant. In addition, the other assumptions associated with the fluid coker option are applicable.

To implement this approach, a preliminary version of the ASPEN process simulation model for the low rank coal baseline case was modified to replace Plant 8-1, the ROSE-SR solid/liquid extraction plant, with Plant 8-2, the fluid coking plant. Besides the plant substitution, this revision involved modifying the flowsheet connectivity within the model, adjusting the initial flow rates of several streams, and changing the flowsheet convergence logic.

Two new alternate FORTRAN user block models were developed as substitutes for Plant 8-2. The first, Plant 8-3, was developed to represent the delayed coking unit. The second, Plant 8-4, was developed to represent the ASCOT unit. These additional alternate user models were generated by developing new parameters for the original fluid coker empirical yields model to represent these new alternate bottoms conversion units.

This empirical yields model essentially consists of a set of distribution factors which reflect the appearance or disappearance of each pure component or boiling range cut as it passes through the unit. For example, all the unreacted coal disappears and is converted to coke. The appropriate parameters were developed using the feed and product distributions as reported by Foster Wheeler. This model formulation works well when there are small perturbations in the entering feedstock composition from the design basis. For large feedstock composition changes, improper yield predictions can be generated. Finally, appropriate parameters were developed to represent the utilities consumptions and ISBL (inside battery limits) field cost as a function of plant capacity. To scale the unit cost as a function, an exponential cost scaling factor of 0.75 was assumed for each case.

The FORTRAN user block model for Plant 2, the coal liquefaction plant, was modified to represent the revised product fractionation system for these new cases. The net atmospheric bottoms column product goes either to the delayed coker, Plant 8-3, or the ASCOT unit, Plant 8-4. This modification involved supplying revised component distribution factors in the product fraction section to put all the atmospheric tower bottoms into the bottoms stream which is routed to either Plant 8-3 or Plant 8-4. Thus, the overall configuration of the resulting process flowsheet is essentially identical to Figure 99 except that either Plant 8-3, the delayed coker, or Plant 8-4, the ASCOT unit, is substituted for Plant 8-2.

Table 91 summarizes the results of the computer simulation runs for these two alternate bottoms processing options and compares them with the model predictions for the low rank coal baseline case which uses Kerr-McGee's ROSE-SR unit. The top portion of this table provides an overall material balance for each of the three cases. Both the delayed coker and ASCOT cases consume more coal, natural gas, and raw water than the baseline case. They also cost more and require more operators and boardmen. However, they also produce more C_4+ liquid product. The ASCOT case produces 74,020 bbl/day of C_4+ liquid product which is 6789 bbl/day more than the baseline case. The delayed coker case produces 71,607 bbl/day of C_4+ liquid product which is 4376 bbl/day more than the baseline case. The ASCOT case produces 2.71 bbl of C_4+ liquids per ton of maf coal, whereas both the baseline and delayed coker cases produce about 2.69 bbl of C_4+ liquids per ton of maf coal.

The middle portion of the table shows the feed rate to and product rates from the three bottoms processing units. In this implementation, the feed to both the delayed coking and ASCOT plants is lighter than the design feed used to generate the model parameters, and therefore, these results are not exactly correct. The delayed coker option produces somewhat less coke, 48.5 wt%, than the design value of 50.3 wt%. This is reasonable since the feed is lighter than the design feed. However, the ASCOT unit

produces 41.9 wt% coke compared with the design value of 37 wt% coke. This overprediction in the amount of coke production is a result of the feedstock difference between that used for developing the empirical model and the lighter feedstock in this case. In retrospect, these bottoms processing options would have been better evaluated using a design similar to that of the baseline case where there is a recycle stream between the bottoms processing unit and the coal liquefaction plant. The economic effect of this coke overprediction in the ASCOT case will be discussed later.

The lower portion of the table compares the utilities consumptions and operator requirements for the three cases. Both the delayed coking and ASCOT cases consume more utilities and require more operators than the baseline case. The ASCOT case requires 52 operators for 24 hour operation, and the delayed coker case requires 24 operators, whereas the baseline ROSE-SR case requires only 8 operators.

The ISBL field cost for the ASCOT plant is \$166.4 MM; that for the delayed coker plant is \$160.4 MM; and that for the ROSE-SR unit is only \$33.4 MM. However, the differences in the total installed capital costs given near the top section of the table are much larger than these individual unit cost differences reflecting the increased costs of most of the other ISBL processing plants and the OSBL (outside battery limits) plants. For example, the \$6.0 MM difference in ISBL field cost between the ASCOT and delayed coker plants increases to \$37.5 MM for the entire complex because of the additional 2413 bbl/day of liquid products.

Economics Calculations:

The three processing cases just described were evaluated using the LOTUS spreadsheet economics model with the same optimistic assumptions that were used for all the other economic evaluations.⁽³⁵⁾ These assumptions are shown in Table 92, which is the LOTUS economics model summary for the low

rank coal baseline case at a 15% return on investment. Many of these economics assumptions were specified in the original statement of work for the Illinois No. 6 coal project. For consistency, they were maintained at the same values for all subsequent economic evaluations.

The same syncrude premium factors that were developed from the PIMS modeling of a typical PADD II refinery also were used for these cases. No price adjustments were made for transporting the products from Wyoming to a petroleum refinery for further upgrading.

The pertinent ASPEN process simulation model results are shown in the top section of the first page of Table 92. The remainder of this page contains some base year costs and other economics items. The Nth plant assumption is reflected in the high operating factor and the rapid initial start-up of the plant in the first three years of operation.

The second page of Table 92 contains the values of the products and some other economic parameters. The top line, labeled REF. CRUDE (PADD II), \$/BBL (BASE YR), is the crude oil equivalent price (COE) in the base year that is required to generate a 15% return on investment. It is shown as \$32.74/bbl for this low rank coal baseline case. The SC. PREM and SC, \$/BBL items listed in the little table at the top right of the second page are the average calculated syncrude premium and the average required syncrude selling price for a 15% return on investment, respectively. This average required syncrude selling price is essentially the cost of production including that of capital at a 15% return on investment. It is calculated by multiplying the crude oil equivalent price in the base year by the average syncrude premium.

The LOTUS spreadsheet summaries are not shown for the delayed coker and ASCOT cases because they contain little additional information other than that given in Tables 91 and 92.

In the following discussion, all calculated crude oil equivalent prices are being rounded to the nearest \$0.05, which is well within the accuracy of the calculations.

The calculated crude oil equivalent prices for all three cases are shown in the last line of Table 91. The crude oil equivalent price for the delayed coker case is \$33.50/bbl, which is \$0.75/bbl above the baseline case value of \$32.75/bbl. This is a somewhat optimistic value because the coker gas oil contains about 16% of 1000+°F material, and it was evaluated as if it all were 850-°F material as in the low rank coal baseline case. Generally, 1000+°F material (resid) has a value of about 70 to 90% of crude oil. Because this case is not economically advantageous compared with the baseline case, no attempt was made to quantify the effect of this higher boiling material on the COE.

The calculated crude oil equivalent price for the ASCOT case is \$32.85/bbl, which is \$0.10/bbl above the low rank coal baseline case. Within the accuracy of the calculations, this is essentially the same value as that of the baseline case.

However, by extrapolation, the COE was estimated for a case closer to the design case which produced 37 wt% coke. It was \$32.35/bbl or \$0.50/bbl less than the baseline case. This case would consume 27,876 tons/day of dry coal, generate 75,735 bbl/day of C₄+ product, and cost \$4108 MM.

In all of the above cases, the same annual catalyst cost of \$80 MM was assumed. If the annual catalyst cost is proportional to the C₄+ liquid's production rate, the annual catalyst cost for the ASCOT case would be \$88 MM. From a sensitivity study, this would increase the COE by \$0.29/bbl. However, this is probably an overcorrection since there would be no change in the catalyst cost of Plant 2, the coal liquefaction plant, since the same amount of coal is liquefied in all cases.

Adjusting the ASCOT extrapolated coke case by the calculated \$0.32/bbl for the increased catalyst cost would raise the COE to \$32.65/bbl. However, the true COE is somewhere between the adjusted and unadjusted values, or about \$32.50/bbl.

Summary:

The delayed coker and ASCOT bottoms processing options were evaluated as optional processing options for the low rank coal baseline case.

Empirical yield models were developed based on Foster Wheeler's designs and evaluated in the same manner as the fluid coker option was evaluated in the Illinois No. 6 coal baseline study case.

The delayed coker case cost \$160.4 MM more than the low rank coal baseline design case, and had a calculated crude oil equivalent price of at least \$33.50/bbl. This COE is \$0.75/bbl above the low rank coal baseline design case.

The ASCOT case cost \$166.4 MM more than the low rank coal baseline design case and had a calculated crude oil equivalent price of at least \$32.85/bbl. This COE is \$0.10/bbl above the low rank coal baseline design case. However, after adjusting this case to a more appropriate coke make and for increased catalyst cost, the COE is about \$32.50/bbl, or roughly \$0.25/bbl less than the low rank coal baseline design case.

In retrospect, perhaps it would have been better to evaluate these two options as a direct substitute for Kerr-McGee's ROSE-SR unit with material being recycled to the coal liquefaction plant for further upgrading. This situation corresponds to Foster Wheeler's design basis, and the empirical models which were developed should better reflect the design.

Furthermore, such an evaluation should be more favorable for the ASCOT process since it should reduce the amount of liquefied material going to

the gasifier for hydrogen production and result in a lower crude oil equivalent price.

II. Economic Evaluation of Coal Cleaning with Sulfurous Acid

Background:

In 1994, Bechtel developed a conceptual design for a mine mouth, direct coal liquefaction plant processing 24,951 tons/day (dry basis) of Wyoming Black Thunder sub-bituminous coal.⁽³²⁾ Figure 98 shows a simplified block flow diagram of this low rank coal liquefaction plant.

The original Baseline Design and System Analysis contract developed a baseline case for the direct liquefaction of Illinois No. 6 coal and for seven optional processing schemes.⁽³³⁾ In addition, ASPEN process simulation models of all the baseline and low rank coal cases were developed.^(33,34) These process simulation models generate material balances for the entire coal liquefactions complex, calculate the utilities requirements and number of operators, and estimate the total installed cost of the complex. The original process simulation models were developed on the ASPEN/SP process simulation program and later converted to the ASPEN PLUS process simulation program. The low rank coal simulation models were developed on the ASPEN PLUS process simulation program from the converted original models.

Although these ASPEN process simulation models do not exactly match the process designs from which they were developed, they do provide a more than adequate representation of them. Differences between the design and model predictions generally are less than 0.1% for the flow rates of the major streams, and the capital cost predictions are within 1%. These differences are well within the uncertainties of the process design. For consistency in this evaluation, all comparisons are based on model predictions for the low rank coal case rather than the design values.

Economics studies were performed for the above cases using a LOTUS spreadsheet economics model.^(34,35) This spreadsheet model does a detailed

cash flow analysis for a 29 year project consisting of 4 years of construction followed by 25 years of operation. It was developed to analyze the economics of various coal liquefaction processes under various economic scenarios using results generated by the process simulation models. The primary results from this spreadsheet model are the crude oil equivalent (COE) price, which will generate a 15% return on investment for the entire project, and the net present value of the project at a 15% rate of return on equity for a given product selling price.

Bechtel's linear programming tool, PIMS (Process Industry Modeling System), was used to develop a relationship between the value of the coal liquid products and that of crude oil.⁽³⁶⁾ This was done by simulating a typical PADD II (Midwestern) refinery and allowing the coal liquids to be brought in as alternate feeds to the naphtha reforming or fluid catalytic cracking units, or as blendstocks.

In 1993, Cronauer reported results of beneficiating Wyoming Black Thunder coal with sulfurous acid.⁽³⁷⁾ Based on these results, the economics of beneficiating Wyoming Black Thunder coal was studied by modifying the previously developed ASPEN process simulation model for the low rank coal base case to include SO₂ coal cleaning.

Process Modeling:

A preliminary version of the ASPEN process simulation model for the low rank coal baseline case was modified to add SO₂ coal cleaning. In this case, Plant 1, the coal cleaning and preparation plant, includes coal grinding, and Plant 1.4 is only a coal drying plant. The coal beneficiation with sulfurous acid step was added to Plant 1.4. Empirical distribution factors were developed to represent the SO₂ beneficiation of Wyoming Black Thunder coal as reported by Cronauer.⁽³⁷⁾ These factors allow the model to adjust for different coal compositions. Appropriate

utility consumption and cost factors also were developed to represent this revised plant configuration.

Figure 100 shows the additional equipment required between the coal grinding and the coal drying steps for the SO_2 coal cleaning operation. The ground coal in Stream 2 is washed for 10 minutes in a stainless steel treater with a 5 wt% sulfurous acid solution produced by dissolving SO_2 gas in water. The treated coal which leaves in Stream 6 is dewatered on a belt filter. The dewatered coal in Stream 7 is then dried in a nitrogen atmosphere to 2 wt% moisture before going to the liquefaction plant.

The filtrate stream (Stream 8), containing excess SO_2 and a mixture of sulfate and bisulfite salts, passes to an aerator where the various sulfur anions are oxidized to precipitate sulfate salts. Five minutes of residence time is provided in the aerator. A Lamella separator concentrates the sulfate salts into a reject stream, Stream 15, which is mixed with the fines from the size beneficiation unit in Stream 3 to form Stream 16. This stream is sent to Plant 9, the hydrogen production by coal gasification plant.

The SO_2 is obtained from the combustor in the sulfur recovery plant, Plant 11. The SO_2 storage tank shown in Figure 100 is sized to maintain a sufficient reserve supply for five days of operation.

From a previous study for similar coal cleaning operation, the cost of the additional equipment required to produce 1494 Mlb/hr of SO_2 beneficiated coal was estimated to be \$32.1 MM during the fourth quarter of 1993.⁽³⁸⁾

No additional beneficiation procedures, such as a sink/float gravity separation or agglomeration procedures, were included because they were not proven to be effective.

Table 93 shows the overall material balance for the coal grinding and SO₂ cleaning operations producing the same amount of dry cleaned coal as the low rank coal baseline case, 1643.5 Mlb/hr. In this table, all flows are given on a dry basis. As shown, 84.0 wt% of the entering dry coal is recovered as cleaned coal. The ash content of the cleaned coal is reduced from 6.3 wt% (dry basis) to 3.5 wt%. However, the sulfur content of the cleaned coal increases to 0.8 wt% from 0.5 wt%.

The SO₂ beneficiation section of this plant consumes an extra 1800 KW of electric power and requires one additional operator per shift per plant train compared with the low rank coal baseline design case. Table 93 also shows the utilities consumptions, operator requirements, and cost for the SO₂ coal cleaning and drying plant.

Figure 101 shows how this modified SO₂ coal cleaning and drying plant is integrated into the entire coal liquefaction complex. Two additional streams are needed. The first is an SO₂ stream that is generated in the combustor section of the Claus plant and is sent to the modified Plant 1.4. The second is a stream containing the reject fines from the coal cleaning operation that goes to the coal gasification plant. In the baseline design case, the fines from the coal grinding operation in Plant 1 were not segregated, and from a material balance standpoint, it was immaterial whether they went either to the coal liquefaction plant or to the coal gasification plant. When SO₂ cleaning is used, the fines stream now is sent to the coal gasification plant, Plant 9, for hydrogen production.

In developing the SO₂ coal cleaning case designs, it was assumed that the net sulfur production would be reduced by 15% to account for losses associated with the SO₂ coal cleaning operations.

In the following analysis, generally, the cost and utility predictions generated by the model were used without adjustment. However, manual

adjustments were required for the cost of the coal liquefaction plant in each of the two coal cleaning cases. These adjustments were made assuming that the coal liquefaction reactor section represented 60% of the Plant 2 cost, and the product separation and recycle gas compression sections were 27% of the cost.

Table 94 compares the results of the computer simulation model runs for the low rank coal baseline design case and with those for two SO₂ coal cleaning cases. SO₂ coal cleaning case A has the same dry clean coal rate to Plant 2, the coal liquefaction plant, as the low rank coal baseline design case. SO₂ coal cleaning case B uses a 10% higher coal feed rate to Plant 2.

SO₂ coal cleaning case A was developed assuming that the coal liquefaction reactors in Plant 2 would give the same 92.7% coal conversion as the baseline design case at the same coal feed rate. Thus, because of the SO₂ coal cleaning step, more pounds of carbon, hydrogen, and sulfur are fed to the coal liquefactions reactors because the coal contains less ash. Consequently, more liquid products are produced.

Case A uses more coal than the baseline case because of the additional products that are produced during coal liquefaction and for generation of more hydrogen in Plant 9, the hydrogen production by coal gasification plant. The net result is that an additional 1609 tons/day of dry coal produce an extra 1909 bbl/day of C₄+ products.

Although the coal liquefaction section of Plant 2 is identical in these two cases, the cost of the entire coal liquefaction plant increases by about \$4.3 MM to account for the increased cost of the recycle gas compression and product separation sections.

Because there is a smaller amount of ash entering the coal liquefaction plant, the ROSE-SR solvent deashing plant receives about 5% less feed.

This results in a smaller ash concentrate stream being sent to the gasification plant and a larger deashed residuum stream being recycled to Plant 2.

The total installed capital cost of SO₂ coal cleaning case A is \$3856 MM, whereas that of the low rank coal baseline case is \$3692 MM. Some of this increased cost is attributable to the generally larger size of many of the processing plants, and some is from the need to build additional trains for Plant 1 (coal cleaning and preparation plant), Plant 9 (coal gasification plant), and Plant 10 (air separation plant). The net result is a higher capital cost per barrel of C₄+ product of \$55.3 M/bbl for coal cleaning case A compared to \$54.9 M/bbl for the low rank coal baseline case.

SO₂ coal cleaning Case B was developed assuming that the coal liquefaction reactors in Plant 2 would give the same 92.7% coal conversion as the baseline design case but at a 10% increased coal feed rate. As expected, this case produces more liquid products, consumes more coal, and costs more.

The ISBL field cost of the coal liquefaction plant for coal cleaning Case B is \$22.3 MM larger than that of the baseline design case because of the larger coal handling, recycle gas compression, and product separation sections. The cost of the coal liquefaction reactor section is unchanged from that of the other two cases.

The capital cost per barrel of C₄+ product drops to \$55.0 M/bbl for this case because of the improved efficiency of the coal liquefaction reactors in Plant 2. This is not below that of the low rank coal baseline case because some more additional trains were required in Plant 6.1 (hydrogen purification by membrane permeation plant) and Plant 10 (air separation plant).

Economics Calculations:

The three processing cases just described were evaluated using the LOTUS spreadsheet economics model with the same optimistic assumptions that were used for all the other economic evaluations.⁽⁵⁾ These assumptions are shown in Table 95, which is the LOTUS economics model summary for the SO₂ coal cleaning case A at a 15% return on investment. Table 92 is the corresponding model summary for the low rank coal baseline case. Many of these economics assumptions were specified in the original statement of work for the Illinois No. 6 coal project. For consistency, they were maintained at the same values for all subsequent economic evaluations.

The same syncrude premium factors that were developed from the PIMS modeling of a typical PADD II refinery also were used for these cases. No price adjustments were made for transporting the products from Wyoming to a petroleum refinery for further upgrading.

The pertinent ASPEN process simulation model results are shown in the top section of the first page of Table 95. The remainder of this page contains some base year costs and other economics items. The Nth plant assumption is reflected in the high operating factor and the rapid initial start up of the plant in the first three years of operation.

The second page of Table 95 contains the values of the products and some other economic parameters. The top line, labeled REF. CRUDE (PADD II), \$/BBL (BASE YR), is the crude oil equivalent price (COE) in the base year that is required to generate a 15% return on investment. It is shown as \$33.72/bbl for this coal cleaning case. The SC. PREM and SC, \$/BBL items listed in the little table at the top right of the second page are the average calculated syncrude premium and the average required syncrude selling price for a 15% return on investment, respectively. This average required syncrude selling price is essentially the cost of production including that of capital at a 15% return on investment. It is calculated

by multiplying the crude oil equivalent price in the base year by the average syncrude premium.

The LOTUS spreadsheet summary is not shown for SO₂ coal cleaning Case B since it would contain little additional information other than that given in Tables 94 and 95.

In the following discussion, all calculated crude oil equivalent prices are being rounded to the nearest \$0.05, which is well within the accuracy of the calculations.

The calculated crude oil equivalent prices for all three cases are shown in the last line of Table 92. The crude oil equivalent price for SO₂ coal cleaning Case A is \$33.70/bbl, which is \$0.95/bbl above the baseline case value of \$32.75/bbl. This higher COE is mainly attributable to the higher capital requirement per barrel of product than that of the baseline case.

The calculated crude oil equivalent price for the SO₂ coal cleaning Case B is \$33.00/bbl, which is \$0.25/bbl above the baseline case value of \$32.75/bbl. Even though this case assumed a 10% increase in coal reactivity, it was not enough to compensate for the increased capital and operating costs of the coal cleaning operation and those of processing the additional product.

Conclusions:

This analysis has shown that SO₂ coal cleaning is not economically attractive compared with the low rank coal baseline case even when it increases the reactivity of the coal by 10% over the base case. However, it has a crude oil equivalent price that is only \$0.25/bbl above the low rank coal baseline case.

By extrapolation from the two SO₂ coal cleaning cases that were run, it appears that SO₂ coal cleaning will be economic if the coal reactivity could be increased by 17%.

CONCLUSIONS AND RECOMMENDATIONS

1. Aqueous SO₂ treatment of Black Thunder coal reduced the ash level to 4 wt%; further reduction to 2 wt% was obtained using agglomeration and froth flotation.
2. Coals with varying rank (bituminous, subbituminous, lignite) can be swollen by a number of solvents, where the most effective ones are those with hetero-functionality. A synergistic effect was demonstrated with solvent blends, which were more effective for coal swelling than pure solvents.
3. During simultaneous swelling and impregnation, catalyst uptake into coal is higher when a nonswelling solvent (toluene) or higher impregnation temperature is used. Molyvan L precursor has more extensive uptake into coal than Mo octoate.
4. STEM/EDXS analysis determined that Mo in Molyvan L-impregnated samples was finely dispersed, whereas Mo octoate as a precursor caused higher surface concentration in coal particles. Some degree of surface concentration was seen in Molyvan L-impregnated SO₂-treated coal samples, which seemed to have higher concentrations of impurities, including coke.
5. Some enhancement in initial coal conversion was seen when Black Thunder coal was treated with SO₂ and liquefied with slurry catalysts. Using hydrogen donor as a liquefaction solvent was also beneficial. Noncatalytic reactions showed no benefit from SO₂ treatment.
6. Coupling SO₂ treatment with coal swelling and slurry catalysts showed no benefit; however, liquefying untreated swollen Black Thunder coal

with no catalyst had a higher coal conversion than that of nonswollen coal.

7. Simultaneous coal swelling and catalyst impregnation was detrimental to coal and pyrene conversion in both batch and continuous pilot plant experiments.
8. Swelling solvent type and length of swelling influenced the catalyst conversion activity. Most catalysts, such as Molyvan L, had the highest activity when they were added directly into the liquefaction reactor, i.e. had minimal contact with the swelling solvent. Generally Mo catalysts had the highest activity followed by Ni and Co catalysts.
9. Unlike the differences seen in the batch studies at low severity (770°F), the effects of swelling and catalysts were minimal in a continuous operation. However, a considerable increase in Black Thunder coal conversion (to about 90%) was seen at 800°F and long residence time (3 hr) with Molyvan L and SO₂-treated swollen coal. Similar coal conversion was seen in earlier results (previous DOE contract) with untreated Black Thunder coal, Molyvan L, and similar operating conditions. When the operating temperature was increased to 825°F, the coal conversion results were worse, probably due to retrogressive reactions.
10. Long-term deactivation experiment showed that although SO₂-treated coal had higher initial activity, its deactivation was more severe than that of untreated Black Thunder coal. These experiments were done using supported AMOCAT™ 1C catalyst.
11. There was no increase in coal conversion or hydrogenation when Illinois No. 6 coal was either swelled or Molyvan L was introduced during swelling step.

12. The average liquid yield from Foster Wheeler's ASCOT process exceeded that of Wilsonville's process (vacuum tower and ROSE unit) and that of delayed coking.
13. The liquid product from ASCOT process is of high quality.
14. The coal liquefaction bottoms product generated by pilot plants at Amoco was superior to that of Wilsonville.
15. The economic analysis of delayed coker and ASCOT cases showed that the calculated crude oil equivalent cost for delayed coker case was \$33.50/bbl, which is \$0.75/bbl above the low rank coal baseline case, whereas for ASCOT it was \$32.50/bbl, which is \$0.25/bbl below the baseline case.
16. SO_2 treatment is not economically attractive compared to low rank coal baseline even when it increases the reactivity of coal by 10%. An about 17% increase in reactivity is needed for this treatment to be economic.

ACKNOWLEDGEMENTS

This work is being supported by the United States Department of Energy under Contract DE-AC22-91PC91051. Appreciation is particularly extended to Mr. C. Gutterman of Foster Wheeler Development Corporation, Dr. C. W. Curtis of Auburn University, Dr. S. Chander of Pennsylvania State University, Dr. K. D. Vorres from Argonne National Laboratory, and Dr. H. W. Haynes, Jr., from the University of Wyoming for participating in this program. Appreciation is also due to S. J. Kramer and J. E. Myers for carrying out the economic analysis. Special thanks are due to Dr. R. J. Torres-Ordonez for coordinating the laboratory work on catalyst swelling and impregnation studies, and L. R. Guerine for the pilot plant work and analysis of the data. M. D. Manila, R. Cervantes, and D. B. Nolan deserve thanks for their diligence and efforts in the pilot plant work.

REFERENCES

1. Derbyshire, F. J. "Catalysis in Coal Liquefaction: New Directions for Research"; IEACR/08, IEA Coal Research, London, June 1988.
2. Charcosset, H.; Genard, A. "Catalysis in Direct Coal Liquefaction"; EUR11191, Comm. Eur. Communities, Synth. Fuels Coal, 1987, pp 339-381.
3. Narain, N. K.; Cillo, D. L.; Stiefel, G. J. Tischer, R. E. "Disposable Catalysts in Coal Liquefaction"; in *Coal Science and Chemistry*, Volborth, A. (Ed.), Elsevier, Amsterdam, 1987, pp 111-149.
4. Crank, J. "Diffusion with Rapid Irreversible Immobilization"; *Trans. Faraday Soc.*, 1954, 53, 1083-1091.
5. Cronauer, D. C.; Swanson, A. J. *ACS Preprints, Fuel Chem. Div.*, 1991, 36(1), 67.
6. Cronauer, D. C.; Joseph, J. T.; Davis, A.; Quick, J. C.; Luckie, P. T. *Fuel*, 1992, 71, 65-73.
7. Cronauer, D. C.; Swanson, A. J.; Valente, A. M. Presentation, EPRI Contractor's Meeting, Palo Alto, CA, May 1991.
8. Ollendorff, R. L.; Cronauer, D. C.; Swanson, A. J.; Sajkowski, D. J. DOE Final Technical Report, 1992, Contract No. DEAC22-88PC-88819.
9. Joseph, J. T.; Forrai, T. R. *Fuel*, 1992, 71, 75-80.
10. Joseph, J. T. *Fuel* 1991, 70, 139-144.
11. Vahrman, M. *Fuel*, 1970, 49, 5-16.

12. Palmer, T. J.; Vahrman, M. *Fuel*, 1972, 51, 22-26.
13. Shapiro, L-L. D.; Al'terman, L. S. *Solid Fuel Chem.*, 1977, 11(3), 13-17.
14. Larsen, J. W.; Lee, D.; Shawver, S. E. *Fuel Process. Techn.*, 1986, 12, 51-62.
15. Larsen, J. W.; Shawver, S. E. *Energy Fuels*, 1990, 4, 74-77.
16. Jones, J. C.; Boother, M.; Brown, M. *J. Chem. Tech. Biotechnol*, 1991, 52, 257-264.
17. Van Krevelen, D. W. *Coal*, Elsevier, Amsterdam, 1961; and *Fuel*, 1966, 45, 99, 229.
18. Cronauer, D. C. Quarterly Report, July-September 1992, Contract DE-AC22-91PC91051.
19. Torres, R. J.; Quinga, E. M.; Cronauer, D. C. *ACS Preprints, Fuel Chem. Div.*, 1993, 38(3), 1039-1044.
20. Brannan, C. J.; Curtis, C. W.; Cronauer, D. C. ACS Fuel Chem. Div. Prep. 38, 3, 1001, 1993.
21. Brannan, C. J.; Curtis, C. W.; Cronauer, D. C. Submitted to *Energy and Fuels*, 1994.
22. Torres-Ordonez, R. J., Quinga, E. M., Cronauer, D. C. ACS Fuel Chem. Div. Prep. 38, 3, 1039, 1993.
23. Kim, H.; Curtis, C. W. *Energy Fuels*, 1990, 4, 214 -219.

24. Ting, P. S.; Curtis, C. W.; Cronauer, D. C. *Energy Fuels*, 1992, 511-518.
25. Tang, Y.; Curtis, C. W. *Energy Fuels*, 1994, 8, 63-70.
26. Tang, Y.; Curtis, C. W. *ACS Preprints, Fuel Chem. Div.*, 1993, 38(1), 163-171.
27. Derbyshire, F. J.; Whitehurst, D. D. *Fuel*, 1981, 60, 655-662;
Derbyshire F. J., Varghese, P., Whitehurst D. D. *Fuel*, 1982, 61, 859-864.
28. Curtis, C. W.; Cassell, F. N. *Energy Fuels*, 1988, 2, 1-8.
29. Leung, K.; Haynes, H. W., Jr. *Chem. Eng. Commun.* 31, 1, 1984.
30. Freeman, G. B.; Heink, J.; Long, N. J.; Davis, B. H. *Appl. Catal.* 23, 309, 1986.
31. Sajkowski, D. J.; Pacheco, M. A.; Fleisch, T. H.; Meyers, B. L.
"Deactivation of Coal Liquefaction Catalysts"; Proc. 9th Intl. Congr. on Catal., Calgary, 223, 1988.
32. DOE Contract DE-AC22-90PC89857, Direct Coal Liquefaction--Low Rank Coal Study Design and System Analysis, Topical Report on "Design, Capital Cost and Economics for the Low Rank Coal Study"; Bechtel Corporation, in press.
33. DOE Contract DE-AC22-90PC89857, Direct Coal Liquefaction--Baseline Design and System Analysis, "Task II Topical Report--Baseline"; Volume III, March 1992.

34. DOE Contract DE-AC22-90PC89857, Direct Coal Liquefaction--Baseline Design and System Analysis, "Task V Topical Report--Process Simulation Model for Baseline and Options"; December 1992.
35. DOE Contract DE-AC22-90PC89857, Direct Coal Liquefaction--Baseline Design and System Analysis, "Task V Topical Report: LOTUS Spreadsheet Economics Model (Restricted Addendum)"; December 1992.
36. DOE Contract DE-AC22-90PC89857, Direct Coal Liquefaction--Baseline Design and System Analysis, "Final Report on Baseline and Improved Baseline"; March 1993.
37. Cronauer, D. C., et al. "Advanced Liquefaction Using Coal Swelling and Catalyst Dispersion"; DOE Liquefaction Contractors Review Conference, Pittsburgh, Penn., September 1993.
38. Amoco Oil Company proprietary memorandum, M90-117.

FIGURE 1

Schematic of SO₂ Coal Treating Process

FIGURE 2

SWELLING RATIOS

FIGURE 3

SWELLING RATIOS

FIGURE 4

FIGURE 5

Swelling Ratios of 325-mesh Coal with the IPA/Tetralin System

FIGURE 6

Swelling Ratios of 325-mesh Black Thunder Coal with the THF/Water System

FIGURE 7

Swelling Ratios of 325-mesh Black Thunder Coal with the Methanol/Water System

FIGURE 8

Swelling Ratios of 325-mesh Black Thunder Coal with Solvent Blends

24-hr Swelling Ratio

FIGURE 9

Swelling Rates of 325-mesh Black Thunder Coal

FIGURE 10 -- Reproducibility of experiments

30/70 solvent/toluene blends, 100 ppm Mo initial
 -70 mesh coal with THF, 70 F
 8 x 60 mesh coal with DMSO, 150 F

FIGURE 11a -- Effect of Solvent on Molyvan-L Uptake
(IPA, THF, and Toluene at Ambient)

-70 mesh SO₂-treated Black Thunder
~ 100 ppm Mo initial, 70 F

FIGURE 11b -- Effect of Solvent on Molyvan-L Uptake
(IPA, THF, and DMSO at Ambient)

8 x 60 mesh SO₂-treated Black Thunder
~ 100 ppm Mo initial, 70 F
30/70 blends of swelling solvent with toluene

FIGURE 11c -- Effect of Swelling Solvent Concentration on Molyvan-L Uptake

8 x 60 mesh SO₂-treated Black Thunder
 ~ 100 ppm Mo Initial, THF/toluene blends

FIGURE 12 -- Effect of Temperature on Molyvan-L Uptake
(Toluene, THF, and DMSO Solvents)

-70 mesh (toluene) or 8 x 60 mesh (THF, DMSO)
~ 100 ppm Mo initial
30/70 solvent/toluene blends

FIGURE 13a -- Effect of Coal Size on Molyvan-L Uptake
(IPA/Toluene at Ambient Temperature)

~ 100 ppm Mo initial, SO₂-treated Black Thunder
30/70 IPA/toluene blend

FIGURE 13b -- Effect of Coal Size on Molyvan-L Uptake
(THF/Toluene at Ambient and Elevated Temperatures)

FIGURE 14 -- Effect of Initial Catalyst Concentration on Molyvan-L Uptake
(IPA/Toluene at Ambient Temperature)

8x60 mesh SO₂-treated Black Thunder
30/70 IPA/toluene blend

FIGURE 15a -- Effect of Catalyst Precursor on Uptake
(IPA/Toluene)

8x60 mesh SO₂-treated Black Thunder
30/70 IPA/toluene blend, 100 ppm Mo initial
Mo oct. uptake at 70 F calculated as $1 - Mo_i/Mo_o$

FIGURE 15b -- Effect of Catalyst Precursor on Uptake
(DMSO/Toluene at Ambient and Elevated Temperatures)

8x60 mesh SO₂-treated Black Thunder
30/70 DMSO/toluene blend, 100 ppm Mo initial
Mo oct. uptake calculated as $1 - Mo_i / Mo_o$

FIGURE 15c -- Effect of Catalyst Precursor on Uptake
(THF/Toluene at Elevated Temperature)

SO₂-treated Black Thunder, 120 F
30/70 THF/toluene blend, 100 ppm Mo initial

FIGURE 16

**ELEMENT PROFILES FOR RAW BLACK THUNDER
IMPREGNATED WITH MOLYVAN-L**

FIGURE 17

ELEMENT PROFILES FOR SO₂-TREATED BLACK THUNDER
IMPREGNATED WITH MOLYVAN-L

FIGURE 18

**ELEMENT PROFILES FOR RAW BLACK THUNDER
IMPREGNATED WITH MO OCTOATE**

FIGURE 19

**ELEMENT PROFILES FOR SO₂-TREATED BLACK THUNDER
IMPREGNATED WITH MO OCTOATE**

TEM
4/94

16103-34-E2
x92,500

200 nm

FIGURE 20

FIGURE 21

500 nm

16103-165-AB2 TEM
x33,750
4/94

FIGURE 22

16103-34-E2-750 X25,000 A-1

TN-5500 AMOCO CORPORATION RESEARCH
CURSOR: 0.000keV = 0
MED 30-MAR-54 17:21

TN-5500 AMOCO CORPORATION RESEARCH
CURSOR: 0.000keV = 0
MED 30-MAR-54 17:14

TN-5500 AMOCO CORPORATION RESEARCH
CURSOR: 0.000keV = 0
MED 30-MAR-54 17:15

FIGURE 23

TN-5500 AMOCO CORPORATION RESEARCH
Cursor: 0.000keV = 0

WED 30-MAR-54 17:15

TN-5500 AMOCO CORPORATION RESEARCH
Cursor: 0.000keV = 0

WED 30-MAR-54 17:17

TN-5500 AMOCO CORPORATION RESEARCH
Cursor: 0.000keV = 0

WED 30-MAR-54 17:17

TN-5500 AMOCO CORPORATION RESEARCH
Cursor: 0.000keV = 0

WED 30-MAR-54 17:16

FIGURE 23 (cont)

FIGURE 24a

FIGURE 24b

FIGURE 25a

FIGURE 25b

FIGURE 26a

FIGURE 26b

16103-34-E1
x62,000

TEM
4/94

500 nm

TN-5500 AMOCO CORPORATION RESEARCH
Cursch: 0.000keV = 2

WED 08-MAR-54 21:45

FIGURE 27

FIGURE 28 Swelling Apparatus

FIGURE 29

Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal Without Solvents

	Untreated	SO ₂ Treated
Coal Conversion	48.2	85.7
Pyrene Conversion	3.4	26.3

Catalyst--Molybdenum Naphthenate

Reaction Solvent--None

Reaction conditions: 410 C, 30 min, 1250 psig H₂

FIGURE 30

Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal Without Solvents

	Untreated	SO ₂ Treated
Coal Conversion	72.9	90.3
Pyrene Conversion	22.9	28.0

Catalyst--Molyvan-L

Reaction Solvent--None

Reaction conditions: 410 C,30 min,1250 psig H₂

FIGURE 31

Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal Without Solvents

	Untreated	SO ₂ Treated
Coal Conversion	73.8	84.4
Pyrene Conversion	25.6	21.9

Catalyst--Nickel Octoate

Reaction Solvent--None

Reaction conditions: 410 C, 30 min, 1250 psig H₂

FIGURE 32

Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal With Solvents

	Untreated	SO ₂ Treated
Coal Conversion	82.4	88.5
Pyrene Conversion	30.0	27.8

Catalyst--Molyvan-L

Reaction Solvent--1-Methylnaphthalene

Reaction conditions: 410 C,30 min,1250 psig H₂

FIGURE 33

Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal With Solvents

		Untreated	SO ₂ Treated
Coal Conversion	■	70.7	76.3
Pyrene Conversion	▨	6.8	12.5

Catalyst--Nickel Octoate

Reaction Solvent--1-Methylnaphthalene

Reaction conditions: 410 C, 30 min, 1250 psig H₂

FIGURE 34

Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal With Solvents

	Untreated	SO2 Treated
Coal Conversion	84.7	90.5
Pyrene Conversion	14.9	20.8

Catalyst--Molyvan-L

Reaction Solvent--V1074

Reaction conditions: 410 C,30 min,1250 psig H₂

FIGURE 35

Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal With Solvents

	Untreated	SO ₂ Treated
Coal Conversion	81.5	82.1
Pyrene Conversion	6.8	2.0

Catalyst--Nickel Octoate

Reaction Solvent--V1074

Reaction conditions: 410 C, 30 min, 1250 psig H₂

FIGURE 36

Effect of Preswelling on Reactions of Untreated Black Thunder Coal in 1-Methylnaphthalene With Molyvan-L Catalyst

	THF	Methanol	Isopropanol	DMSO
Coal Conversion	87.3	88.0	88.1	79.9
Pyrene Conversion	18.6	24.3	18.7	11.6

Reaction conditions: 410 C, 30 min, 1250 psig H₂

FIGURE 37

Effect of Preswelling on Reactions of Untreated Black Thunder Coal in 1-Methylnaphthalene With Nickel Octoate Catalyst

	THF	Methanol	Isopropanol	DMSO
Coal Conversion	77.0	85.5	77.6	63.6
Pyrene Conversion	2.4	10.9	2.2	5.0

Reaction conditions: 410 C,30 min,1250 psig H₂

FIGURE 38

Effect of Preswelling on Reactions of SO₂ Treated Black Thunder Coal in 1-Methylnaphthalene With Molyvan-L Catalyst

	THF	Methanol	Isopropanol	DMSO
Coal Conversion	91.2	90.0	91.3	78.1
Pyrene Conversion	25.4	30.0	21.3	13.7

Reaction conditions: 410 C, 30 min, 1250 psig H₂

FIGURE 39

Effect of Preswelling on Reactions of SO₂ Treated Black Thunder Coal in 1-Methylnaphthalene With Nickel Octoate Catalyst

	THF	Methanol	Isopropanol	DMSO
Coal Conversion	72.5	78.7	73.9	50.1
Pyrene Conversion	2.2	4.9	3.9	7.1

Reaction conditions: 410 C,30 min,1250 psig H₂

FIGURE 40

Impregnation vs. Direct Addition of Catalyst

THF Swelling Solvent; Molynaphthanate + S Cat.

Untreated Black Thunder Coal in 1-Methylnaph.

		Direct Addition	Impregnation
Coal Conversion	■	73.8	76.8
Pyrene Conversion	▨	34.4	35.4

Reaction conditions: 385 C;30 min;1250 psig H₂

FIGURE 41

Impregnation vs. Direct Addition of Catalyst **THF Swelling Solvent; Molyvan-L Catalyst** **Untreated Black Thunder Coal in 1-Methylnaph.**

	Direct Addition	Impregnation
Coal Conversion	72.5	50.4
Pyrene Conversion	25.7	4.5

Reaction conditions: 385 C; 30 min; 1250 psig H₂

FIGURE 42

Impregnation vs. Direct Addition of Catalyst

Isopropanol Solvent; Molyvan-L Catalyst
Untreated Black Thunder Coal in 1-Methylnaph.

	Direct Addition	Impregnation
Coal Conversion	76.7	55.9
Pyrene Conversion	23.1	5.0

Reaction conditions: 385 C;30 min;1250 psig H₂

FIGURE 43

Impregnation vs. Direct Addition of Catalyst

**Isopropanol Solvent; Nickel Octoate Catalyst
Untreated Black Thunder Coal in 1-Methylnaph.**

	Direct Addition	Impregnation
Coal Conversion	65.3	62.2
Pyrene Conversion	7.7	5.0

Reaction conditions: 385 C;30 min;1250 psig H₂

FIGURE 44

Impregnation vs. Direct Addition of Catalyst **THF Swelling Solvent; Molyvan-L Catalyst** **Untreated Black Thunder Coal in 1-Methylnaph.**

	Direct Addition	Impregnation
Coal Conversion	87.3	81.9
Pyrene Conversion	18.6	15.1

Reaction conditions: 410 C;30 min;1250 psig H₂
 Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 45

Impregnation vs. Direct Addition of Catalyst

**IPA Swelling Solvent; Molyvan-L Catalyst
Untreated Black Thunder Coal in 1-Methylnaph.**

	Direct Addition	Impregnation
Coal Conversion	88.1	79.9
Pyrene Conversion	18.7	16.9

Reaction conditions: 410 C;30 min;1250 psig H2
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 46

Impregnation vs. Direct Addition of Catalyst

IPA Swelling Solvent; Nickel Octoate Catalyst
Untreated Black Thunder Coal in 1-Methylnaph.

	Direct Addition	Impregnation
Coal Conversion	77.6	75.2
Pyrene Conversion	2.2	3.9

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 47

Catalyst Added to Swelling Solvent

Various Swelling Solvents; Molyvan-L Cat.

SO₂ Treated Black Thunder Coal in 1-Methylnaph.

	THF	IPA	MeOH
Coal Conversion	86.0	87.6	85.1
Pyrene Conversion	31.4	26.0	26.8

Reaction conditions: 410 C;30 min;1250 psig H₂
 Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 48

Direct Addition of Catalyst

Various Swelling Solvents; Molyvan-L Catalyst

SO₂ Treated Black Thunder Coal in 1-Methylnaph.

	THF	MeOH	IPA
Coal Conversion	91.2	90.0	91.3
Pyrene Conversion	25.4	30.0	21.3

Reaction conditions: 410 C; 30 min; 1250 psig H₂

Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 49

Direct Addition of Catalyst **Various Swelling Solvents; Nickel Octoate Cat.** **SO₂ Treated Black Thunder Coal in 1-Methylnaph.**

	THF	IPA	MeOH
Coal Conversion	72.5	73.9	78.7
Pyrene Conversion	2.2	3.9	4.9

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 50

Catalyst Added to Swelling Solvent

Various Swelling Solvents; Nickel Octoate Cat.
SO₂ Treated Black Thunder Coal in 1-Methylnaph.

	THF	IPA	MeOH
Coal Conversion	71.4	67.9	78.4
Pyrene Conversion	6.9	5.0	7.1

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 51

Impregnation vs. Direct Addition of Catalyst

THF Swelling Solvent; Molyvan-L Cat.
Untreated Black Thunder Coal in V-1074

	Direct Addition	Impregnation
Coal Conversion	82.8	76.0
Pyrene Conversion	28.0	14.1

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 52

Impregnation vs. Direct Addition of Catalyst

THF Swelling Solvent; Nickel Octoate Cat.

Untreated Black Thunder Coal in V-1074

	Direct Addition	Impregnation
Coal Conversion	77.2	79.5
Pyrene Conversion	6.4	4.6

Reaction conditions: 410 C;30 min;1250 psig H₂

Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 53

Impregnation vs. Direct Addition of Catalyst

THF Swelling Solvent; Molyvan-L Cat.

Untreated Black Thunder in Dihydroanthracene

	Direct Addition	Impregnation
Coal Conversion	87.3	84.5
Pyrene Conversion	23.5	8.9

Reaction conditions: 410 C;30 min;1250 psig H₂

Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 54

Effect of Reaction Solvents on Untreated Black

Thunder Coal; THF Swelling Solvent; Molyvan-L
Direct Addition of Catalyst

	1-Mn	V1074	DHA
Coal Conversion	87.3	82.8	87.3
Pyrene Conversion	18.6	28.0	23.5

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 55

Effect of Reaction Solvents on Untreated Black

Thunder Coal; THF Swelling Solvent; Molyvan-L

Catalyst Added to Swelling Solvent

	1-Mn	V1074	DHA
Coal Conversion	81.9	76.0	84.5
Pyrene Conversion	15.1	14.1	8.9

Reaction conditions: 410 C; 30 min; 1250 psig H₂
 Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 56

Effect of Reaction Solvents on Untreated Black Thunder Coal; IPA Swelling Solvent; 1-Mn Reaction Solvent; Catalyst Added to Reactor

	Molyvan-L	Nickel Octoate
Coal Conversion	88.1	77.6
Pyrene Conversion	18.7	2.2

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 57

Effect of Reaction Solvents on Untreated Black Thunder Coal; IPA Swelling Solvent; Molyvan-L Catalyst Added to Swelling Solvent

	1-Mn	20% DHA 80% V1074
Coal Conversion	79.9	81.2
Pyrene Conversion	16.9	7.7

Reaction conditions: 410 C;30 min;1250 psig H₂
 Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 58

Effect of Reaction Solvents on Untreated Black Thunder Coal; IPA Swelling Solvent; Molyvan 822 Catalyst Added to Swelling Solvent

	1-Mn	20% DHA 80% V1074
Coal Conversion	83.3	88.0
Pyrene Conversion	24.3	21.0

Reaction conditions: 410 C;30 min;1250 psig H₂
 Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 59

Effect of Reaction Solvents on Untreated Black Thunder Coal; IPA Swelling Solvent; Ni Octoate Catalyst Added to Swelling Solvent

		1-Mn	20% DHA 80% V1074
Coal Conversion	■	75.2	75.3
Pyrene Conversion	▨	3.9	5.7

Reaction conditions: 410 C;30 min;1250 psig H2
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 60

Effect of Swelling Solvents on Untreated Black

Thunder Coal; 1-Mn Reaction Solvent

Molyvan-L Catalyst Added to Swelling Solvent

	THF	Methanol	Isopropanol	20% IPA/80% Water	20% IPA/80% Toluene	Water
Coal Conversion	81.9	68.4	79.9	89.6	60.7	80.1
Pyrene Conversion	15.1	3.0	16.9	34.7	4.8	25.0

Reaction conditions: 410 C;30 min;1250 psig H₂
 Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 61

Effect of Swelling Solvents on Untreated Black Thunder Coal; 1-Mn Reaction Solvent Molyvan 822 Catalyst Added to Swelling Solvent

	IPA	20% IPA/80% Water	40% THF/60% Water
Coal Conversion	83.3	60.6	69.4
Pyrene Conversion	24.3	4.6	9.8

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 62

Effect of Swelling Solvents on Untreated Black Thunder Coal; 1-Mn Reaction Solvent Ni Octoate Catalyst Added to Swelling Solvent

	Methanol	Isopropanol
Coal Conversion	70.1	75.2
Pyrene Conversion	3.5	12.9

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 63

Effect of IPA Swelling Solvent on Untreated Black Thunder Coal; 1-Mn Reaction Solvent Catalyst Added to Swelling Solvent

		Molyvan-L	Molyvan 822	Ni Octoate
Coal Conversion	■	79.9	83.3	75.2
Pyrene Conversion	▨	16.9	24.3	12.9

Reaction conditions: 410 C;30 min;1250 psig H₂

Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 64

Effect of Swelling Solvents on Untreated Black

Thunder Coal; 20% DHA-80% V1074 Reaction Solvent

Molyvan-L Catalyst Added to Swelling Solvent

	Isopropanol	20% IPA/80% Water
Coal Conversion	81.2	87.5
Pyrene Conversion	7.7	28.6

Reaction conditions: 410 C;30 min;1250 psig H₂
Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 65

Effect of Swelling Solvents on Untreated Black

Thunder Coal; 20% DHA-80% V1074 Reaction Solvent

Molyvan 822 Catalyst Added to Swelling Solvent

	Isopropanol	20% IPA/80% Water
Coal Conversion	88.0	83.2
Pyrene Conversion	21.0	11.5

Reaction conditions: 410 C;30 min;1250 psig H₂

Catalyst: 600 ppm; Not Agitated while swelling

FIGURE 66

Effect of Molyvan-L Loading on Untreated Black Thunder Coal; 1-Mn Reaction Solvent Catalyst Added to THF Swelling Solvent

	100-150 ppm	600-800 ppm	1200-1600 ppm
Coal Conversion	53.7	81.9	84.8
Pyrene Conversion	2.1	15.1	28.6

Reaction conditions: 410 C; 30 min; 1250 psig H₂
Catalyst: Not Agitated while swelling for 96 hr.

FIGURE 67

Effect of Molyvan-L Loading on Untreated Black Thunder Coal; 1-Mn Reaction Solvent Catalyst Added to Methanol Swelling Solvent

	100-150 ppm	600-800 ppm	1200-1600 ppm
Coal Conversion	53.1	68.4	88.8
Pyrene Conversion	2.1	3.0	25.7

Reaction conditions: 410 C;30 min;1250 psig H₂

Catalyst: Not Agitated while swelling for 96 hr.

FIGURE 68

Effect of Molyvan-L Loading on Untreated Black Thunder Coal; 1-Mn Reaction Solvent Catalyst Added to Isopropanol Swelling Solvent

	100-150 ppm	600-800 ppm	1200-1600 ppm
Coal Conversion	51.6	79.9	81.9
Pyrene Conversion	1.8	16.9	28.2

Reaction conditions: 410 C;30 min;1250 psig H₂

Catalyst: Not Agitated while swelling for 96 hr.

FIGURE 69

Effect of Swelling Time on Untreated Black Thunder Coal; V1074 Reaction Solvent Catalyst Added to THF Swelling Solvent

	0 hr swelled w/o cat	12 hr swelled w/cat	24 hr swelled w/cat	48 hr swelled w/cat	96 hr swelled w/cat
Coal Conversion	82.8	85.4	84.4	80.4	76.0
Pyrene Conversion	28.0	31.8	23.5	14.7	2.3

Reaction conditions: 410 C;30 min;1250 psig H₂

FIGURE 70

Effect of Swelling Time on Untreated Black Thunder Coal; 1-Mn Reaction Solvent Catalyst Added to THF Swelling Solvent

	0 hr swelled w/o cat	12 hr swelled w/cat	24 hr swelled w/cat	48 hr swelled w/cat	96 hr swelled w/cat
Coal Conversion	87.3	76.8	78.2	74.1	15.1
Pyrene Conversion	18.6	15.2	18.1	8.8	8.8

Reaction conditions: 410 C; 30 min; 1250 psig H₂

FIGURE 71

Effect of Swelling Time on Untreated Black Thunder Coal; 1-Mn Reaction Solvent Catalyst Added to IPA Swelling Solvent

	0 hr swelled w/o cat	12 hr swelled w/cat	24 hr swelled w/cat	48 hr swelled w/cat	96 hr swelled w/cat
Coal Conversion	88.1	71.2	74.1	70.2	79.9
Pyrene Conversion	18.7	7.8	10.1	9.5	16.9

Reaction conditions: 410 C;30 min;1250 psig H₂

FIGURE 72

Effect of Carbon Black Addition **Mo Naphthenate + S Catalyst; THF Swelling Solvent** **Direct Catalyst Addition**

	None	Carbon Black in THF
Coal Conversion	89.9	80.0
Pyrene Conversion	24.8	21.6

FIGURE 73

Effect of Carbon Black Addition

Mo Naphthenate + S Catalyst

Catalyst Added to THF Swelling Solvent

	None	Direct Addition	Carbon Black in THF
Coal Conversion	89.9	78.3	78.8
Pyrene Conversion	26.0	28.9	21.8

FIGURE 74

Effect of V1074 As Swelling and Reaction Solvent Molyvan-L Catalyst

	None	Direct Cat. Addition	Cat. Add to Solvent
Coal Conversion	70.7	76.8	77.9
Pyrene Conversion	5.8	25.9	27.3

FIGURE 75

Untreated Black Thunder Reacted in DHA and V1074 Catalyst in IPA Swelling Solvent

	Mo Naphthenate + S	Molyvan-L	Molyvan 822	Molyvan 822 + S	Ni Naphthenate	Ni Octoate
Coal Conversion	85.3	81.2	88.0	86.5	85.5	75.3
Pyrene Conversion	21.3	7.7	21.0	23.6	11.4	5.7

FIGURE 76

Untreated Black Thunder Reacted in DHA and V1074

Catalyst in 20% IPA/80% Water Swelling Solvent

		Molyvan-L (777 ppm)	Molyvan 822 (632ppm)	Ni Naph. (691ppm)
Coal Conversion	■	87.5	83.2	84.5
Pyrene Conversion	▨	28.6	11.5	12.1

SCHEMATIC OF THE AU-44 FLOW UNIT

SCHEMATIC OF THE AU-51 FLOW UNIT

Liquefaction of Raw Black Thunder Coal

Using AU-44L, Single-stage Coal Liquefaction Unit

Low Severity, 770 deg. F

FIGURE 79

	Non-Swollen/Non-Cat	Swollen/Non-Cat
Pre-asphaltenes	3.24	2.54
Asphaltenes	10.49	7.96
Oils	77.86	81.40

FIGURE 80

Liquefaction of Raw Black Thunder Coal

Using AU-44L, Single-stage Coal Liquefaction Unit

Low Severity, 770 deg. F

	Non-Swollen/Cat	Swollen/Cat
Pre-asphaltenes	3.56	3.08
Asphaltenes	9.91	8.27
Oils	76.91	79.30

FIGURE 81

Liquefaction of Raw Black Thunder Coal

Using AU-44L, Single-stage Coal Liquefaction Unit

Low Severity, 770 F Vs. High Severity, 825 F

	Swollen/Cat 770 F	Swollen/Cat 825 F
Pre-asphaltenes	3.08	3.84
Asphaltenes	8.27	23.62
Oils	79.30	62.87

FIGURE 82

Solubility Class Conversions for Run ZHQ08.

FIGURE 83

Comparison of Cyclohexane Solubility Conversions
for Amocat 1A and Amocat 1C Catalysts.

FIGURE 84

Comparison of Toluene Solubility Conversions for Amocat 1A and Amocat 1C Catalysts.

FIGURE 85

Comparison of Pyridine Solubility Conversions for Amocat 1A and Amocat 1C Catalysts.

FIGURE 86

Cumulative Pore Size Distributions for Fresh Amocat 1A and Amocat 1C Catalysts.

FIGURE 87

Solvent Carbon, Hydrogen and Nitrogen Contents
vs. Catalyst Service for Run ZHQ08

FIGURE 88

Comparison of Cyclohexane Solubility Conversions
for Run ZHQ08 and Run ZHQ10.

FIGURE 89

Comparison of Toluene Solubility Conversions for
Run ZHQ08 and Run ZHQ10.

FIGURE 90

Comparison of Pyridine Solubility Conversions
for Run ZHQ08 and Run ZHQ10.

FIGURE 91

Comparison of Solvent Carbon to Hydrogen Ratio
for Run ZHQ08 and Run ZHQ10.

FIGURE 92

Solvent Carbon, Hydrogen and Nitrogen Contents
vs. Catalyst Service for Run ZHQ10

FIGURE 93 Effect of Temperature on DAO Yield

FIGURE 94 Effect of Temperature on DAO Yield For N-Butane

FIGURE 95 Effect of Butane/Pentane Blend Composition on DAO Yield

FIGURE 96 Relationship of DAO Yield to Deashed Resid Yield

(1) Defined as vol% of deasphalted oil (DAO) corresponding to a 900°F + Resid fraction from its ASTM D-1160 distillation.

DAO Yield vs Investment Cost

Upgrading Liquefied Coal Residue

FIGURE 98

FIGURE 99

Revised 08/26/91

Notes:

1. Flow rates are in Mlb/hr unless noted and on dry basis.
2. Simplified water flow distribution diagram is shown on Figure 41.1
3. Minor streams including steam, water, sour water, and make-up amine are not shown on this diagram.
4. Flow rates around plants #38, 39, 34 are shown on wet basis.

DOE / PETC
COAL LIQUEFACTION
COAL LIQUEFACTION
FLUID COKING OPTION
OVERALL PLANT CONFIGURATION
AND
OVERALL MATERIAL BALANCE

FIGURE 100

PROCESS FLOW DIAGRAM FOR SO₂ TREATMENT AND BENEFICATION OF COAL

FIGURE 101

DOE / PETC
COAL LIQUEFACTION

OVERALL PLANT CONFIGURATION
FOR SO₂ COAL CLEANING

TABLE 1

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 10 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	36.13	36.13	2.39	2.39	36.37	36.37
1 min.	15.97	52.10	2.38	2.39	16.07	52.45
2 min.	16.81	68.91	2.33	2.37	16.93	69.38
4 min.	0.00	68.91	0.00	2.37	0.00	69.38
8 min.	0.00	68.91	0.00	2.37	0.00	69.38
Refuse	31.09	100.00	4.50	3.03	30.62	100.00
Total	100.00		3.03		100.00	

TABLE 2

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 20 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	29.85	29.85	2.49	2.49	30.02	30.02
1 min.	14.18	44.03	2.41	2.46	14.27	44.30
2 min.	14.18	58.21	2.35	2.44	14.28	58.58
4 min.	6.72	64.93	2.44	2.44	6.76	65.34
8 min.	0.00	64.93	0.00	2.44	0.00	65.34
Refuse	35.07	100.00	4.20	3.06	34.66	100.00
Total	100.00		3.06		100.00	

TABLE 3

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	45.69	45.69	1.95	1.95	46.03	46.03
1 min.	21.55	67.24	2.27	2.05	21.64	67.68
2 min.	18.10	85.34	2.13	2.07	18.21	85.88
4 min.	7.76	93.10	2.44	2.10	7.78	93.66
8 min.	0.00	93.10	0.00	2.10	0.00	93.66
Refuse	6.90	100.00	10.52	2.68	6.34	100.00
Total	100.00		2.68		100.00	

TABLE 4

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 100 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	68.06	68.06	1.77	1.77	69.04	69.04
1 min.	15.28	83.33	2.20	1.85	15.43	84.47
2 min.	0.00	83.33	0.00	1.85	0.00	84.47
4 min.	0.00	83.33	0.00	1.85	0.00	84.47
8 min.	0.00	83.33	0.00	1.85	0.00	84.47
Refuse	16.67	100.00	9.80	3.17	15.53	100.00
Total	100.00		3.17		100.00	

TABLE 5

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 500 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	28.69	28.69	2.28	2.28	28.85	28.85
1 min.	20.72	49.40	2.15	2.23	20.87	49.72
2 min.	21.12	70.52	2.18	2.21	21.26	70.98
4 min.	16.33	86.85	2.13	2.20	16.46	87.44
8 min.	0.00	86.85	0.00	2.20	0.00	87.44
Refuse	13.15	100.00	7.17	2.85	12.56	100.00
Total	100.00		2.85		100.00	

TABLE 6

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 500 ml. All the slurry was taken to conduct the experiment. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	12.85	12.85	2.83	2.83	12.89	12.89
1 min.	7.83	20.68	2.65	2.76	7.87	20.76
2 min.	13.86	34.54	2.69	2.73	13.92	34.67
4 min.	15.26	49.80	2.52	2.67	15.35	50.03
8 min.	20.08	69.88	2.51	2.62	20.21	70.24
Refuse	30.12	100.00	4.26	3.12	29.76	100.00
Total	100.00		3.12		100.00	

TABLE 7

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 125 μ l
Collector: Dodecane 1125 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 100 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	55.13	55.13	2.35	2.35	55.61	55.61
1 min.	19.30	74.43	2.89	2.49	19.35	74.96
2 min.	0.00	74.43	0.00	2.49	0.00	74.96
Refuse	25.57	100.00	5.21	3.19	25.04	100.00
Total	100.00		3.19		100.00	

TABLE 8

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 250 μ l
Collector: Dodecane 2250 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*
 Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.
Spherical Agglomeration:
 Slurry from the mill was completed to 1000 ml. 100 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.
Flotation:
 1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.
Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	71.21	71.21	1.83	1.83	72.23	72.23
1 min.	15.74	86.96	2.53	1.96	15.85	88.08
2 min.	0.00	86.96	0.00	1.96	0.00	88.08
Refuse	13.04	100.00	11.52	3.20	11.92	100.00
Total	100.00		3.20		100.00	

TABLE 9

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 500 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*
 Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.
Spherical Agglomeration:
 Slurry from the mill was completed to 1000 ml. 100 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.
Flotation:
 1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.
Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	75.18	75.18	1.82	1.82	76.22	76.22
1 min.	14.37	89.55	2.88	1.99	14.41	90.63
2 min.	0.00	89.55	0.00	1.99	0.00	90.63
Refuse	10.45	100.00	13.15	3.16	9.37	100.00
Total	100.00		3.16		100.00	

TABLE 10

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 1000 μ l
Collector: Dodecane 9000 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 100 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	45.33	45.33	1.97	1.97	45.86	45.86
1 min.	23.68	69.00	1.88	1.94	23.98	69.84
2 min.	16.67	85.67	2.21	1.99	16.82	86.66
Refuse	14.33	100.00	9.82	3.11	13.34	100.00
Total	100.00		3.11		100.00	

TABLE 11

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill in the presence of 20 mg Calgon per kg of coal.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	44.09	44.09	1.82	1.82	44.68	44.68
1 min.	21.26	65.35	2.00	1.88	21.50	66.19
2 min.	17.32	82.68	2.02	1.91	17.52	83.70
4 min.	9.45	92.13	2.47	1.97	9.51	93.21
8 min.	0.00	92.13	0.00	1.97	0.00	93.21
Refuse	7.87	100.00	16.50	3.11	6.79	100.00

TABLE 12

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill in the presence of 100 mg Calgon per kg of coal.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	43.07	43.07	2.00	2.00	43.53	43.53
1 min.	18.25	61.31	1.94	1.98	18.46	61.99
2 min.	16.79	78.10	2.04	1.99	16.96	78.95
4 min.	8.76	86.86	2.36	2.03	8.82	87.78
8 min.	0.00	86.86	0.00	2.03	0.00	87.78
Refuse	13.14	100.00	9.80	3.05	12.22	100.00

TABLE 13

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: Grinding:

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill in the presence of 500 mg Calgon per kg of coal.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	38.58	38.58	1.87	1.87	39.07	39.07
1 min.	17.32	55.91	2.03	1.92	17.51	56.58
2 min.	20.47	76.38	1.87	1.91	20.73	77.31
4 min.	14.96	91.34	2.13	1.94	15.11	92.42
8 min.	0.00	91.34	0.00	1.94	0.00	92.42
Refuse	8.66	100.00	15.20	3.09	7.58	100.00

TABLE 14

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: Grinding:

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill in the presence of 2000 mg Calgon per kg of coal.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 30 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	41.41	41.41	1.93	1.93	41.91	41.91
1 min.	16.41	57.81	1.92	1.93	16.61	58.52
2 min.	18.75	76.56	2.00	1.95	18.97	77.49
4 min.	14.06	90.63	2.11	1.97	14.21	91.70
8 min.	0.00	90.63	14.20	1.97	0.00	91.70
Refuse	9.38	100.00	14.20	3.12	8.30	100.00

TABLE 15

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 00 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	40.74	40.74	1.94	1.94	41.12	41.12
1 min.	19.26	60.00	1.96	1.95	19.43	60.55
2 min.	19.26	79.26	2.03	1.97	19.42	79.97
4 min.	10.37	89.63	2.34	2.01	10.42	90.39
8 min.	0.00	89.63	0.00	2.01	0.00	90.39
Refuse	10.37	100.00	9.95	2.83	9.61	100.00
Total	100.00		2.83		100.00	

TABLE 16

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 04 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	39.84	39.84	1.94	1.94	40.20	40.20
1 min.	22.66	62.50	2.00	1.96	22.85	63.05
2 min.	17.97	80.47	1.96	1.96	18.13	81.18
4 min.	10.94	91.41	2.24	1.99	11.00	92.18
8 min.	0.00	91.41	0.00	1.99	0.00	92.18
Refuse	8.59	100.00	11.54	2.82	7.82	100.00
Total	100.00		2.82		100.00	

TABLE 17

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: *Grinding:*

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 10 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	39.84	39.84	1.91	1.91	40.19	40.19
1 min.	21.09	60.94	1.99	1.94	21.26	61.45
2 min.	18.75	79.69	1.98	1.95	18.90	80.35
4 min.	11.72	91.41	2.51	2.02	11.75	92.09
8 min.	0.00	91.41	0.00	2.02	0.00	92.09
Refuse	8.59	100.00	10.52	2.75	7.91	100.00
Total	100.00		2.75		100.00	

TABLE 18

Experiment type: Spherical Agglomeration/Flotation
Material Type: SO₂ treated sample from AMOCO

Surfactant: BC1 100 μ l
Collector: Dodecane 4500 μ l
Frother: MIBC 50 μ l

Conditions: Grinding:

Wet grinding of a 50 g. sample in 100 ml of water for 40 min in a planetary mill.

Spherical Agglomeration:

Slurry from the mill was completed to 1000 ml. 200 ml slurry was taken and completed to 500 ml. This slurry was kept in an ultrasonic bath for 60 min. It was mixed in a blender for 1 min. at a setting of 2. Oil + surfactant was added and the slurry was blended for 3 more min. at a setting of 4. A final blending of 2 min. at a setting of 2 was applied.

Flotation:

1 min. conditioning – MIBC addition; 1 min. conditioning – flotation.

Feed Ash: 3.2%

Product	Yield(%)	Cumulative Yield(%)	Ash(%)	Cum. Ash (%)	CMR (%)	Cumulative CMR (%)
30 sec.	37.96	37.96	2.04	2.04	38.28	38.28
1 min.	18.25	56.20	2.05	2.04	18.40	56.68
2 min.	21.17	77.37	1.98	2.03	21.36	78.04
4 min.	12.41	89.78	2.18	2.05	12.50	90.53
8 min.	0.00	89.78	0.00	2.05	0.00	90.53
Refuse	10.22	100.00	10.01	2.86	9.47	100.00
Total	100.00		2.86		100.00	

TABLE 19

COAL SWELLING REPRODUCIBILITY TESTS

Solvent	Coal Swelling Ratio, Q		
	Black Thunder Subbituminous	Burning Star Illinois No. 6	Martin Lake Lignite
Cyclohexane:			
Operator 1	1.00	1.00	1.00
	1.00	1.04	1.01
Operator 2	1.00	1.00	1.00
	1.00	1.00	1.00
Average	1.00	1.01	1.00
Std Dev	--	0.02	0.005
Methanol:			
Operator 1	1.23	1.20	1.25
	1.32	1.19	1.25
Operator 2	1.37	1.21	1.27
	1.35	1.24	1.44
Average	1.32	1.21	1.30
Std Dev	0.06	0.02	0.09
Tetrahydrofuran:			
Operator 1	1.69	1.55	1.32
	1.72	1.66	1.35
Operator 2	1.54	1.69	1.41
	1.52	1.57	1.34
Average	1.62	1.62	1.36
Std Dev	0.10	0.07	0.04
Tetrabutylammonium Hydroxide:			
Operator 1	2.39	2.12	2.73
	2.65	2.13	2.94
Operator 2	2.22	2.15	2.79
	2.68	2.21	2.53
Average	2.48	2.15	2.75
Std Dev	0.22	0.04	0.17

TABLE 20

SWELLING REPRODUCIBILITY TESTS FOR MIXTURES

	Coal Swelling Ratio, Q		
Solvent	Black Thunder Subbituminous	Burning Star Illinois No. 6	Martin Lake Lignite
Tetralin:			
	1.04	1.01	1.03
	1.04	1.00	1.03
Average	1.04	1.01	1.03
Tetralin/ Isopropanol:2/1:			
	1.48	1.46	1.35
	1.69	1.52	1.37
	1.47	1.44	1.28
	1.46	1.48	1.27
Average	1.52	1.48	1.32
Std Dev	0.11	0.03	0.05
Tetralin/ Isopropanol:1/2:			
	1.52	1.43	1.32
	1.54	1.42	1.34
	1.59	1.38	1.38
	1.64	1.32	1.35
Average	1.57	1.39	1.35
Std Dev	0.05	0.05	0.03
Isopropanol:			
	1.38	1.17	1.26
	1.44	1.18	1.24
	1.37	1.17	1.29
	1.41	1.12	1.29
Average	1.40	1.16	1.27
Std Dev	0.03	0.03	0.02

TABLE 21

SWELLING RATIO OF COAL/SOLVENT MIXTURES
(325 Mesh Coal with 1 ml Winthrobe Tubes)

Solvent/Time	Black Thunder		Illinois No. 6		Martin Lake Lignite	
	24 Hr	96 Hr	24 Hr	96 Hr	24 Hr	96 Hr
Hexane	--	1.01	--	1.00	--	0.95
Cyclohexane	--	1.00	1.00	1.00	--	--
Benzene	--	1.12	--	1.06	--	1.14
Toluene	--	1.04	--	1.16	--	1.00
Xylene	--	1.02	--	1.04	--	1.05
Tetralin	1.00	1.04	0.96	1.02	1.02	1.03
Methanol	1.28	1.35	1.16	1.23	1.43	1.36
Ethanol	--	1.31	--	1.26	--	1.24
Isopropanol	1.30	1.39	1.06	1.15	1.14	1.25
Isopropanol	1.30	1.39	1.06	1.15	1.14	1.25
33% Tetralin/67% IPA	1.40	1.53	1.31	1.43	1.18	1.37
67% Tetralin/33% IPA	1.39	1.47	1.34	1.49	1.18	1.36
80% Tetralin/20% IPA	1.34	1.42	1.22	1.35	1.10	1.23
90% Tetralin/10% IPA	1.22	1.35	1.13	1.19	1.10	1.18
Tetralin	1.00	1.04	0.96	1.02	1.02	1.03
Cresol	1.16	1.29	1.28	1.48	1.13	1.20
Acetone	--	1.32	--	1.24	--	1.25
Methyl Ethyl Ketone	1.32	1.34	1.29	1.29	1.27	1.3
Methyl Acetate	1.28	1.34	1.20	1.20	1.25	1.25
Tetrahydrofuran	1.45	1.53	1.50	1.63	1.36	1.38
Chloroform	--	1.17	--	1.19	--	1.03
Chlorobenzene	1.08	1.08	1.07	1.16	1.09	1.12
Nitrobenzene	1.11	1.15	1.18	1.19	1.08	1.11
Aniline	1.41	1.64	1.71	1.94	1.12	1.19
Tetrabutylammonium Hydroxide	2.05	2.45	1.59	2.18	2.04	2.66
Dimethyl Sulfoxide	2.19	2.39	2.08	2.15	1.52	1.63

TABLE 22
 SWELLING RATIO OF THREE SAMPLES OF BLACK THUNDER COAL
 (10 ml Conical Centrifuge Tubes)

Solvent/Time	Untreated -325 Mesh				Untreated 8 x 60 Mesh				SO ₂ -Treated 8 x 60 Mesh			
	2 Hr	4 Hr	24 Hr	96 Hr	2 Hr	4 Hr	24 Hr	96 Hr	2 Hr	4 Hr	24 Hr	96 Hr
Isopropanol	--	--	--	--	1.20	--	--	--	1.27	--	1.42	--
50X IPA/50X H ₂ O	--	--	--	1.38	--	--	--	--	--	--	1.40	1.40
20X IPA/80X Tetralin	1.16	--	1.24	--	1.25	--	1.48	--	1.33	1.38	1.41	1.41
20X IPA/80X Toluene	--	--	--	--	1.18	--	1.21	--	1.26	--	1.42	--
30X IPA/70X Toluene	--	--	--	--	1.20	--	1.24	--	1.38	--	1.51	--
40X IPA/60X Toluene	--	--	--	--	1.18	--	1.30	--	1.32	--	1.56	--
Methanol	1.34	1.43	1.43	--	--	--	1.26	1.26	1.24	--	--	--
(repeat)	--	--	1.19	1.33	--	--	--	--	1.18	--	--	--
70X MeOH/30X H ₂ O	--	--	1.32	1.40	1.24	--	1.24	--	--	--	1.25	--
50X MeOH/50X H ₂ O	--	--	1.38	1.36	--	--	--	--	--	--	1.21	--
30X MeOH/70X H ₂ O	--	--	1.21	1.28	--	--	--	--	--	--	--	--
25X MeOH/75X Tetralin	1.43	1.46	1.49	--	--	--	--	--	--	--	--	--
Acetone	--	--	--	--	1.23	--	1.24	--	1.52	--	1.52	--
Tetrahydrofuran	--	--	1.42	1.33	--	--	1.54	1.59	1.83	1.94	2.07	2.08
70X THF/30X H ₂ O	--	--	1.87	1.91	1.71	--	1.86	--	1.93	--	2.15	--
50X THF/50X H ₂ O	--	--	1.78	1.85	--	--	--	--	--	--	--	--
30X THF/70X H ₂ O	--	--	1.52	1.60	1.36	--	1.49	--	1.43	--	1.52	--
20X THF/80X H ₂ O	1.40	1.46	1.46	--	--	--	--	--	--	--	--	--
10X THF/90X H ₂ O	1.24	1.24	1.31	--	--	--	--	--	1.16	--	1.16	--
5X THF/95X H ₂ O	1.40	1.38	1.41	--	1.14	--	1.16	--	1.17	--	1.15	--
(repeat)	--	--	--	--	--	--	--	--	--	--	--	--
Aniline	--	--	--	--	1.17	--	1.37	--	1.22	--	1.68	--
(repeat)	--	--	--	--	--	--	--	--	1.21	--	1.97	--
Diethyl Sulfoxide	2.05	2.37	2.37	2.37	1.60	--	2.09	--	2.28	2.35	2.41	2.58
10X DMSO/90X Tetralin	1.39	1.49	1.58	--	1.21	--	1.60	--	1.41	--	1.83	--
5X DMSO/95X Tetralin	1.19	1.27	1.32	--	1.13	--	1.43	--	1.23	--	1.44	--

TABLE 23 . ANALYSIS OF BLACK THUNDER COAL

	Proximate Analysis			
	Raw		SO ₂ -Treated	
	As received	Dry basis	As received	Dry basis
% Moisture	11.20		9.88	
% Ash	5.43	6.12	3.08	3.42
% Volatile	44.53	50.15	41.74	46.32
% Fixed Carbon	38.84	43.73	45.30	50.26
TOTAL	100.00	100.00	100.00	100.0
BTU/lb	10,606	11,944	10,993	12,198
maf BTU		12,723		12,630
% Sulfur	0.39	0.44	0.73	0.81

	Ultimate Analysis			
	Raw		SO ₂ -Treated	
	As received	Dry basis	As received	Dry basis
% Moisture	11.20		9.88	
% Carbon	61.87	69.67	63.57	70.54
% Hydrogen	4.33	4.88	4.46	4.95
% Nitrogen	0.81	0.91	0.80	0.89
% Sulfur	0.39	0.44	0.73	0.81
% Ash	5.43	6.12	3.08	3.42
% Oxygen (diff.)	15.97	17.98	17.48	19.39

TABLE 24. COMPARISON BETWEEN SINGLE AND MULTIPLE
SAMPLE WITHDRAWALS

CATALYST UPTAKE	$Mo_{\text{coal},i}/Mo_{\text{coal,max}}$	
	Uncorrected ⁽¹⁾	Corrected for sampling ⁽²⁾
70°F swelling/impregnation: Single sample at 24 hr Sixth sample at 24 hr ⁽³⁾	0.43 0.54	0.43 ⁽⁴⁾ 0.56
120°F swelling/impregnation: Single sample at 24 hr Sixth sample at 24 hr ⁽³⁾	0.72 0.80	0.72 ⁽⁴⁾ 0.82

Notes:

[1] Catalyst uptake is approximated by $1 - Mo_i/Mo_o$, where Mo_i is the concentration of Mo in the sample withdrawn at the given time and Mo_o is the concentration of available Mo which is assumed equal to the starting Mo concentration.

[2] Corrections are made for the amount of catalyst removed during sampling as follows: (See Appendix A)

$$Mo_{\text{coal},i} = Mo_{\text{coal},i-1} + (Mo_{i-1} - Mo_i) (V_i/W_{\text{coal}})$$

$$Mo_{\text{max}} = Mo_{\text{max},i-1} - [Mo_{i-1} (V_{\text{wd},i}/W_{\text{coal}})]$$

where:

V_i = volume of solution remaining

$V_{\text{wd},i}$ = sample volume withdrawn (= 25 ml)

$W_{\text{coal}} = 100 \text{ g}$

$Mo_{\text{max},o} = Mo_o (V_o/W_{\text{coal}}) = Mo_o (500/100)$

[3] 25-ml samples were withdrawn at each of time intervals 0.5, 1.0, 2.0, 4.0, and 6.0 hr prior to the sample withdrawal at 24 hr.

[4] There is no correction for single sampling.

TABLE 25. CATALYST STRIPPING FROM IMPREGNATED COAL WITH SUBSEQUENT SWELLING

Catalyst-impregnated coals derived from the following treatment:

Swelling/Impregnation Solvent: 30/70 THF/toluene

Treatment time: 48 hr

Temperature: 70°F

Catalyst: Molyvan-L

Coal mesh	Contact time with THF	ppm Mo in liquid ⁽¹⁾	ppm Mo in dried coal ⁽²⁾	
			Measured	Calculated ⁽³⁾
8x60	48 hr	1.0	370	445
-70	48 hr	1.7	500	511
-70	0 hr	--	420	409
	14 days	0.9	410	409

Notes:

- [1] Mo content of THF solvent that was subsequently contacted with the dried catalyst-impregnated coals
- [2] Mo content of the dried coal solids after subsequent contact with THF
- [3] Calculated Mo content of the catalyst-impregnated coals (applying the sampling corrections outlined in Table II and Appendix A).

TABLE 26. SUMMARY OF EXPERIMENTAL CONDITIONS

Simultaneous swelling in IPA and impregnation with catalyst precursor
Ambient, 48 hours

IDENTIFICATION NUMBERS			CATALYST PRECURSOR	TREATMENT		ppm Mo (ICP)
RUN ID.	AEM ID. ⁽¹⁾	XRD ID		Coal	Heat	
18101-27-2	16103-34- E-MV	18101-52-B	Molyvan-L	None	None	3210
18101-30-4	16103-34- E-MO	18101-52-A	Mo octoate	None	None	4400
18101-27-1	16103-165- AB-MV	18101-52D	Molyvan L	SO ₂	None	4710
18101-30-3	16103-165- AB-MO	18101-52-C	Mo octoate	SO ₂	None	5200
18101-35		18101-35	Molyvan L	None	315°C (600°F)	2980
18101-39		18101-39	Mo octoate	None	315°C (600°F)	5200
18101-33		18101-33	Molyvan L	SO ₂	315°C (600°F)	4200
18101-37		18101-37	Mo octoate	SO ₂	315°C (600°F)	6100
18101-42	16103-34- E1-750	18101-34- E-1	Molyvan L	None	400°C (750°F)	ND
18101-41	16103-34- E2-750	18101-34- E-2	Mo octoate	None	400°C (750°F)	ND
18101-44	16103-165- AB1-750	18101-165- AB-1	Molyvan L	SO ₂	400°C (750°F)	ND
18101-43	16103-165- AB2-750	18101-165- AB-2	Mo octoate	SO ₂	400°C (750°F)	ND

ND = not determined

⁽¹⁾ Used when referring to figures in text

TABLE 27 . Reaction Conditions for Untreated and SO₂ Treated Black Thunder Coals Preswelled with Catalyst

Reaction Conditions	
Coal	Untreated Black Thunder
Temperature	385°C, 410°C
Agitation	500 cpm
H ₂ pressure	1250 psig at ambient
Pyrene	0.67 g
Coal (maf)	-1.33 g
Solvent	2.0 g
Reaction Solvent	1-methylnaphthalene, 80% V1074, and 20% DHA
Catalyst Loading	-600-800 ppm based on maf coal
Reaction Time	30 min
Conditions for Preswelling	
Solvents for Preswelling	THF, isopropanol
Amount of Preswelling Solvent	7 g
Catalyst	Slurry phase or powdered
Catalyst Charge to Swelling Solvent	1.05 x 600 to 800 ppm of active metal
Swelling Time	0-96 hrs
Analysis	1. Coal conversion to THF solubles 2. Pyrene conversion to hydrogenated products 3. Catalyst loading (analysis by Amoco)

TABLE 28. Effect of Catalyst Type on Coal and Pyrene Conversions Using Untreated and SO₂ Treated Black Thunder Coal With and Without Solvents^a

Catalyst	Untreated Black Thunder Coal			SO ₂ Treated Black Thunder Coal		
	% Coal Conversion	% Pyrene Conversion	% Pyrene HYD ^b	% Coal Conversion	% Pyrene Conversion	% Pyrene HYD
No Solvent						
None	59.6±0.9	1.6±0.1	1.0±0.1	57.5±11.5	1.3±0.4	0.8±0.3
Molyvan L	72.9±4.6	22.9±4.6	8.3±1.7	90.3±0.1	28.0±2.8	9.8±1.2
MoNaph	48.2±1.8	3.4±1.7	1.1±0.6	85.7±2.0	26.3±2.5	9.2±0.9
FeNaph	54.2±11.2	1.4±0.1	1.0±0.3	63.4±2.8	4.9±4.2	2.1±1.6
NiNaph	62.7±10.9	13.1±6.8	5.7±1.5	73.9±5.7	15.8±0.4	5.7±0.1
VNaph	64.4	4.2	2.0	66.1±1.8	3.9±0.7	1.9±0.3
NiOct	73.8±6.0	25.6±0.1	9.1±0.0	84.4±7.6	21.9±2.0	7.8±0.7
Cr 2-EH	48.0±7.9	1.2±0.3	0.8±0.2	54.8±1.5	3.3±1.6	1.5±0.6
Solvent: 1-Methylnaphthalene						
None	49.3±0.8	3.5±1.1	2.1±0.6	47.3±1.1	1.5±1.1	0.7±0.7
Molyvan L	82.4±3.0	30.0±5.4	11.2±2.4	88.5±0.7	27.8±3.0	10.4±0.6
NiOct	70.7±4.1	6.8±0.3	2.3±0.1	76.3±4.2	12.5±3.5	4.2±1.2
CrNaph	52.8±1.8	0.0±0.0	0.0±0.0	51.7±1.1	0.0±0.0	0.0±0.0
Solvent: V1074						
Molyvan L	84.7±1.0	14.9±2.8	5.7±1.1	90.5±1.9	20.8±2.2	7.6±0.8
NiOct	81.5±0.9	6.8±4.3	2.4±1.6	82.1±3.0	2.0±2.8	0.7±0.9
Solvent: 9,10-Dihydroanthracene						
Molyvan L	89.7±0.2	15.2±4.5	5.4±1.8	92.4±0.7	20.8±4.4	7.4±1.6
NiOct	87.0±1.7	4.4±1.1	2.1±0.4	92.4±5.0	3.7±1.4	1.8±0.5
CoNaph	83.2±0.1	2.2±0.2	1.3±0.1	85.9±0.8	2.7±0.4	1.6±0.3
CrNaph	76.8±4.2	4.0±0.0	2.6±0.0	78.6±5.7	2.9±1.3	2.0±0.9

^a Reaction Conditions: 410°C, 30 min, 1250 psig H₂ at ambient temperature, agitated at 450 cpm.^b HYD = hydrogenation^c MoNaph = molybdenum naphthenate; FeNaph = iron naphthenate; NiNaph = nickel naphthenate;

VNaph = vanadium naphthenate; NiOct = nickel octoate; Cr2-EH = chromium 2-ethylhexanoate;

CrNaph = chromium naphthenate; CoNaph = cobalt naphthenate

TABLE 29 • Effect of Preswelling on Reactions of Untreated and SO₂ Treated Black Thunder Coal in 1-Methylnaphthalene^a

Swelling Solvent	Catalyst	Untreated Black Thunder Coal			SO ₂ Treated Black Thunder Coal		
		Change in Volume (% ΔV)	Coal Conversion (%)	Pyrene Conversion (%)	Change in Volume (% ΔV)	Coal Conversion (%)	Pyrene Conversion (%)
None	None	NA	49.3±0.8	3.5±1.1	NA	47.3±1.1	1.5±1.1
	Molyvan L	NA	82.4±3.0	30.0±5.4	NA	88.5±0.7	27.8±3.0
	Ni Octoate	NA	70.7±4.1	6.8±0.3	NA	76.3±4.211	12.5±3.5
THF	None	34.2±7.0	59.7±8.9	0.0±0.0	87.6±2.7	58.0±9.5	0.0±0.0
	Molyvan L	37.8±1.9	87.3±1.6	18.6±1.3	79.5±0.8	91.2±1.5	25.4±0.1
	Ni Octoate	41.3±0.6	77.0±0.1	2.4±0.1	97.4±3.7	72.5±5.8	2.2±0.4
Methanol	None	26.7±0.8	53.9±2.8	1.0±0.3	38.4±2.3	41.8±2.4	1.5±0.1
	Molyvan L	18.6±0.6	88.0±0.9	24.3±1.8	36.9±7.4	90.0±1.3	30.0±4.4
	Ni Octoate	18.6±0.6	85.5±0.1	10.9±0.4	31.6±7.4	78.7±1.1	4.9±0.8
Isopropanol	None	16.9±5.5	61.7±1.1	0.8±1.1	45.0±0.0	56.4±3.0	1.6±0.1
	Molyvan L	17.9±6.9	88.1±0.4	18.7±0.8	38.6±5.0	91.3±0.6	21.3±2.4
	Ni Octoate	16.3±3.8	77.6±1.1	2.2±0.4	32.3±6.4	73.9±5.1	3.9±0.6
DMSO	None	111.7±3.7	29.3±4.0	1.2±0.5	176.5±26.2	29.8±3.2	1.3±0.4
	Molyvan L	115.9±2.2	79.9±1.9	11.6±0.1	178.9	78.1	13.7
	Ni Octoate	102.4±9.5	63.6±3.6	5.0±0.8	171.6±11.9	50.1±9.5	7.1±1.1

^a Reaction Conditions: 410 °C, 30 min, 1250 psig at ambient temperature agitated at 450 cpm.

TABLE 30 . Coal and Pyrene Conversions in Reactions of Untreated Black Thunder Coal in 1-Methylnaphthalene at 385 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	%ΔV	Coal Conversion (wt %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Time: 30 minutes Swelling Solvent: THF Catalyst: added to reactor						
Mo Naphthenate+S	655±35	N*	39.7±4.6	73.8±1.6	34.4±1.5	14.2±0.6
Molyvan L	602±6.4	N	34.1±9.6	72.5±3.5	25.7±7.2	10.4±3.3
Ni Octoate	803±108	N	34.9±2.2	69.4±7.8	16.2±11.2	6.7±4.2
Time: 30 minutes Swelling Solvent: THF Catalyst: added to swelling solvent						
Mo Naphthenate+S	646±42.4	N	41.9±1.4	76.8±0.3	35.4±0.1	14.6±0.1
Molyvan L	583±4.9	N	33.4±4.2	50.4±3.9	4.5±1.0	2.3±0.2
Ni Octoate	641±23.3	N	33.4±6.7	57.0±1.0	3.6±0.1	1.9±6.1
Time: 30 minutes Swelling Solvent: Isopropanol Catalyst: added to reactor						
Mo Naphthenate+S	758±8.5	N	11.2±3.5	80.0±7.9	29.0±1.8	11.7±0.5
Molyvan L	650±50	N	14.3±6.7	76.7±0.3	23.1±8.0	9.2±3.0
Ni Octoate	698±112	N	14.0±0.4	65.3±0.9	7.7±1.3	3.5±0.4
Time: 30 minutes Swelling Solvent: Isopropanol Catalyst: added to swelling solvent						
Mo Naphthenate+S	616±1.4	N	11.7±3.7	79.3±3.8	32.3±0.8	13.2±0.3
Molyvan L	633±19.1	N	13.6±0.0	55.9±0.3	5.0±0.4	2.6±0.1
Ni Octoate	725±94.0	N	14.3±6.7	62.2±2.7	5.0±0.4	2.6±0.2

* N = not agitated for 96 hr swelling period.

TABLE 31. Coal and Pyrene Conversions for Untreated Black Thunder Coal
Reacted in 1-Methylnaphthalene at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min Swelling Solvent: None						
None	0	NA*	NA	49.3 $\pm$ 0.8	3.5 $\pm$ 1.1	2.1 $\pm$ 0.6
Molyvan L	709 $\pm$ 39	NA	NA	82.4 $\pm$ 3.0	30.0 $\pm$ 5.4	11.2 $\pm$ 2.4
Ni Octoate	604 $\pm$ 6	NA	NA	70.7 $\pm$ 4.1	6.8 $\pm$ 0.3	2.3 $\pm$ 0.1
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Reactor						
None	0	N*	34.2 $\pm$ 7.0	59.7 $\pm$ 8.9	0.0	0.0
Molyvan L	661 $\pm$ 33	N	37.8 $\pm$ 1.9	87.3 $\pm$ 1.6	18.6 $\pm$ 1.3	6.2 $\pm$ 0.4
Ni Octoate	615 $\pm$ 6	N	41.3 $\pm$ 0.6	77.0 $\pm$ 0.1	2.4 $\pm$ 0.1	1.2 $\pm$ 0.1
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Swelling Solvent						
Mo Naphthenate	672 $\pm$ 16	A	35.0 $\pm$ 4.5	62.3 $\pm$ 0.6	3.5 $\pm$ 0.2	1.8 $\pm$ 0.4
Molyvan L	607 $\pm$ 88	N	40.4 $\pm$ 1.8	81.9 $\pm$ 1.6	15.1 $\pm$ 1.8	5.7 $\pm$ 0.4
Molyvan L	653 $\pm$ 94	A	52.3 $\pm$ 3.2	73.6 $\pm$ 3.0	14.7 $\pm$ 5.0	5.7 $\pm$ 1.9
Molyvan L	1188 $\pm$ 64	D	41.0 $\pm$ 2.7	84.8 $\pm$ 1.1	28.6 $\pm$ 2.5	11.0 $\pm$ 1.2
Ni Octoate	624 $\pm$ 78	N	38.9 $\pm$ 5.7	74.8 $\pm$ 12.9	11.1 $\pm$ 11.0	4.7 $\pm$ 4.1
Reaction Time: 20 min Swelling Solvent: THF Catalyst Added to Swelling Solvent						
Mo Naphthenate	608 $\pm$ 9.2	A	37.1 $\pm$ 12.0	53.1 $\pm$ 3.3	2.6 $\pm$ 0.5	1.7 $\pm$ 0.2
Molyvan L	599 $\pm$ 7	N	38.7 $\pm$ 3.2	67.5 $\pm$ 5.4	4.8 $\pm$ 3.5	2.1 $\pm$ 1.3
Ni Octoate	652 $\pm$ 74	N	34.1 $\pm$ 3.3	60.8 $\pm$ 3.2	2.4 $\pm$ 0.3	1.3 $\pm$ 0.1
Reaction Time: 10 min Swelling Solvent: THF Catalyst Added to Swelling Solvent						
Molyvan L	599 $\pm$ 16	N	43.2 $\pm$ 3.3	49.4 $\pm$ 3.7	6.1 $\pm$ 0.9	2.6 $\pm$ 0.2
Reaction Time: 30 min Swelling Solvent: Methanol Catalyst Added to Reactor						
None	0	N	26.7 $\pm$ 0.8	53.9 $\pm$ 2.8	1.0 $\pm$ 0.3	0.8 $\pm$ 0.2
Molyvan L	690 $\pm$ 19	N	18.6 $\pm$ 0.6	88.0 $\pm$ 0.9	24.3 $\pm$ 1.8	8.5 $\pm$ 1.1
Ni Octoate	698 $\pm$ 70	N	18.6 $\pm$ 0.6	85.5 $\pm$ 0.1	10.9 $\pm$ 0.4	4.0 $\pm$ 0.4
Reaction Time: 30 min Swelling Solvent: Methanol Catalyst Added to Swelling Solvent						
Molyvan L	666 $\pm$ 31	N	25.2 $\pm$ 4.9	68.4 $\pm$ 0.0	3.0 $\pm$ 0.8	1.7 $\pm$ 0.5
Molyvan L	1269 $\pm$ 4	D	26.2 $\pm$ 3.4	88.8 $\pm$ 0.5	25.7 $\pm$ 2.7	9.9 $\pm$ 1.3
Ni Octoate	644 $\pm$ 13	N	23.3 $\pm$ 0.8	70.1 $\pm$ 1.1	3.5 $\pm$ 0.4	1.9 $\pm$ 0.1

TABLE 31 (cont). Coal and Pyrene Conversions for Untreated Black Thunder Coal
Reacted in 1-Methylnaphthalene at 410 °C(Continued)

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 20 min Swelling Solvent: Methanol Catalyst Added to Swelling Solvent						
Molyvan L	652 $\pm$ 21	N	25.4 $\pm$ 9.1	67.6 $\pm$ 0.1	2.8 $\pm$ 0.8	1.9 $\pm$ 0.1
Ni Octoate	613 $\pm$ 6.4	N	20.6 $\pm$ 4.5	64.4 $\pm$ 0.4	2.3 $\pm$ 0.4	1.4 $\pm$ 0.3
Reaction Time: 30 min Swelling Solvent: Isopropanol Catalyst Added to Reactor						
None	0	N	16.9 $\pm$ 5.5	61.7 $\pm$ 1.1	0.8 $\pm$ 1.1	0.6 $\pm$ 0.8
Molyvan L	623 $\pm$ 37	N	17.9 $\pm$ 6.9	88.1 $\pm$ 0.4	18.7 $\pm$ 0.8	6.6 $\pm$ 0.3
Ni Octoate	658 $\pm$ 1.4	N	16.3 $\pm$ 3.8	77.6 $\pm$ 1.1	2.2 $\pm$ 0.4	1.1 $\pm$ 0.1
Reaction Time: 30 min Swelling Solvent: Isopropanol Catalyst Added to the Swelling Solvent						
Molyvan L	645 $\pm$ 26	N	18.2 $\pm$ 1.1	79.9 $\pm$ 0.8	16.9 $\pm$ 2.3	6.5 $\pm$ 0.8
Molyvan L	NM	D	22.8 $\pm$ 1.5	81.9 $\pm$ 1.8	28.2 $\pm$ 0.4	10.9 $\pm$ 0.3
Ni Octoate	667 $\pm$ 70	N	15.6 $\pm$ 3.7	75.2 $\pm$ 0.8	3.9 $\pm$ 0.6	1.9 $\pm$ 0.3
Reaction Time: 20 min Swelling Solvent: Isopropanol Catalyst Added to the Swelling Solvent						
Molyvan L	583 $\pm$ 16	N	18.6 $\pm$ 0.6	68.2 $\pm$ 4.0	4.5 $\pm$ 1.8	1.9 $\pm$ 0.7
Ni Octoate	678 $\pm$ 30	N	15.6 $\pm$ 3.7	64.8 $\pm$ 3.7	4.3 $\pm$ 0.4	2.2 $\pm$ 0.1

* A = agitated: samples were agitated with catalyst for 96 hr; N = not agitated for 96 hr swelling period; D = catalyst level doubled; NA = not applicable.

TABLE 32. Coal and Pyrene Conversions for SO₂ Treated Black Thunder Coal
Reacted in 1-Methylnaphthalene at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min Swelling Solvent: None						
None	0	NA ^a	NA	47.3±1.1	1.5±1.1	0.7±0.7
Molyvan L	623±12	NA	NA	88.5±0.7	27.8±3.0	10.4±0.6
Ni Octoate	696±143	NA	NA	76.3±4.2	12.5±3.5	4.2±1.2
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Reactor						
None	0	N ^b	87.6±2.7	58.0±9.5	0.0±0.0	0.0±0.0
Molyvan L	683±53	N	79.5±0.8	91.2±1.5	25.4±0.1	9.1±0.1
Ni Octoate	665±23	N	97.4±3.7	72.5±5.8	2.2±0.4	1.2±0.1
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Swelling Solvent						
Molyvan L	617±30	N	76.1±18.2	86.0±2.2	31.4±0.8	12.5±0.4
Ni Octoate	632±38	N	58.9±26.7	71.4±4.1	6.9±1.2	3.1±0.4
Reaction Time: 30 min Swelling Solvent: Methanol Catalyst Added to Reactor						
None	0	N	38.4±2.3	41.8±2.4	1.5±0.1	1.0±0.0
Molyvan L	672±18	N	36.9±7.4	90.0±1.3	30.0±4.4	11.2±1.5
Ni Octoate	655±2.1	N	31.6±7.4	78.7±1.1	4.9±0.8	1.8±0.6
Reaction Time: 30 min Swelling Solvent: Methanol Catalyst Added to Swelling Solvent						
Molyvan L	648±37	N	43.7±5.2	85.1±5.7	26.8±2.8	11.1±1.6
Ni Octoate	685±1	N	33.4±4.8	78.4±0.2	7.1±0.5	3.1±0.1
Reaction Time: 30 min Swelling Solvent: Isopropanol Catalyst Added to Reactor						
None	0	N	45.0±0.0	56.4±3.0	1.6±0.1	1.1±0.1
Molyvan L	642±25	N	38.6±5.0	91.3±0.6	21.3±2.4	8.0±1.1
Ni Octoate	674±26	N	32.3±6.4	73.9±5.1	3.9±0.6	2.1±0.0
Reaction Time: 30 min Swelling Solvent: Isopropanol Catalyst Added to Swelling Solvent						
Molyvan L	638±1.0	N	32.5±1.2	87.6±1.0	26.0±0.2	10.4±0.1
Ni Octoate	637±25	N	25.0±0.0	67.9±2.3	5.0±0.2	2.4±0.0

^a NA = not applicable. ^b N = not agitated during 96 hrs swelling period.

TABLE 33. Coal and Pyrene Conversions for Untreated Black Thunder
Coal Reacted in V1074 at 410 °C

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min Swelling Solvent: None Catalyst Added to Reactor						
Molyvan L	652±18	NA ^a	NA	84.7±1.0	14.9±2.8	5.7±1.1
Ni Octoate	668±41	NA	NA	79.8±3.5	5.5±4.4	2.0±1.6
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Reactor						
None	0	N ^b	25.0±3.3	72.0±1.7	5.3±0.1	3.0±0.1
Molyvan L	670±57	N	38.7±9.7	82.8±2.0	28.0±0.3	11.8±0.3
Ni Octoate	663±4.2	N	35.0±4.5	77.2±1.8	6.4±0.0	3.3±0.1
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Swelling Solvent						
Molyvan L	648±0.0	N	38.3±1.1	76.0±8.1	14.1±2.3	6.1±0.8
Ni Octoate	683±0.5	N	26.7±0.8	79.5±3.5	4.6±1.5	2.5±0.7

^a NA = not applicable. ^b N = not agitated for 96 hr swelling period.

**TABLE 34. Coal and Pyrene Conversions for Untreated Black Thunder
Coal Reacted in Dihydroanthracene at 410 °C**

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (mol %)	Pyrene Conversion (mol %)	Pyrene Hydrogenation (%)
Reaction Time: 30 min Swelling Solvent: None Catalyst Added to Reactor						
Molyvan L	677 $\pm$ 23	NA ^a	NA	89.7 $\pm$ 0.2	15.2 $\pm$ 4.5	5.4 $\pm$ 1.8
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Reactor						
None	0	N ^b	36.5 $\pm$ 2.3	82.4 $\pm$ 2.1	9.3 $\pm$ 0.2	6.0 $\pm$ 0.1
Molyvan L	658 $\pm$ 33	N	22.2 $\pm$ 0.7	87.3 $\pm$ 2.8	23.5 $\pm$ 4.7	9.4 $\pm$ 1.8
Reaction Time: 30 min Swelling Solvent: THF Catalyst Added to Swelling Solvent						
Molyvan L	641 $\pm$ 41	N	41.0 $\pm$ 6.4	84.5 $\pm$ 0.4	8.9 $\pm$ 2.3	4.6 $\pm$ 0.8

^a NA = not applicable. ^b N = not agitated for 96 hr swelling period.

TABLE 35. Effect of Reaction Solvent on Untreated Black Thunder Coal and Pyrene Conversions^a

Reaction Solvent	Catalyst Type	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Swelling Solvent: THF Catalyst added to THF				
1-Methylnaphthalene	Molyvan L	81.9±1.6	15.1±1.8	5.7±0.4
V1074	Molyvan L	76.0±8.1	14.1±2.3	6.1±0.8
DHA	Molyvan L	84.5±0.4	8.9±2.3	4.6±0.8
1-Methylnaphthalene	Ni Octoate	74.8±12.9	11.1±11.0	4.7±4.1
V1074	Ni Octoate	79.5±3.5	4.6±1.5	2.5±0.7
Swelling Solvent: THF Catalyst added to Reactor				
1-Methylnaphthalene	Molyvan L	87.3±1.6	18.6±1.3	6.2±0.4
V1074	Molyvan L	82.8±2.0	28.0±0.3	11.8±0.3
DHA	Molyvan L	87.3±2.8	23.5±4.7	9.4±1.8
1-Methylnaphthalene	Ni Octoate	77.0±0.1	2.4±0.1	1.2±0.1
V1074	Ni Octoate	77.2±1.8	6.4±0.0	3.3±0.1
Swelling Solvent: Isopropanol Catalyst added to Isopropanol				
1-Methylnaphthalene	Molyvan L	79.9±0.8	16.9±2.3	6.5±0.8
20% DHA 80% V1074	Molyvan L	81.2±1.1	7.7±1.6	3.6±0.6
1-Methylnaphthalene	Molyvan 822	83.3±0.8	24.3±0.1	9.6±0.1
20% DHA 80% V1074	Molyvan 822	88.0±0.1	21.0±1.1	9.1±0.6
1-Methylnaphthalene	Ni Octoate	75.2±0.8	3.9±0.6	1.9±0.3
20% DHA 80% V1074	Ni Octoate	75.3±1.5	5.7±2.5	2.9±0.8
Swelling Solvent: Isopropanol Catalyst added to Reactor				
1-Methylnaphthalene	Molyvan L	88.1±0.4	18.7±0.8	6.6±0.3
1-Methylnaphthalene	Ni Octoate	77.6±1.1	2.2±0.4	1.1±0.1

^a Conditions: Swelled for 96 hr; reacted at 410 °C for 30 min with 1250 psi H₂ introduced at ambient temperature.

TABLE 36. Coal and Pyrene Conversions for Untreated Black Thunder Coal
Reacted in Dihydroanthracene

Catalyst Type	Catalyst Loading (ppm)	%HYD (% Coal)	Added Coal			Conversion		Total Recovery [% R]
			%ΔV	g coal	wt%	Pyrene (mol %)	Coal (wt%)	
Time: 30 min								

TABLE 37. Effect of Molyvan L Loading on Untreated Black Thunder Coal and Pyrene Conversions^a

Swelling Solvent	Catalyst Loading (ppm)	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Reaction Solvent: 1-Methylnaphthalene		Catalyst Added to Swelling Solvent		
THF	100-150	53.7±1.3	2.1±1.3	1.3±0.0
THF	600-800	81.9±1.6	15.1±1.8	5.7±1.9
THF	1200-1600	84.8±1.1	28.6±2.5	11.0±1.2
Methanol	100-150	53.1±2.3	2.1±0.4	1.3±0.2
Methanol	600-800	68.4±0.0	3.0±0.8	1.7±0.5
Methanol	1200-1600	88.8±0.5	25.7±2.7	9.9±1.3
Isopropanol	100-150	51.6±4.0	1.8±0.4	1.2±0.1
Isopropanol	600-800	79.9±0.8	16.9±2.3	6.5±0.8
Isopropanol	1200-1600	81.9±1.8	28.2±0.4	10.9±0.3
Isopropanol	600-800 SS ^b 600-800 R ^c	87.3±1.3	25.9±0.8	10.4±0.4
Isopropanol	300-400 SS 300-400 R	83.0±1.8	17.7±7.9	7.1±3.3

^a Conditions: Swelling for 96 hr, reacted at 410 °C for 30 min with 1250 psi H₂ introduced at ambient temperature.

^b SS = added directly to swelling solvent.

^c R = added directly to reactor.

TABLE 38. Effect of Swelling Time on Untreated Black Thunder Coal and Pyrene Conversions^a

Swelling Time (hr)	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (%)	Pyrene Hydrogenation
Swelling Solvent: THF Reaction Solvent: V1074 Catalyst Added to Swelling Solvent				
0	38.7±9.7 ^b	82.8±2.0	28.0±0.3	11.8±0.3
12	40.7±6.1 ^c	85.4±1.4	31.8±1.6	13.4±0.7
24	32.6±1.7 ^c	84.4±0.6	23.5±7.8	9.8±3.0
48	34.1±3.2 ^c	80.4±1.1	14.7±1.1	6.3±0.3
96	38.3±1.1 ^c	76.0±8.1	14.1±2.3	6.1±0.8
Swelling Solvent: THF Reaction Solvent: 1-MN Catalyst Added to Swelling Solvent				
0	37.8±1.9 ^b	87.3±1.6	18.6±1.3	6.2±0.4
6	41.9±1.4 ^c	76.8±4.0	15.2±6.9	5.9±2.5
16	36.5±9.1 ^c	78.2±5.0	18.1±10.3	7.2±4.2
28	41.0±6.4 ^c	74.1±1.1	8.8±2.3	3.6±1.0
96	40.4±1.8 ^c	81.9±1.6	15.1±1.8	5.7±0.4
Swelling Solvent: Isopropanol Reaction Solvent: 1-MN Catalyst Added to Swelling Solvent				
0	17.9±6.7 ^b	88.1±0.4	18.7±0.8	6.6±0.3
12	14.3±0.0 ^c	71.2±9.4	7.8±2.9	3.7±0.9
24	11.9±3.4 ^c	74.1±5.7	10.1±3.9	4.5±1.3
48	16.3±3.8 ^c	70.2±0.5	9.5±0.3	4.2±0.0
96	18.2±1.1 ^c	79.9±0.8	16.9±2.3	6.5±0.8

^a Conditions: varied swelling times; reacted at 410 °C for 30 min with 1250 psig H₂ introduced at ambient temperature.

^b Coal swelled without catalyst

^c Coal swelled with catalyst.

TABLE 39. Effect of Contact with THF and Catalytic Activity of Molyvan L

Catalyst Type	Catalyst Loading (ppm)	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Time: 30 min			Catalyst added to Reaction		
Molyvan L	661 $\pm$ 32.5	37.8 $\pm$ 1.9	87.3 $\pm$ 1.6	18.6 $\pm$ 1.3	6.2 $\pm$ 0.4
Time: 30 min			Catalyst Placed in THF, separated and added to Reactor		
Molyvan L	656 $\pm$ 23.3	33.4 $\pm$ 4.2	85.2 $\pm$ 1.8	22.9 $\pm$ 4.2	9.0 $\pm$ 1.6

TABLE 41. Effect of Carbon Black Addition on Coal and Pyrene Conversion

Catalyst Type	Catalyst Loading	Compound Added	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Swelling Solvent: THF			Catalyst in Reactor			
Mo Naphthenate + S	659±21	None	36.4±6.4	89.9±1.2	24.8±0.8	10.2±0.2
Mo Naphthenate + S	643±74	Carbon Black in Reactor	31.1±1.0	78.2±0.9	15.8±11.6	6.5±4.7
Mo Naphthenate + S	657±21	Carbon Black in THF	52.0±25	80.0±2.8	21.6±1.3	9.2±0.3
Swelling Solvent: THF			Catalyst in THF			
Mo Naphthenate + S	655±66	None	35.1±11.0	89.9±0.1	26.0±0.5	10.7±0.2
Mo Naphthenate + S	578±9	Carbon Black in Reactor	31.8±12.9	78.3±1.1	21.1±0.6	9.0±0.4
Mo Naphthenate + S	593±47	Carbon Black in THF	46.7±17.5	78.8±1.1	21.8±1.6	9.2±0.7

TABLE 42. Coal and Pyrene Conversion Using V1074 as Swelling and Reaction Solvent

Catalyst Type	Catalyst Loading (ppm)	Condition	%ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
None	0.0	N ^a	NM ^d	70.7±1.3	5.8±0.9	3.0±0.4
Molyvan L	645±55	NoPS ^b	NM	76.8±2.3	25.9±2.4	10.7±1.3
Molyvan L	655±33	NC ^c	NM	77.9±0.4	27.3±0.9	11.6±0.5

^a N = not agitated during preswelling; preswelling solvent used as reaction solvent.

^b NoPS = No preswelling; catalyst added directly to the reactor.

^c Catalyst added to preswelling solvent; preswelling solvent used as reaction solvent.

TABLE 43. Effect of Adding Phosphorous on Catalytic and Thermal Reactions of Untreated Black Thunder Coal

Catalyst Type	Catalyst Loading (ppm)	Phosphorus Loading (ppm)	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Swelling Solvent: THF			Catalyst in Reactor		
None	0.0	0.0	59.7±8.9	0.0±0.0	0.0±0.0
None	0.0	1348±1	54.3±5.7	4.0±0.2	2.4±0.1
Molyvan 822	611±11	0.0	73.4±0.8	8.8±3.7	3.6±1.3
Molyvan 822	625±15	1343±3	83.6±1.8	26.6±1.6	10.7±0.7
Molyvan L	661±33	0.0	87.3±1.6	18.6±1.3	6.2±0.4
Swelling Solvent: THF			Catalyst in Swelling Solvent		
Molyvan 822	600±16	0.0	64.7±9.5	5.5±0.2	3.0±0.1
Molyvan 822	640±23	1338±2	58.5±0.8	4.7±0.0	2.6±0.0
Molyvan L	607±88	0.0	81.9±1.6	15.1±1.8	5.7±0.4
Molyvan L	680±27	1431±130	79.9±3.1	19.6±1.8	7.9±0.6

TABLE 44 . Coal and Pyrene Conversions for Untreated Black Thunder Coal
Reacted in DHA and V1074

Catalyst Type	Catalyst Loading (ppm)	Conditions During Swelling	% ΔV	Coal Conversion (wt%)	Pyrene Conversion (mol%)	Pyrene Hydrogenation (%)
Swelling Solvent: Isopropanol			Catalyst: In Swelling Solvent			
Mo Naphthenate + S	608 $\pm$ 4.9	N	10.9 $\pm$ 3.0	85.3 $\pm$ 0.6	21.3 $\pm$ 1.4	9.9 $\pm$ 0.6
Molyvan L	626 $\pm$ 26.9	N	20.1 $\pm$ 3.7	81.2 $\pm$ 1.1	7.7 $\pm$ 1.6	3.6 $\pm$ 0.6
Molyvan 822	498 $\pm$ 0.7	N	26.7 $\pm$ 0.8	88.0 $\pm$ 0.1	21.0 $\pm$ 1.1	9.1 $\pm$ 0.6
Molyvan 822 + S	664 $\pm$ 40.3	N	25.0 $\pm$ 3.3	86.5 $\pm$ 0.1	23.6 $\pm$ 0.1	10.1 $\pm$ 0.5
Ni Naphthenate	682 $\pm$ 0.0	N	25.7 $\pm$ 4.2	85.5 $\pm$ 1.5	11.4 $\pm$ 0.7	5.1 $\pm$ 0.2
Ni Octoate	626 $\pm$ 38.2	N	17.8 $\pm$ 0.6	75.3 $\pm$ 1.5	5.7 $\pm$ 2.5	2.9 $\pm$ 0.8
Co Naphthenate	660 $\pm$ 9.2	N	28.2 $\pm$ 14.1	73.4 $\pm$ 0.6	4.8 $\pm$ 0.3	3.0 $\pm$ 0.2
Ni Acetylacetonate	671 $\pm$ 55.9	N	20.9 $\pm$ 2.6	80.0 $\pm$ 1.3	7.3 $\pm$ 2.1	3.6 $\pm$ 0.8
Ni Citrate	603 $\pm$ 12.0	N	13.6 $\pm$ 0.0	77.5 $\pm$ 1.4	6.3 $\pm$ 1.2	3.3 $\pm$ 0.1
MoO ₃	746 $\pm$ 36.1	N	18.7 $\pm$ 7.2	83.6 $\pm$ 0.9	9.6 $\pm$ 0.8	4.5 $\pm$ 0.2
MoO ₂ AcAc	697 $\pm$ 21.9	N	19.6 $\pm$ 3.0	78.9 $\pm$ 3.2	6.2 $\pm$ 0.4	3.2 $\pm$ 0.1
Swelling Solvent: 20% Isopropanol/80% Water			Catalyst: In Swelling Solvent			
Molyvan L	777 $\pm$ 83.4	N	28.0 $\pm$ 0.9	87.5 $\pm$ 1.9	28.6 $\pm$ 0.8	11.5 $\pm$ 0.6
(NH ₄) ₂ MoS ₄	632 $\pm$ 10.6	N	18.6 $\pm$ 0.6	89.5 $\pm$ 0.6	27.6 $\pm$ 1.4	11.6 $\pm$ 0.6
Molyvan 822	605 $\pm$ 15.6	N	38.7 $\pm$ 3.2	83.2 $\pm$ 2.8	11.5 $\pm$ 0.9	5.0 $\pm$ 0.4
Ni Naphthenate	619 $\pm$ 25.5	N	23.8 $\pm$ 0.0	84.5 $\pm$ 2.3	12.1 $\pm$ 2.9	5.2 $\pm$ 0.8

TABLE 45. IMPREGNATED ARGONNE COAL SAMPLES

Sample	Coal	Metal	Loading (ppm)	Metal	Loading (ppm)
BT-1-Mo ^a	Black Thunder	Mo	829		
BT-1-Fe	Black Thunder	Fe	548		
BT-1-Co	Black Thunder	Co	212		
BT-1-Ni	Black Thunder	Ni	257		
BT-2-Mo	Black Thunder	Mo	418		
BT-2-Fe	Black Thunder	Fe	483		
BT-2-Co	Black Thunder	Co	83		
BT-2-Ni	Black Thunder	Ni	464		
WY-Mo ^b	Wyodak	Mo	847		
WY-Fe	Wyodak	Fe	552		
Wy-Co	Wyodak	Co	668		
Wy-Ni	Wyodak	Ni	822		
Fe-Mo-1	Black Thunder	Fe	456	Mo	210
Fe-Mo-2	Black Thunder	Fe	484	Mo	70
Fe-Ni-1	Black Thunder	Fe	408	Ni	224
Fe-Ni-2	Black Thunder	Fe	472	Ni	106

^a Note that BT-1 and BT-2 were two batches of Black Thunder Coal received by Argonne Laboratories from Amoco.

^b Wyodak coal was SO₂ treated.

30°
TABLE 46. COAL AND PYRENE CONVERSIONS USING NICKEL AND
COBALT TREATED BLACK THUNDER COAL

Catalyst [Label]	Added Coal		Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [%R]
	(g)	wt %			
Solvent: 1-Methylnaphthalene					
Nickel [Ni 1]	1.6517	30.9	2.5	63.6	4.4038[101.8]
Nickel [Ni 1]	1.6498	30.9	2.7	64.3	4.6376[107.4]
Nickel [Ni 2]	1.6522	30.9	3.4	70.1	4.8328[111.7]
Nickel [Ni 2]	1.6539	30.9	2.5	61.9	4.3385[100.3]
Cobalt [Co 1]	1.6510	30.9	2.7	62.3	4.6384[107.3]
Cobalt [Co 1]	1.6493	30.9	3.1	64.4	4.9445[114.4]
Cobalt [Co 2]	1.6540	30.9	3.4	67.1	4.2309[97.8]
Cobalt [Co 2]	1.6511	30.9	2.5	63.1	4.4005[101.7]
Molybdenum [Mo 1]	1.6409	30.8	5.5	67.8	4.0856[94.7]
Molybdenum [Mo 1]	1.6421	30.8	5.1	63.3	4.1202[95.4]
Molybdenum [Mo 2]	1.6444	30.8	3.6	59.4	4.4652[103.5]
Molybdenum [Mo 2]	1.6424	30.8	2.7	67.3	4.5634[105.8]
Iron [Fe 1]	1.6444	30.8	4.4	61.3	4.4515[103.1]
Iron [Fe 1]	1.6410	30.8	2.5	59.0	4.3598[101.1]
Iron [Fe 2]	1.6414	30.8	2.8	63.5	4.2976[99.6]
Iron [Fe 2]	1.6462	30.8	3.3	68.3	4.4908[103.9]
Iron-Nickel [Fe-Ni 1]	1.6424	30.8	4.0	65.4	4.4631[103.4]
Iron-Nickel [Fe-Ni 1]	1.6444	30.8	3.8	69.6	4.4811[103.8]
Iron-Nickel [Fe-Ni 2]	1.6437	30.8	4.1	64.3	4.5355[105.1]
Iron-Nickel [Fe-Ni 2]	1.6404	30.8	3.9	68.5	4.3298[100.4]
Iron-Molybdenum [Fe-Mo 1]	1.6433	30.8	5.4	67.1	4.3737[101.3]
Iron-Molybdenum [Fe-Mo 1]	1.6429	30.8	5.2	71.2	4.4062[102.3]
Iron-Molybdenum [Fe-Mo 2]	1.6428	30.8	4.7	64.8	4.3892[101.6]
Iron-Molybdenum [Fe-Mo 2]	1.6411	30.8	4.9	68.2	4.4332[102.7]

TABLE 47. PYRENE PRODUCT DISTRIBUTIONS WITH NICKEL AND COBALT TREATED BLACK THUNDER COAL

Catalyst [Label]	% H (% Coal)	Product Distribution (mol %)			
		PYR	DHP	THP	HHP
Solvent: 1-Methylnaphthalene					
Nickel [Ni 1]	1.5(30.9)	97.5	1.5	0	1.0
Nickel [Ni 1]	1.5(30.9)	97.3	1.8	0	0.9
Nickel [Ni 2]	1.7(30.9)	96.6	2.5	0	0.9
Nickel [Ni 2]	1.4(30.9)	97.5	1.7	0	0.8
Cobalt [Co 1]	1.6(30.9)	97.3	1.6	0	1.1
Cobalt [Co 1]	1.7(30.9)	96.9	2.1	0	1.0
Cobalt [Co 2]	1.9(30.9)	96.6	2.3	0	1.1
Cobalt [Co 2]	1.5(30.9)	97.5	1.5	0	1.0
Molybdenum [Mo 1]	2.5(30.8)	94.5	4.6	0	0.9
Molybdenum [Mo 1]	2.3(30.8)	94.9	4.2	0	0.9
Molybdenum [Mo 2]	2.0(30.8)	96.4	2.5	0	1.1
Molybdenum [Mo 2]	1.5(30.8)	97.3	1.8	0	0.9
Iron [Fe 1]	2.2(30.8)	95.6	3.3	0	1.1
Iron [Fe 1]	1.4(30.8)	97.5	1.6	0	0.9
Iron [Fe 2]	1.6(30.8)	97.2	1.9	0	0.9
Iron [Fe 2]	1.7(30.8)	96.7	2.4	0	0.9
Iron-Nickel [Fe-i 1]	2.0(30.8)	96.0	3.0	0	1.0
Iron-Nickel [Fe-Ni 1]	1.9(30.8)	96.2	2.8	0	1.0
Iron-Nickel [Fe-Ni 2]	2.1(30.8)	95.9	3.0	0	1.1
Iron-Nickel [Fe-Ni 2]	2.0(30.8)	96.1	2.9	0	1.0
Iron-Molybdenum [Fe-Mo 1]	2.5(30.8)	94.6	4.4	0	1.0
Iron-Molybdenum [Fe-Mo 1]	2.4(30.8)	94.8	4.2	0	1.0
Iron-Molybdenum [Fe-Mo 2]	2.2(30.8)	95.3	3.8	0	0.9
Iron-Molybdenum [Fe-Mo 2]	2.5(30.8)	95.1	3.5	0	1.4

TABLE 48. COAL AND PYRENE CONVERSIONS USING METAL TREATED WYODAK COALS

Catalyst (ppm)	Added Coal		Pyrene Conversion (mole %)	Coal Conversion (mole %)	Total Recovery (g) [%R]
	(g)	wt %			
Solvent: 1-Methylnaphthalene					
Iron	2.0284	28.3	3.3	74.8	4.9569[105.4]
Iron	2.0289	28.3	3.3	74.6	4.6361[98.6]
Cobalt	2.0295	28.3	3.1	56.9	5.0320[107.0]
Cobalt	1.8280	28.2	1.9	49.8	4.4978[105.9]
Molybdenum	2.0284	28.3	6.2	75.1	5.0478[107.4]
Molybdenum	2.0341	28.3	2.8	73.3	5.0565[107.4]
Nickel	2.0291	28.3	2.8	75.5	4.8974[104.3]
Nickel	2.0315	28.3	3.5	75.6	5.0471[107.2]

TABLE 49. PYRENE PRODUCT DISTRIBUTIONS WITH METAL TREATED WYODAK COAL

Catalyst (ppm)	% H (% Coal)	Product Distribution (mole %)			
		PYR	DHP	THP	HHP
Solvent: 1-Methylnaphthalene					
Iron	2.0(28.3)	96.7	2.0	0	1.3
Iron	1.9(28.3)	96.7	2.1	0	1.2
Cobalt	1.9(28.3)	96.9	1.7	0	1.4
Cobalt	1.4(28.2)	98.1	0.8	0	1.1
Molybdenum	3.0(28.3)	93.8	4.8	0	1.4
Molybdenum	1.5(28.3)	97.2	1.9	0	0.9
Nickel	1.5(28.3)	97.2	1.9	0	0.9
Nickel	2.1(28.3)	96.5	2.1	0	1.4

TABLE 50

SOLVENT ANALYSES

Designation	V-1074 (650-1000°F)	FSN-113 (Resid)	Blend 80/20
Elemental Analyses, Wt%			
Carbon	87.23	89.56	88.41
Hydrogen	9.68	8.26	8.97
Nitrogen	0.53	0.80	0.66
Oxygen	2.52	1.33	1.92
Sulfur	0.04	0.05	0.04
Distillation, wt%			
IBP-650 F	--	8.8	--
650-975 F	--	53.7	--
975+ F	--	37.5	--
Solubility, wt%			
THF Insolubles	0.01	0.09	0.05
Toluenes Insolubles	0.12	1.31	0.71
Hexane Insolubles	1.32	15.33	8.32

TABLE 51

RESULTS OF THE CONTINUOUS AU-51 UNIT RUNS
(Based on normalized results)

Run Number	93	102	113	115
Coal (1)	--	--	Swollen	Swollen
Catalyst	None	MV-L	--	MV-L
Solvent	V-1074	V-1074	80/20 V-1074/Resid	80/20 V-1074/Resid
Space Time, Min	80.7	89.0	78.7	71.4
<u>Conversion, %MAF (2)</u>				
THF Solubles	79.2	81.4	82.2	72.0
Tcl Solubles	68.9	63.0	69.8	48.8
Hexane Solubles	-8.1	-45.5	-37.9	-96.0
C1-C3 Gases	5.4	9.1	8.4	13.9
C4+ Gases	2.7	3.6	2.4	12.3
CO, CO2	4.4	5.4	4.8	6.8

Notes:

1. In Runs 93 and 102, SO₂-treated Black Thunder coal was used.
In Run 113, SO₂-treated BT coal preswelled with 80/20 toluene/THF.
In Run 115, THF was added to the liquefaction solvent before the run.
2. Conversions are based on moisture, ash free feed coal (using approach of forcing slurry weight to give 100% material balance).

RLO/ml/94366
11/17/94

TABLE 52

ANALYSES OF AU-51 PRODUCT STREAMS

Run Number 16103-93C

Sample	Solids	Pre-Asph	Asphaltenes	Oils
Yield, %	20.8	10.3	77.0	---
Elemental				
Carbon	74.28	84.14	87.59	89.41
Hydrogen	4.03	5.61	6.41	9.05
Nitrogen	1.30	1.58	1.22	0.40
Oxygen	7.66	7.35	3.65	1.29
Sulfur	0.95	0.28	0.18	0.07
Ash		--	--	--
Total	88.22	98.96	99.05	100.22

Run Number 16103-102C

Sample	Solids	Pre-Asph	Asphaltenes	Oils
Yield, %	18.6	18.4	100+	---
Elemental				
Carbon	81.22	85.26	87.45	89.78
Hydrogen	4.20	5.49	5.53	8.58
Nitrogen	1.36	1.33	1.52	0.49
Oxygen	5.75	5.87	4.91	1.39
Sulfur	0.47	0.19	0.18	0.09
Ash		--	--	--
Total	93.00	98.14	99.59	100.33

Run Number 16103-113C

Sample	Solids	Pre-Asph	Asphaltenes	Oils
Yield, %	17.8	12.4	100+	---
Elemental				
Carbon	77.45	85.46	88.27	89.42
Hydrogen	3.99	5.73	6.02	8.77
Nitrogen	1.28	1.42	1.29	0.43
Oxygen	6.20	6.04	3.43	1.06
Sulfur	0.78	0.12	0.16	0.09
Ash		--	--	--
Total	89.70	98.77	99.17	99.77

Run Number 16103-115C

Sample	Solids	Pre-Asph	Asphaltenes	Oils
Yield, %	28.0	23.2	100+	---
Elemental				
Carbon	78.98	86.68	88.60	89.22
Hydrogen	4.01	5.54	6.32	8.99
Nitrogen	1.23	1.30	1.16	0.41
Oxygen	5.09	5.49	3.19	1.20
Sulfur	0.77	0.19	0.17	0.52
Ash		--	--	--
Total	90.08	99.20	99.44	100.34

TABLE 53

AVERAGED ANALYSES OF AU-51 PRODUCT STREAMS
Run Numbers 16103-93C, 102C, 113C, 115C
(DCC entered 6/14/93)

Sample	Solids	Pre-Asph	Asphaltenes	Oils	Feed Coal SO ₂ -Treated	20/80 Solvent
Carbon	77.98	85.39	87.98	89.46	71.26	88.41
Hydrogen	4.06	5.59	6.07	8.85	5.29	8.97
Nitrogen	1.29	1.41	1.30	0.43	1.03	0.66
Oxygen	6.18	6.19	3.80	1.24	18.38	1.92
Sulfur	0.74	0.20	0.17	0.19	0.80	0.04
Ash		--	--	--	3.24	---
Total	90.25	98.77	99.31	100.17	100.00	100.00

Elemental Ratios of the Fractions:

H/C	0.625	0.787	0.829	1.188	0.892	1.219
N/C	0.014	0.014	0.013	0.004	0.012	0.006
O/C	0.059	0.054	0.032	0.010	0.193	0.016
S/C	0.004	0.001	0.001	0.001	0.004	0.000

TABLE 54

Summary of Operating Data
(SO₂-Treated Black Thunder Coal)
(AU-51 Unit Runs for DOE 70-6186)

Run Number:	18119-27A	18119-27B	18119-27C	18119-44AB	18119-44C	18119-66B	18119-66C	18119-66E	18119-66F	18119-66A
Slurry Feed:										(Solvent only)
SO ₂ -Treated BT Coal	33.0%	33.0%	31.15%	29.82%	29.82%	30.86%	30.86%	32.83%	32.83%	—
Raw V-1074	40.2%	40.2%	37.95%	34.52%	34.52%	36.84%	36.84%	39.32%	39.32%	60.00%
Hydrogenated V-1074	26.8%	26.8%	25.31%	22.85%	22.85%	24.85%	24.85%	26.24%	26.24%	40.00%
Resid	—	—	—	3.07%	3.07%	—	—	—	—	—
Swelling Solvent: IPA	—	—	1.10%	1.80%	1.80%	1.22%	1.22%	—	—	—
Swelling Solvent: Tol	—	—	4.49%	7.24%	7.24%	4.90%	4.90%	—	—	—
Red Mud + TPS-32	—	—	—	0.30+0.30%	0.30+0.30%	0.30+1.18%	0.30+1.18%	0.32+1.25%	0.32+1.25%	—
MVL/MN with swelling*	—	—	—	100ppm-MVL	100ppm-MVL	100ppm-MN	100ppm-MN	—	—	—
MVL/MN added to tank	—	—	—	—	100ppm-MVL	—	100ppm-MN	100ppm-MN	200ppm-MN	2ppm-MN soft
Slurry Feed Rate, Lb/Hr	1.30	1.042	1.283	1.427	1.427	1.478	1.381	1.231	1.171	0.783
*(Molyvan-L (MVL) or MoNaphthenate (MN) specified as ppm Mo on coal.)										
Operating Data:										
Initial Date	9/20/93	9/21/93	9/21/93	10/13/93	10/14/93	11/9/93	11/9/93	11/11/93	11/12/93	11/8/93
Final Date	9/20/93	9/21/93	9/21/93	10/14/93	10/14/93	11/9/93	11/10/93	11/12/93	11/12/93	11/9/93
Initial Time	2100	0000	0900	1710	0700	1500	2350	2008	0930	2140
Final Time	0000	0730	1500	0700	2350	2350	0800	0730	1500	0730
Op'n Time	3.0	7.5	6	13.83	16.83	8.83	8.17	11.4	5.5	9.33
Initial Feed Scale	35.89	31.99	34.12	55.33	36.29	47.13	33.48	43.14	28.54	26.22
Final	31.99	23.89	28.41	38.29	12.28	34.08	22.38	29.11	20.10	18.91
Feed Slurry, Lbs.	3.90	8.10	7.70	*19.73	24.01	13.05	11.12	14.03	6.44	7.31
* Corrected for 0.5 hr off-stream										
Product weights										
Slurry	3.85	6.70	7.63	17.12	18.68	10.98	10.30	11.05	12.20	7.29
Light Ends										
Reactor 1 Temp, F	821	827	821	817	825	825	826	824	825	750
Reactor 2 Temp, F	820	820	793	787	781	823	821	822	823	750
Reactor Pressure, Psig	1995	1997	2002	1996	1996	1999	1999	1997	1997	1997
Room Temperature, F	69	66	72	67	67	63	64	64	63	63
WTM FQ-01	1.31	3.89	3.76	55.33	67.66	39.91	33.45	42.99	20.17	32.55
Brooks, scf	4.88	4.88	4.88	4.90	4.99	4.89	4.89	4.89	4.89	4.90

TABLE 55a

**Summary of Extraction Results
(SO₂-Treated Black Thunder Coal)
(AU-51 Unit Runs for DOE 70-8186)**

Run Number:	18119-27A	18119-27B	18119-27C	18119-44AB	18119-44C	18119-66B	18119-66C	18119-66E	18119-66F	18119-66A
Slurry Feed:										Solvent only
Coal Conc., wt%	33.0%	33.0%	31.15%	29.82%	29.82%	30.66%	30.66%	32.83%	32.83%	—
Solvent (Raw/H ₂ V-1074)	40/27	40/27	38/25	35/23	35/23	37/25	37/25	39/26	39/26	60/40
Swelling Solvent	None	None	IPA/Tol	IPA/Tol	IPA/Tol	IPA/Tol	None	None	None	None
Catalyst - Red Mud	None	None	None	1% on Coal	1% on Coal	1% on Coal	1% on Coal	1% on Coal	1% on Coal	None
-MVL/MN (S,T)*	None	None	None	S-MVL	S+T- MVL	S-MN	S+T- MN	T- MN	T 200 MN	T- MN
Slurry Feed Rate, Lb/Hr	1.30	1.04	1.28	1.43	1.43	1.48	1.36	1.23	1.17	0.78#/Hr
Space Time, Min.	55.0	66.1	55.7	54.5	50.1	48.4	49.8	58.1	61.1	

*Catalyst (100ppm) added during swelling (S) or directly to feed tank (T), MVL is Molyvan-L and MN is Molybdenum Naphthenate.

Extraction Data:

THF Ins:	4.12	5.24	6.17	8.52	5.79	4.80	4.11	2.88	3.16	0.24
Toluene Ins:	4.82	5.80	7.41	9.92	8.01	6.28	6.01	3.74	3.77	0.10
Hexane Ins:	21.67	25.91	25.70	20.73	28.79	26.26	18.31	19.27	10.31	0.41
Pre-asph:	0.70	0.55	1.24	2.49	2.23	1.48	1.90	0.86	0.61	-0.14
Asph:	16.85	20.11	18.29	10.81	20.78	19.98	12.30	15.53	6.53	0.31
Oils:	78.33	74.09	74.30	74.69	71.21	73.74	81.69	80.73	89.69	99.59

Extraction Yields (MAF Coal Basis: Forced Material Balances)

Conversion (THF Sol)	87.8	82.5	79.0	66.0	79.0	83.2	87.5	93.1	92.2	
Conversion (Tol Sol)	86.4	80.4	74.1	53.6	69.5	77.0	79.6	89.7	89.8	

TABLE 55b

**Summary of Extraction and Distillation Results
(SO₂-Treated Black Thunder Coal)
(AU-51 Unit Runs for DOE 70-6186)**

Run No. 18119-	27A	27B	27C	44AB	44C
Swelling solvent	None	None	IPA/Tol	IPA/Tol	IPA/Tol
Red Mud	None	None	None	1% on coal	1% on coal
MVL/MN (S,T) ^[1]	None	None	None	S-MVL	S+T-MVL
Feed rate, lb/hr	1.30	1.04	1.28	1.43	1.43
XProduct recovery	98.7	82.6	99.2	94.4	77.8
Yields, % MAF coal:					
THF-solubles	88.0	86.1	79.2	68.1	84.5
Toluene-solubles	86.6	84.3	74.4	56.4	77.1
Oils	40.6	19.5	3.9	5.3	7.5
Asphaltenes	45.9	64.8	70.5	51.1	69.6
Preasphaltenes	1.4	1.8	4.8	11.7	7.4
C ₁ - C ₃ Gases	0	0	0	0.27	0.07
C ₄ ⁺ Gases	0	0	0	0.03	0.01
CO, CO ₂	0	0	0	0.19	0.05
Distillation yields (wt% slurry): ^[2]					
IBP-360°F	4.4	5.5	7.1	5.2	5.2
360-650°F	30.0	32.5	29.6	28.0	27.3
650-1000°F	56.6	52.2	53.1	55.7	55.6
1000°F ⁺	9.0	9.8	10.2	11.1	11.9
% HDN	0.5	25.0	0.0	0.0	0.0
% HDO	88.0	90.4	85.7	70.0	50.4
% H ₂ Consumption	4.0	(-1.5)	3.5	2.1	11.6

- [1] Catalyst (100 ppm) added during swelling (S) and/or directly to feed tank (T); MVL = Molyvan L; MN = Mo naphthenate
- [2] High-temperature simulated distillation results

TABLE 55b (cont)

**Summary of Extraction and Distillation Results
(SO₂-Treated Black Thunder Coal)
(AU-51 Unit Runs for DOE 70-6186)**

Run No. 18119-	66B	66C	66E	66F
Swelling solvent	IPA/Tol	None	None	None
Red Mud	1% on coal	1% on coal	1% on coal	1% on coal
MVL/MN (S,T) ^[1]	S-MN	S+T-MN	T-MN	T-200MN
Feed rate, lb/hr	1.48	1.36	1.23	1.17
%Product recovery	84.0	87.9	101.5 ^[2]	100.0 ^[2]
Yields, % MAF coal:				
THF-solubles	87.7	89.5	93.1	92.2
Toluene-solubles	82.6	82.5	89.7	89.8
Oils	13.5	37.2	28.0	64.2
Asphaltenes	69.1	45.3	61.8	25.7
Preasphaltenes	5.1	6.9	3.4	2.4
C ₁ - C ₃ Gases	0.11	0.11	0.10	0.09
C ₄ ⁺ Gases	0.01	0.01	0.01	0.01
CO, CO ₂	0.05	0.06	0.06	0.04
Distillation yields (wt% slurry): ^[3]				
IBP-360°F	18.6	15.6	11.9	7.8
360-650°F	23.9	25.2	26.1	26.0
650-1000°F	37.5	33.8	40.1	51.4
1000°F ⁺	17.5	17.5	16.5	12.3
% HDN	0.0	0.0	0.0	1.4
% HDO	82.1	83.0	74.1	71.7
% H ₂ Consumption	(-1.5)	2.5	7.2	6.8

- [1] Catalyst (100 ppm, except for 66F where it is 200 ppm) added during swelling (S) and/or directly to feed tank (T); MVL = Molyvan L; MN = Mo naphthenate
- [2] Actual recoveries not used because of errors in weighing products; results shown here were calculated using forced (100%) material balances.
- [3] Oldershaw (ASTM) distillation results; note difference in high-boiling cutpoint (compared to simulated distillation results for Runs 27 and 44).

TABLE 56

**Summary of Feed Slurry Extraction Results
(SO₂-Treated Black Thunder Coal)
(AU-51 Unit Runs for DOE 70-8186)**

	18119-27A&B Feed	18119-27C Feed	18119-44A Feed	18119-44C&D Feed	18119-66A Feed	18119-66F Feed
Slurry Feed:						
SO ₂ -Treated	33.0%	31.15%	29.82%	29.82%	—	32.83%
Raw V-1074	40.2%	37.85%	34.52%	34.52%	60.00%	39.32%
H ₂ V-1074	26.8%	25.31%	22.95%	22.95%	40.00%	26.24%
Resid	—	—	3.07%	3.07%	—	—
Swelling Solvent: IPA	—	1.10%	1.80%	1.80%	—	—
Swelling Solvent: Tol	—	4.49%	7.24%	7.24%	—	—
Red Mud + TPS-32	—	—	0.30+0.30%	0.30+0.30%	—	0.32+1.25%
MVL/MN with swelling	—	—	100ppm MVL	100ppm MVL	—	—
MVL/MN added to tank (ppm Mo on coal)	—	—	—	100ppm MVL 132 MN on sol/t	—	200ppm MN
Extraction Data:						
THF Ins	25.95	26.38	31.92	30.20	4.20	29.54
Toluene Ins	27.80	28.04	36.30	34.22	4.55	31.57
Hexane Ins	28.24	28.42	37.80	35.35	5.31	32.28
Pre-asphaltenes	1.85	1.96	4.36	4.02	0.35	2.03
Asphaltenes	0.44	0.39	1.60	1.13	0.76	0.71
Oils	71.76	71.58	62.10	64.65	94.69	67.72
Ash	2.81	3.02	4.30	3.95	2.94	3.26
Analyses, wt%						
HF Insolubles						
Carbon	69.03	69.72	69.36	68.86		68.53
Hydrogen	5.81	5.88	5.40	5.36		5.51
Nitrogen	0.78	0.64	1.21	1.08		1.04
Oxygen	17.57	17.87	18.53	18.71		18.71
Sulfur	0.76	0.77	0.80	0.78		0.69
Ash	2.81	3.02	4.30	3.95		
Total	96.76	97.90	99.60	98.74		94.48
Preasphaltenes						
Carbon	75.54	76.27	77.56	76.23		76.99
Hydrogen	7.23	7.37	6.82	7.17		7.74
Nitrogen	0.95	0.91	1.13	1.31		0.98
Oxygen	12.70	12.72	12.64	13.22		11.92
Sulfur	0.29	0.29	0.32	0.33		0.29
Total	96.42	97.27	98.15	97.93		97.63
Asphaltenes						
Carbon	79.95	81.48	83.94	82.68		82.14
Hydrogen	6.77	6.77	6.42	6.22		6.50
Nitrogen	1.49	1.85	1.74	1.94		2.29
Oxygen	7.90	6.20	5.52	6.28		6.56
Sulfur	0.58	0.65	0.60	1.15		1.89
Total	96.11	96.40	97.62	97.12		97.49
Oils (Hexane Sol)						
Carbon	88.24	89.11	88.57	88.60		87.13
Hydrogen	9.61	9.96	9.95	10.49		10.16
Nitrogen	0.50	0.50	1.15	0.75		0.82
Oxygen	0.60	0.50	0.95	1.37		0.94
Sulfur	0.04	0.05	0.12	0.13		0.50
Total	98.95	100.07	100.62	101.21		99.05

TABLE 57

Summary of Analyses of Extracted Fractions
(SO₂-Treated Black Thunder Coal)
(AU-51 Unit Runs for DOE 70-8188)

Run Number:	18119-27A	18119-27B	18119-27C	18119-44AB	18119-44C	18119-66B	18119-66C	18119-66E	18119-66F	18119-66A
Slurry Feed:										Solvent only
Coal Conc., wt%	33.0%	33.0%	31.15%	29.82%	29.82%	30.66%	30.66%	32.83%	32.83%	—
Solvent (Raw/H ₂ V-1074)	40/27	40/27	38/25	35/23	35/23	37/25	37/25	39/28	39/28	60/40
Swelling Solvent	None	None	IPA/Tol	IPA/Tol	IPA/Tol	IPA/Tol	None	None	None	None
Catalyst - Red Mud	None	None	None	1% on Coal	1% on Coal	1% on Coal	1% on Coal	1% on Coal	1% on Coal	None
-MVL/MN (S,T)*	None	None	None	S-MVL	S+T-MVL	S-MN	S+T-MN	T-MN	T 200 MN	T-MN
Slurry Feed Rate, Lb/Hr	1.30	1.04	1.28	1.43	1.43	1.48	1.38	1.23	1.17	0.78
*Catalyst (100ppm) added during swelling (S) or directly to feed tank (T).										
Analyses, wt%										
THF Insolubles										
Carbon	70.54	74.25	75.32	67.07	67.75	63.91	64.23	62.99	62.60	
Hydrogen	3.87	3.82	4.00	3.87	3.47	3.38	3.43	3.29	3.67	
Nitrogen	1.32	1.19	1.45	1.44	1.33	1.68	1.43	1.27	1.46	
Oxygen	7.51	5.19	5.37	8.45	5.98	6.04	5.91	6.09	8.71	
Sulfur	1.55	1.32	1.24	2.91	3.12	3.98	4.20	4.81	4.25	
Ash	17.54	13.30	13.59	18.12	19.27	22.24	23.91	25.34	23.08	
Total	102.33	99.17	100.97	101.88	100.92	101.19	103.11	103.79	103.75	
Preasphaltenes										
Carbon	82.90	85.02	84.74	83.51	84.21	84.18	84.08	84.99	84.07	
Hydrogen	7.78	7.34	8.59	5.90	5.77	6.00	5.92	6.05	6.11	
Nitrogen	0.50	0.68	0.83	1.50	1.81	1.24	1.55	1.32	1.46	
Oxygen	6.44	5.27	6.11	7.89	6.84	6.54	6.97	6.58	7.11	
Sulfur	0.14	0.18	0.18	0.27	0.21	0.21	0.21	0.24	0.24	
Total	97.82	98.49	98.27	98.80	98.43	97.94	98.52	98.94	98.75	
Asphaltenes										
Carbon	88.58	88.98	88.93	87.31	87.48	88.78	87.94	88.80	87.18	
Hydrogen	5.75	6.28	6.39	5.64	6.32	6.30	5.84	5.93	5.52	
Nitrogen	1.55	0.77	1.15	1.48	1.82	1.04	1.48	1.39	1.83	
Oxygen	3.54	2.04	2.65	4.58	4.28	3.10	4.19	3.32	4.94	
Sulfur	0.14	0.10	0.12	0.21	0.12	0.12	0.16	0.12	0.20	
Total	99.40	99.05	99.12	98.99	99.88	99.22	99.45	99.44	99.47	
Oils (Hexane Sol)										
Carbon	88.95	90.69	89.81	88.94	88.23	88.80	88.94	88.85	88.89	
Hydrogen	8.98	9.09	8.98	9.54	9.21	8.73	9.70	9.83	9.50	
Nitrogen	0.50	0.50	0.83	0.71	0.52	0.74	0.68	0.52	0.52	
Oxygen	0.05	0.03	0.04	1.73	1.22	1.24	1.07	1.11	1.31	
Sulfur	0.94	0.78	0.55	0.05	0.08	0.04	0.08	0.13	0.05	
Total	99.46	100.31	99.44	100.92	99.15	97.51	100.37	100.31	100.22	

Liquefaction of SO₂ Treated Black Thunder Coal
Using AU-51L, Two-stage Coal Liquefaction Unit
High Severity 825 F

TABLE 58

	IBP--350	350--650	650-900	900+
Swollen, Cat(100Mn)	11.9	26.1	41.6	20.4
Swollen, Cat(200Mn)	16.1	23.7	48.7	11.5

Actual Distillation Data

TABLE 59

**Summary of AU-44 Operating Data
Raw Black Thunder Runs
(Swollen and Molyvan-L Series)
(AU-44 Unit Runs for DOE 70-6186)**

Run Number:	18119-171	18119-174	18119-188	18119-190	18119-191
Slurry Feed	Raw BT V1074 Non-Cat 1.28 #/Hr	Raw BT V1074 100ppm MVL 1.32 #/Hr	Swollen BT 1074(IPA/T) Non-Cat 1.34 #/Hr	Swollen BT 1074(IPA/T) 100ppm MVL 1.05 #/Hr	Swollen BT 1074(IPA/T) 100ppm MVL 1.26 #/Hr
Initial Date	4/25/94	4/26/94	6/7/94	6/8/94	6/8/94
Final Date	4/26/94	4/26/94	6/8/94	6/8/94	6/8/94
Initial Time	1500	1400	1400	0900	1600
Final Time	0800	2300	0800	1300	2100
Run Time, Hr	17.00	9.00	18.00	4.00	5.00
Initial Feed Scale	43.52	16.04	42.48	18.32	11.42
Final	23.04	4.20	19.74	14.14	5.12
Feed Slurry, Lbs	20.48	11.84	22.74	4.18	6.30
Product weights					
Receiver, Lbs		10.04	18.20	4.24	5.33
Slurry Sample, L	20.30	9.50	21.91	4.04	5.77
Light Ends, g	--	--	18.18	4.28	5.35
Water, g	--	--	53.90	12.68	15.85
Reactor Temp, F	767	771	772	771	824
Furnace Temp, F	935	940	964	949	1012
Reactor Press, psig	1965	1953	1966	1971	1963
Room Temp, F	79	83	72	70	69
Wet Test Meter, cc	2519	978	1700	246	387
Brooks H2 Gas, scf	0.820	0.738	0.861	0.882	0.881

**Summary of Extraction Results
Raw Black Thunder Runs
(Unswollen, Swollen, and Molyvan-L Series)
(AU-44 Unit Runs for DOE 70-6186)**

Run Number:	18119-171	18119-174	18119-188	18119-190	18119-191	18119-171-FEED	18119-188-FEED	18119-190-FEED
Slurry Feed	Raw BT V1074 Non-Cat 1.28 #/Hr	Raw BT V1074 100ppm MVL 1.32 #/Hr	Raw Swollen BT V1074 Non-Cat 1.34 #/Hr	Raw Swollen BT V1074 100ppm MVL 1.05 #/Hr	Raw Swollen BT V1074 100ppm MVL 1.28 #/Hr	Raw BT V1074 Non-Cat 1.28 #/Hr	Raw Swollen BT V1074 Non-Cat 1.34 #/Hr	Raw Swollen BT V1074 100ppm MVL 1.05 #/Hr
THF Ins:	8.35	9.62	8.10	9.34	9.67	25.96	22.45	28.92
Toluene Ins:	11.64	13.18	10.84	12.42	13.51	27.29	22.82	29.22
Hexane Ins:	22.14	23.09	18.60	20.70	37.13	28.54	23.52	29.98
Pre-asph:	3.29	3.58	2.54	3.08	3.84	1.33	0.37	0.30
Asph:	10.49	9.91	7.96	8.27	23.62	1.25	0.70	0.78
Oils:	77.86	76.91	81.40	79.30	62.87	71.46	78.48	70.02

TABLE 60b

Summary of Extraction and Distillation Results
(SO₂-Treated Black Thunder Coal)
(AU-44 Unit Runs for DOE 70-6186)

Run No. 18119-	171	174	188	190	191
Swelling solvent	None	None	IPA/Tol	IPA/Tol	IPA/Tol
Catalyst ^[1]	None	MVL	None	MVL	MVL
ppm Mo	0	100	0	100	100
Temperature, °F	767	771	772	771	824
Feed rate, lb/hr	1.28	1.32	1.34	1.05	1.26
Space time, min	29.5	30.6	25.4	32.2	32.0
%Product recovery	101.1	81.5	98.0	98.2	95.0
Yields, % MAF coal:					
THF-solubles	70.9	73.2	71.1	65.8	66.5
Toluene-solubles	57.4	61.4	60.2	52.7	51.1
Oils	14.4	28.5	26.7	17.9	-42.8
Asphaltenes	43.0	32.9	33.5	34.8	93.9
Preasphaltenes	13.5	11.8	10.9	13.0	15.4
C ₁ - C ₃ Gases	1.8	1.2	1.4	0.9	4.3
C ₄ ⁺ Gases	0.9	0.6	0.5	0.7	3.3
CO, CO ₂	5.4	3.6	3.2	2.1	4.8
Distillation yields (wt% slurry): ^[2]					
IBP-360°F	0.7	0.7	1.0	0.9	2.1
360-650°F	18.2	18.8	18.9	19.6	24.0
650-1000°F	71.0	70.9	67.9	68.9	61.2
1000°F ⁺	10.2	9.6	12.3	10.6	12.7
% HDN	0.0	12.2	7.4	5.4	0.0
% HDO	40.4	55.6	66.8	64.4	65.8
% H ₂ Consumption	3.8	(-1.6)	6.4	4.8	1.1

[1] Catalyst added directly to feed tank; MVL = Molyvan L

[2] High-temperature simulated distillation results on product slurry for Runs 171 and 174; on THF-solubles for the other runs.

TABLE 61

Summary of Stream Analyses
Raw (Untreated) Black Thunder Run
(Swollen and Molyvan-L Series)
(AU-44 Unit Runs for DOE 70-8188)

Run Number:	18119-171	18119-174	18119-188	18119-190	18119-191	18119-171-FEE	18119-188-FEED	18119-190-FEE
Slurry Feed	Raw BT V1074 Non-Cat 1.28 #/Hr	Raw BT V1074 100ppm M 1.32 #/Hr	Swollen BT V1074 Non-Cat 1.34 #/Hr	Swollen BT V1074 100ppm MVL 1.05 #/Hr	Swollen BT V1074 100ppm MVL 1.28 #/Hr	Raw BT V1074 Non-Cat	Swollen BT V1074 Non-Cat	Swollen BT V1074 100ppm MV-L
Analyses, wt%								
THF Insolubles								
Carbon	85.17	85.73	85.47	88.02	88.37	88.89	88.82	86.41
Hydrogen	4.14	4.18	4.17	4.13	3.74	5.28	4.99	4.89
Nitrogen	0.93	1.10	1.07	1.10	1.04	1.00	1.00	0.92
Oxygen	12.95	13.78	15.15	14.93	10.92	19.32	17.98	18.28
Sulfur	0.52	0.54	0.63	0.58	0.59	0.47	0.51	0.26
Ash	18.69	18.22	14.42	14.50	15.80	8.23	5.55	8.90
Total	100.40	101.53	100.91	101.28	100.28	101.19	98.83	97.64
Preasphaltenes								
Carbon	80.71	81.08	80.14	77.11	83.82	78.53	80.13	78.52
Hydrogen	8.10	8.18	8.48	8.47	5.98	8.47	8.48	7.78 ³²⁷
Nitrogen	1.48	1.31	1.18	1.22	1.41	1.38	1.14	1.12 ³²⁷
Oxygen	9.70	9.88	10.79	10.39	7.82	9.88	9.07	9.28
Sulfur	0.27	0.25	0.32	0.29	0.24	0.25	0.23	0.10
Total	98.28	98.48	98.87	95.48	99.07	98.49	99.03	98.80
Asphaltenes								
Carbon	84.60	84.28	83.87	83.08	85.51	84.73	78.88	82.91
Hydrogen	5.98	5.92	6.11	6.20	4.85	6.07	5.97	6.22
Nitrogen	1.44	1.45	1.42	1.48	2.20	2.10	1.78	1.98
Oxygen	6.75	7.24	7.27	7.53	4.08	8.23	9.78	5.93
Sulfur	0.28	0.28	0.31	0.28	0.19	0.23	0.27	0.88
Total	99.01	99.13	98.78	98.55	78.81 •	99.38	98.88	97.70
Oils (Hexane Sol)								
Carbon	88.97	85.54	88.45	88.83	89.81	88.48	88.57	89.09
Hydrogen	9.44	9.38	9.95	9.54	9.48	9.29	9.57	9.49
Nitrogen	0.51	0.50	0.42	0.40	0.40	0.51	1.08	0.48
Oxygen	2.04	1.28	1.21	1.18	1.18	1.81	0.78	0.78
Sulfur	0.08	0.10	0.11	0.09	0.12	0.07	0.85	0.08
Total	101.04	98.80	100.14	99.84	100.79	100.14	100.83	99.88

TABLE 62
Summary of Operating and Performance Data
(Black Thunder Coal)
(AU-51 Unit Runs for DOE 70-6186)

Run No.	18101-58	18101-60	16103-93	16103-102	16103-113	16103-115
Coal treatment	SO ₂ -trt.	None	SO ₂ -trt.	SO ₂ -trt.	SO ₂ -trt.	SO ₂ -trt.
Swelling solvent	IPA/tol	IPA/tol	None	None	THF/tol ^[3]	THF/tol ^[3]
Catalyst addition ^[1]	T		No cat.	T	No cat.	S
Liquef. solvent		T			Blend ^[4]	Blend ^[4]
Contact time, min	V1074	V1074	V1074	V1074	78.7	71.4
Temperature, °F	180.5	87.3	80.7	89.0	800	800
	800	800	800	800		
%Product recovery	65.0	92.7	100.0 ^[2]	74.8	99.6	86.2
Yields, % MAF coal:						
THF-solubles						
Toluene-solubles	97.6	80.0	79.2	86.7	82.2	75.9
Oils	97.5	74.4	68.9	72.8	69.8	57.7
Asphaltenes						
Preasphaltenes	66.4	4.4	-8.2	-9.2	-37.9	-71.9
C ₁ - C ₆ Gases	31.1	70.0	77.1	82.0	107.7	129.6
C ₇ + Gases	0.2	5.6	10.3	13.9	12.4	18.2
CO, CO ₂	0.13	0.02	5.4	9.1	8.4	13.9
	0.01	0.01	2.70	3.6	2.4	12.3
	0.05	0.02	4.4	5.4	4.8	6.8
% HDN	33.7	1.9	0.7	0.0	0.0	0.0
% HDO	85.2	78.1	67.2	69.5	68.0	76.0
% H ₂ Consumption ^[5]	(-6.7)	1.8	1.1	(-6.6)	1.9	(-1.7)

- [1] Catalyst (100 ppm Mo on coal basis as Molyvan L) added during swelling (S) and/or directly to feed tank (T)
- [2] Actual recovery was 106.3%; results shown are for a forced 100% material balance (product slurry weight adjusted to get 100% closure)
- [3] 20% THF + 80% toluene
- [4] 80% V1074 + 20% resid
- [5] Negative values may be due to analytical errors

TABLE 63

**Summary of Operating and Performance Data
(Black Thunder Coal)
(AU-51 Unit Runs for DOE 70-6186)
(Material Balance Forced to 100%)**

Run No.	18101-58	18101-60	16103-93	16103-102	16103-113	16103-115
Coal treatment	SO ₂ -trt.	None	SO ₂ -trt.	SO ₂ -trt.	SO ₂ -trt.	SO ₂ -trt.
Swelling solvent	IPA/tol		None	None	THF/tol ⁽³⁾	THF/tol ⁽³⁾
Catalyst addition ⁽¹⁾	T	IPA/tol	No cat.	T	No cat.	S
Liquef. solvent		T			Blend ⁽⁴⁾	Blend ⁽⁴⁾
Contact time, min	V1074	V1074	V1074	V1074	78.7	71.4
Temperature, °F	180.5	87.3	80.7	89.0	800	800
	800	800	800	800		
% Product recovery	100.0	92.7	100.0 ⁽²⁾	100.0	99.6	100.0
Yields, % MAF coal:						
THF-solubles						
Toluene-solubles	92.4	80.0	79.2	81.4	82.2	72.0
Oils	92.2	74.4	68.9	63.0	69.8	51.2
Asphaltenes						
Preasphaltenes	44.2	4.4	-8.2	-45.5	-37.9	-96.9
C ₁ - C ₆ Gases	48.0	70.0	77.1	108.5	107.7	148.1
C ₁ ⁺ Gases	0.2	5.6	10.3	18.4	12.4	20.8
CO, CO ₂	0.0	0.02	5.4	9.1	8.4	13.9
	0.0	0.01	2.7	3.6	2.4	12.3
	0.0	0.02	4.4	5.4	4.8	6.8
% HDM	0.0	1.9	0.7	0.0	0.0	0.0
% HDO	77.2	78.1	67.2	59.6	68.0	72.5
% H ₂ Consumption ⁽⁵⁾	6.9	1.8	1.1	(-1.5)	1.9	1.2

- [1] Catalyst (100 ppm Mo on coal basis as Molyvan L) added during swelling (S) and/or directly to feed tank (T)
- [2] Actual recovery was 106.3%; results shown are for a forced 100% material balance (product slurry weight adjusted to get 100% closure)
- [3] 20% THF + 80% toluene
- [4] 80% V1074 + 20% resid
- [5] Negative values may be due to analytical errors

TABLE 64

Summary of AU-44 Operating Data
 Illinois No. 6 Runs
 (Swollen and Molyvan-L Series)
 (AU-44 Unit Runs for DOE 91PC91051)

Run Number:	16103-197	16103-198-I	16103-198-II	18119-01	18119-04	18119-05
Slurry Feed:						
Coal	Raw IL	Raw IL	Raw IL	27.74% Coal	27.74% Coal	27.74% Coal
Liq'n Solvent	V1074	V1074	V1074	55.39% V1074	55.39% V1074	55.39% V1074
Sw Solv. Toluene	None	None	None	13.49% Tol	13.49% Tol	13.49% Tol
IPA	None	None	None	3.48% IPA	3.48% IPA	3.48% IPA
MV-L: To Swellin	None	None	None	None	100 ppm	100 ppm
To Feed	None	100 ppm	100 ppm	None	None	100 ppm
Operating Data:						
Initial Date	6/30/93	6/30/93	7/01/93	7/19/93	7/20/93	7/20/93
Final Date	6/30/93	7/01/93	7/01/93	7/19/93	7/20/93	7/20/93
Initial Time	1530	2315	1135	1401	1300	1800
Final Time	1832	0730	1530	1701	1600	2100
Run Time, Hr	3.03	8.25	3.92	3.00	3.00	3.00
Initial Feed Scale	35.42	43.00	25.50	17.40	42.64	36.44
Final	30.50	29.86	21.56	14.36	38.96	32.62
Feed Slurry, Lbs	4.92	13.14	3.94	3.04	3.68	3.82
Product weights						
Receiver, Lbs	4.82	12.69	3.72	2.35	3.19	3.17
Slurry Sample, L	4.36	12.61	2.38	2.23	3.19	3.37
Light Ends, g	2.80	7.15	7.70	—	—	—
Water, g	12.50	28.23	26.60	—	—	—
Feed Rate, Lb/Hr	1.64	1.59	1.01	1.01	1.23	1.27
Space Time, Min	22.2	22.7	35.9	35.6	29.4	28.3
Reactor Temp, F	824.00	823.00	825.00	826.00	824.00	825.00
Furnace Temp, F	992.00	997.00	965.00	953.00	1008.00	1001.00
Reactor Press, psig	1946	1961	1972	1981	1959	1954
Room Temp, F	72	73	75	86	82	82
Wet Test Meter, cc	1712.00	5509.00	2821.00	4776.00	2227.00	2214.00
Brooks H2 Gas, scf	14.64	14.92	15.03	15.05	14.96	15.05

TABLE 65

Summary of Extraction Results
 Illinois No. 6 Runs at 825F
 (Swollen and Molyvan-L Series)
 (AU-44 Unit Runs for DOE 91PC91051)

Run Number:	16103-197 Average	16103-198-I Average	16103-198-II Average	18119-01 Average	18119-04 Average	18119-05 Average	16103-198 Fd Average
Slurry Feed:	IL No.6 V1074 Non-Cat 1.616 #/Hr 22 Min.	IL No.6 V1074 100ppm MVL 1.593 #/Hr 23 Min.	IL No.6 V1074 100ppm MVL 1.006 #/Hr 36 Min.	Swollen IL No.6 V1074 Non-Cat 1.013 #/Hr 36 Min.	Swollen IL No.6 V1074 W/ 100ppm MVL 1.227 #/Hr 29 Min.	Swollen IL No.6 V1074 W/100+100 MVL 1.273 #/Hr 28 Min.	IL No.6 V1074 100ppm MVL —
Extraction Data:							
THF Ins:	7.90	7.25	5.89	7.24	7.16	7.62	28.88
Toluene Ins:	12.25	11.77	8.83	10.37	10.67	10.96	31.05
Hexane Ins:	23.63	22.43	19.11	20.83	20.95	22.06	31.73
Pre-asph:	4.35	4.52	2.95	3.14	3.52	3.34	2.18
Asph:	11.38	10.65	10.28	10.46	10.28	11.10	0.67
Oils:	76.37	77.57	80.89	79.17	79.05	77.94	68.27
Extraction Yields: (MAF Coal basis)							
Conversion (THF Sol)	83.30	85.90	91.10	87.20	84.50	84.00	
Conversion (Tol Sol)	68.00	70.20	81.10	76.80	71.50	72.20	

TABLE 66

Summary of Stream Analyses
 Illinois No. 6 Runs
 (Swollen and Molyvan-L Series)
 (AU-44 Unit Runs for DOE 91PC91051)

Run Number:	16103-197	16103-198-I	16103-198-II	18119-01	18119-04	18119-05	16103-198 Fd
Slurry Feed:	IL No.6 V1074 Non-Cat 1.616 #/Hr 22 Min.	IL No.6 V1074 100ppm MVL 1.593 #/Hr 23 Min.	IL No.6 V1074 100ppm MVL 1.006 #/Hr 36 Min.	Swollen IL No.6 V1074 Non-Cat 1.013 #/Hr 36 Min.	Swollen IL No.6 V1074 W/ 100ppm MVL 1.227 #/Hr 29 Min.	Swollen IL No.6 V1074 W/100+100 MVL 1.273 #/Hr 28 Min.	IL No.6 V1074 100ppm MVL —
Analyses, wt%:							
THF Insolubles							
Carbon	43.22	42.72	44.35	50.48	50.66	43.11	65.91
Hydrogen	2.19	2.36	2.44	3.06	3.08	2.71	4.74
Nitrogen	0.77	1.01	1.12	1.06	1.40	1.02	1.05
Oxygen	9.19	9.31	7.48	6.40	6.24	7.15	13.79
Sulfur	4.07	4.18	4.18	2.98	3.08	4.36	2.86
Ash	41.48	42.74	45.00	36.33	37.79	44.71	
Total	100.92	102.32	104.57	100.31	102.25	103.06	88.35
Preasphaltenes							
Carbon	78.01	77.33	78.95	78.78	80.28	80.35	77.40
Hydrogen	5.51	5.41	5.69	6.29	6.75	6.62	6.11
Nitrogen	1.66	1.60	1.78	1.92	1.93	1.83	0.96
Oxygen	11.59	11.92	11.68	11.34	9.29	7.76	11.51
Sulfur	0.98	1.01	0.85	0.94	0.90	0.90	2.51
Total	97.75	97.27	98.95	99.27	99.15	97.46	98.49
Asphaltenes							
Carbon	83.50	83.30	84.47	84.90	83.91	83.97	81.90
Hydrogen	5.57	5.71	5.71	6.28	6.21	6.31	6.10
Nitrogen	1.75	1.67	1.73	1.92	1.88	1.94	2.34
Oxygen	6.75	6.61	5.99	5.57	6.20	5.74	7.45
Sulfur	2.10	1.17	1.05	0.98	1.08	1.11	1.68
Total	99.67	98.46	98.95	99.65	99.28	99.07	99.47
Oils (Hexane Sol)							
Carbon	88.29	87.87	88.49	89.83	86.94	88.34	88.80
Hydrogen	9.47	9.67	9.70	8.92	9.91	9.96	10.10
Nitrogen	0.30	0.33	0.34	<0.5	<0.5	<0.5	0.28
Oxygen	0.98	1.30	0.95	0.74	0.84	0.98	0.69
Sulfur	0.07	0.08	0.08	0.10	0.12	0.12	0.05
Total	99.11	99.25	99.56	99.59	97.81	99.40	99.92

TABLE 67: Spent Catalyst Properties for Amocat™ 1A and Amocat™ 1C Catalysts

	ZHQ06(Amocat™ 1A)	ZHQ08 (Amocat™ 1C)
Run Duration (hrs)	507	505
Catalyst Charged (g)	5.0019	5.0019
Dried Extracted Spent Catalyst Weight (%)	0.2178	0.4415
Loss on Ignition (%)	16.6	27.5
Percent Recovery (%)	153.7	139.6
Percent Metals* (%)	53.7	36.9
Percent Carbon* (%)	28.5	45.7
Percent Hydrogren* (%)	1.1	1.8
Percent Nitrogen*(%)	0.5	0.6
Surface Area (Fresh), m2/g	174	229
Surface Area (Used),m2/g	143	185

TABLE 68: Comparison of Used Catalyst Properties for ZHQ10 and ZHQ08 (AmocatTM 1C)

	ZHQ08	ZHQ10
Run Duration (hrs)	505	397
Catalyst Charged (g)	5.0019	5.0013
Spent Catalyst Wt. (g)	9.4415	10.1646
Loss on Ignition (%)	27.5	37.8
Percent Recovery (%)	136.9	126.4
Percent Metals* (%)	36.9	26.4
Percent Carbon* (%)	45.7	76.8
Percent Hydrogen* (%)	1.8	2.3
Percent Nitrogen* (%)	0.9	1.1
Surface Area (fresh) m ² /g	229	229
Surface Area (used) m ² /g	185	95

TABLE 69

**Feedstock Inspections
Wilsonville Atmospheric Residue ⁽¹⁾**

FW Identification No.	22777
Specific Gravity @ 60/60 °F	1.187
Asphaltenes ⁽²⁾ , wt%	10.9
Toluene Insolubles, wt%	23.2
Quinoline Insolubles, wt%	22.2
Ash, wt%	11.49
Softening Point (R&B), °F	124
Conradson Carbon Residue, wt%	38.1
Carbon, wt%	77.6
Hydrogen, wt%	7.4
Sulfur, wt%	1.40
Nitrogen, wt%	1.12
Metals, ppm	
Fe	16200
Ni	36
V	43
Cu	46
Na	426
ASTM Distillation (D-1160, °F ⁽³⁾)	
IBP	592
2 vol%	677
5	721
10	764
20	812
30	846
40	883
50	931 ⁽⁴⁾

(1) Source: Liquefaction of Wyoming Black Thunder subbituminous coal

(2) Asphaltenes Precipitation with Normal Heptane. Method IP 143

(3) Corrected to atmospheric pressure

(4) Cracking at still temperature of 650°F

TABLE 70

**Wilsonville Feedstock Characterization⁽¹⁾
FW# 22777**

	wt %
Oil ⁽²⁾	65.9
Asphaltenes	10.9
Preasphaltenes ⁽³⁾	1.0
Insoluble Organic Matter ⁽⁴⁾	10.7
Ash ⁽⁵⁾	11.5
TOTAL	100.0

(1) This estimation was developed from following feedstock inspections:
Asphaltenes, Toluene Insolubles, Quinoline Insolubles, and Ash.

(2) Toluene solubles minus asphaltenes

(3) Quinoline solubles minus toluene solubles

(4) Defined as quinoline insolubles minus ash. Includes coal fines (mmf)

(5) Includes catalyst fines with coal's mineral matter

TABLE 71

**Feedstock Inspections
Amoco Atmospheric Residue ⁽¹⁾**

FW Identification No.		22779A
Specific Gravity @ 60/60 °F		1.148
Asphaltenes ⁽²⁾ , wt%		18.0
Toluene Insolubles, wt%		18.1
Quinoline Insolubles, wt%		6.7
Ash, wt%		0.97
Softening Point (R&B), °F		96
Conradson Carbon Residue, wt%		26.8
Carbon, wt%		89.5
Hydrogen, wt%		6.2
Sulfur, wt%		0.27
Nitrogen, wt%		1.68
Metals, ppm		
Fe		4180
Ni		30
V		80
Cu		8
Na		< 20
ASTM Distillation (D-1160, °F ⁽³⁾)		
IBP	654	
2 vol%	672	
5	687	
10	711	
20	756	
30	793	
40	830	
50	869	
60	919	
70	994 ⁽⁴⁾	

(1) Source: Liquefaction of Wyoming Black Thunder subbituminous coal

(2) Asphaltenes Precipitation with Normal Heptane. Method IP 143

(3) Corrected to atmospheric pressure

(4) Feedstock cracked

Amoco Feedstock Characterization ⁽¹⁾
FW# 22779A

	wt %
Oil ⁽²⁾	63.9
Asphaltenes	18.0
Preasphaltenes ⁽³⁾	11.4
Insoluble Organic Matter ⁽⁴⁾	5.73
Ash ⁽⁵⁾	0.97
TOTAL	100.0

(1) This estimation was developed from following feedstock inspections:
Asphaltenes, Toluene Insolubles, Quinoline Insolubles, and Ash.

(2) Toluene solubles minus asphaltenes

(3) Quinoline solubles minus toluene solubles

(4) Defined as quinoline insolubles minus ash. Includes coal fines (mmf)

(5) Includes catalyst fines with coal's mineral matter

TABLE 73 Summary of Batch Deasphalting Test Results

Run No.	Solvent	S/F Ratio V/V @ 60°F	Temp. °F	Yields - wt %			Ash - wt%	
				Oil	Asphalt	Recov	Oil	Asphalt
3015	Heptane	8	475	60.4	32.0	92.4	0.010	27.75
3016	Heptane	8	500	58.5	30.5	89.0	0.006	27.23
3017	Xylene	8	565	80.6	25.3	105.9	2.27	33.06
3018	Heptane	4	500	60.6	35.8	96.4	0.030	27.85
3019	Heptane	8	520	60.9	28.8	89.7	0.060	28.44
3020	Heptane	8	550	65.3	40.3	105.6	0.024	28.00
3021	Hexane	4	430	59.8	33.7	93.5	0.017	30.70
3022	Pentane	4	380	63.6	35.7	99.3	0.020	26.00
3023	Butane	4	290	32.5	69.8	102.3	0.017	15.88
3024	Butane	4	240	30.4	68.4	98.8	0.006	17.04
3025	Butane	4	265	49.5	52.5	102.0	0.0044	20.33
3026	80%C ₄ ,20%C ₅	4	290	47.9	49.4	97.3	0.0037	21.51
3027	70%C ₄ ,30%C ₅	4	290	50.0	47.0	97.0	0.0053	23.77
3028	50%C ₄ ,50%C ₅	4	290	54.0	46.3	100.3	0.0055	25.63
3029	70%C ₄ ,30%C ₅	8	290	57.9	38.4	96.3	0.0071	25.98
3030	20%C ₄ ,80%C ₅	4	290	50.5	44.8	95.3	0.014	25.48

S/F Ratio = Solvent/Feed Ratio

TABLE 74

ASPHALT PRODUCTION FOR TRANSPORT TESTS

Run	Solvent	S/F Ratio (V/V at 60°F)	Temp (°F)	Yields (Wt%)			Ash (Wt%)	
				Oil	Asphalt	Recov	Oil	Asphalt
3031	90%C4,10%C5	4	290	41.0	58.0	99.0	0.001	21.03
3034	Pentane	4	340	54.1	48.9	103.0	0.008	24.14
3035	Hexane	4	400	59.8	41.3	101.1	0.003	27.23

**TABLE 75 Inspection of Products from Solvent Deasphalting
(Asphalt Considered a Candidate Feed to Delayed Coking)**

Run No.	3039/3040 Blend	3034	3035
Deasphalted Oil (DAO)			
DAO yield, wt%	40.2	54.1	59.8
API Gravity @ 60°F	9.8	7.3	6.3
Conradson Carbon Residue, wt%	4.10	7.62	10.23
Heptane Insolubles, wt%	0.89	1.94	6.36
Ash, wt%	0.010	0.008	0.003
Carbon, wt%	87.40	87.56	87.77
Hydrogen, wt%	9.99	9.68	9.50
Sulfur, wt%	0.02	0.03	0.04
Nitrogen, wt%	0.63	0.70	0.90
Metals, ppm			
Fe	5	11	2.6
Ni	0.4	0.2	0.2
V	0.2	0.1	0.1
Cu	0.1	0.1	0.1
Na	0.3	1.6	0.5
ASTM Distillation (D-1160)°F			
IBP	537	526	532
2 vol%	603	602	618
5	665	668	687
10	717	716	728
20	753	754	765
30	779	778	791
40	801	800	820
50	827	828	853
60	859	858	894
70	912	907	963
80	996	983	1107(75%)
90	1045(83%)	1023(84%)	

**TABLE 75 (cont) Inspection of Products from Solvent Deasphalting
(Asphalt considered a Candidate Feed to Delayed Coking)**

Run No.	3039/3040⁽¹⁾ Blend	3034	3035
Asphalt			
Yield, wt%	59.8	48.9	41.3
Specific Gravity @ 60/60°F	1.357	1.449	1.532
Conradson Carbon Residue, wt%	58.31	68.58	69.28
Asphaltenes, wt%	19.12	14.45	14.09
Toluene Insolubles, wt%	42.04	57.52	60.82
Quinoline Insoluble, wt%	33.93	49.40	51.23
Ash, wt%	19.09	24.14	27.23
Softening Point, °F	242	348	NA
Carbon, wt%	78.82	73.73	69.62
Hydrogen, wt%	6.36	5.13	4.40
Sulfur, wt%	2.01	2.50	2.73
Nitrogen, wt%	1.18	1.24	1.20
Metals, ppm			
Fe	38900	45300	43600
Ni	21	21	21
V	95	116	137
Cu	29	95	158
Na	480	637	764

NA - Not applicable. Sample decomposed before melting.

(1) - Selected Feedstock for Delayed Coking.

**TABLE 76 Delayed Coking Asphalt ⁽¹⁾ Product From Solvent
Deasphalting Wilsonville Atmospheric Residue**

FWDC Run No.	3047	
Operating Conditions		
Coke Drum Pressure, psig	5	
Throughput Ratio (Total feed/Fresh feed)	1.0	
Steam/Feed Ratio, w/w	0.134	
Maximum Drum Temperature, °F (Avg.)	901	
Material Balance		
Product Distribution-Wt%		
	As Measured	Normalized
Gas	2.2	2.3
Distillate Oil	36.2	38.6
Coke	55.3	59.1
Recovery	93.7	100.0
Overall ASCOT™ Liquid Yield	wt%	
Solvent Deasphalting Yield	40.2	
Asphalt Coking Yield (59.8 x 0.386)	23.1	
Total Liquid Yield (on atm residue)	63.3	
Total Liquid Yield (Solids-Free Basis) ⁽²⁾ (63.3/0.778)	81.4	

(1) Asphalt produced by blending solvent deasphalting product from SDA Run Nos. 3039/3040.

(2) Feedstock solids defined as Quinoline Insolubles (22.2 wt%).

**TABLE 77 Inspection of Run 3047 Delayed Coking Products
ASCOT™ Process**

Distillate Oil			
API Gravity @ 60°F		5.7	
Carbon, wt%		87.68	
Hydrogen, wt%		9.02	
Sulfur, wt%		0.05	
Nitrogen, wt%		1.01	
Ash, wt%		0.018	
Metals, ppm (w)			
Iron		61	
Nickel		0.2	
Vanadium		0.1	
Copper		4	
Sodium		2.2	
ASTM Distillation, °F		D1160	
IBP		140	
2 Vol%		373	
5		504	
10		618	
20		732	
30		773	
40		798	
50		823	
60		848	
70		880	
80		924	
90		1032	
EP (90.7%)		1076	
Coke			
Proximate Analysis, wt%		Ultimate Analysis, wt%	
Fixed Carbon	54.73	Carbon	62.06
Volatile Matter	14.81	Hydrogen	2.55
Ash	29.98	Oxygen	0.09
Moisture	0.48	Nitrogen	1.37
Total	100.0	Sulfur	3.47
		Ash	29.98
		Moisture	0.48
		Total	100.0

TABLE 77 (cont) Inspection of Run 3047 Delayed Coking Products

Gas (Composite Sample)	
	Mol% of Gas
Hydrogen	62.01
Carbon Monoxide	0.93
Carbon Dioxide	3.62
Hydrogen Sulfide	0.58
Methane	18.97
Ethane	6.08
Ethylene	0.56
Propane	3.02
Propylene	0.89
Isobutane	1.21
n-Butane	ND
Propadiene	—
Butene-1	0.56
Isobutene	0.93
trans-Butene-2	0.16
cis-Butene-2	0.08
Butadiene	—
Isopentane	0.28
n-Pentane	ND
Pentene-1	0.04
cis/trans-pentene-2	—
2-Methyl butene-2	0.08
n-hexane	—
Unknown C ₅ 's	—

- none detected

ND Not Determined. N-butane and n-pentane comprised the solvent present with the asphalt feedstock. Their presence in the product gas masked the much smaller yields (< 1.0% each) of these compounds that occurred from coking the asphalt. The gas composition is calculated on a n-butane/n-pentane - free basis.

TABLE 78 Delayed Coking Asphalt ⁽¹⁾ Product From Solvent Deasphalting Wilsonville Atmospheric Residue

FWDC Run No.	3048	
Operating Conditions		
Coke Drum Pressure, psig	5	
Throughput Ratio (Total feed/Fresh feed)	1.0	
Steam/Feed Ratio, w/w	0.163	
Maximum Drum Temperature, °F (Avg.)	962	
Material Balance		
Product Distribution-Wt%		
	As Measured	Normalized
Gas	3.9	4.0
Distillate Oil	35.1	35.7
Coke	59.2	60.3
Recovery	98.2	100.0
Overall ASCOT Liquid Yield	wt%	
Solvent Deasphalting Yield	40.2	
Asphalt Coking Yield (59.8 x 0.357)	21.3	
Total Liquid Yield (on atm residue)	61.5	
Total Liquid Yield (Solids-Free Basis) ⁽²⁾ (61.5/0.778)	79.0	

(1) Asphalt produced by blending solvent deasphalting product from SDA Run Nos. 3039/3040.

(2) Feedstock solids defined as Quinoline Insolubles (22.2 wt%).

**TABLE 79 Inspection of Run 3048 Delayed Coking Products
ASCOT™ Process**

Distillate Oil			
API Gravity @ 60°F		4.9	
Carbon, wt%		86.69	
Hydrogen, wt%		8.69	
Sulfur, wt%		0.07	
Nitrogen, wt%		0.97	
Ash, wt%		0.05	
Metals, ppm (w)			
Iron		170	
Nickel		0.5	
Vanadium		0.2	
Copper		5.8	
Sodium		3.4	
ASTM Distillation, °F		D1160	
IBP		342	
2 Vol%		430	
5		516	
10		625	
20		741	
30		782	
40		807	
50		832	
60		861	
70		893	
80		933	
90		1022	
EP (91%)		1078	
Coke			
Proximate Analysis, wt%		Ultimate Analysis, wt%	
Fixed Carbon	55.42	Carbon	61.96
Volatile Matter	13.51	Hydrogen	2.21
Ash	29.77	Oxygen	0.15
Moisture	1.30	Nitrogen	1.23
Total	100.0	Sulfur	3.38
		Ash	29.77
		Moisture	1.30
		Total	100.0

TABLE 79 (cont) Inspection of Run 3048 Delayed Coking Products

Gas (Composite Sample)	
	Mol% of Gas
Hydrogen	56.91
Carbon Monoxide	1.67
Carbon Dioxide	6.59
Hydrogen Sulfide	—
Methane	20.94
Ethane	5.83
Ethylene	0.95
Propane	2.65
Propylene	1.33
Isobutane	0.83
n-Butane	ND
Propadiene	—
Butene-1	0.61
Isobutene	0.72
trans-Butene-2	0.15
cis-Butene-2	0.08
Butadiene	—
Isopentane	0.27
n-Pentane	ND
Pentene-1	0.08
cis/trans-pentene-2	0.11
2-Methyl butene-2	0.08
n-hexane	—
Unknown C ₅ 's	0.20

- none detected

ND Not Determined. N-butane and n-pentane comprised the solvent present with the asphalt feedstock. Their presence in the product gas masked the much smaller yields (< 1.0% each) of these compounds that occurred from coking the asphalt. The gas composition is calculated on a n-butane/n-pentane - free basis.

**TABLE 80 Direct Delayed Coking Wilsonville Atmospheric Residue
From Black Thunder Subbituminous Coal**

FWDC Run No.		3042	
Operating Conditions			
Coke Drum Pressure, psig		5	
Throughput Ratio (Total feed/Fresh feed)		1.0	
Steam/Feed Ratio, w/w		0.088	
Maximum Drum Temperature, °F (Avg.)		855	
Material Balance			
Product Distribution-Wt%			
	As Measured	Normalized	Normalized Solids-Free Feed ⁽¹⁾
Gas	2.8	2.8	3.6
Distillate Oil	50.4	50.0	64.3
Coke	47.5	47.2	32.1
Recovery	100.7	100.0	100.0

(1) Feedstock solids defined as Quinoline Insolubles (22.2 wt%).
Solids-free basis calculated by subtracting solids from coke product.

350
TABLE 81 Inspection of Run 3042 Delayed Coking Products
Direct Delayed Coking Wilsonville Feed

Distillate Oil			
API Gravity @ 60°F		10.4	
Carbon, wt%		87.95	
Hydrogen, wt%		9.99	
Sulfur, wt%		0.05	
Nitrogen, wt%		0.79	
Ash, wt%		0.007	
Metals, ppm (w)			
Iron		22	
Nickel		< 1	
Vanadium		< 1	
Copper		1	
Sodium		3	
ASTM Distillation, °F		D86	D1160
IBP		352	393
2 Vol%		—	468
5		504	540
10		710	635
20			726
30			762
40			787
50			809
60			831
70			856
80			885
90			937
95			1010
EP			1023
Coke			
Proximate Analysis, wt%		Ultimate Analysis, wt%	
Fixed Carbon	59.14	Carbon	67.26
Volatile Matter	15.21	Hydrogen	3.02
Ash	25.24	Oxygen	0.09
Moisture	0.41	Nitrogen	1.20
Total	100.0	Sulfur	2.78
		Ash	25.24
		Moisture	0.41
		Total	100.0

TABLE 81 (cont)¹ Inspection of Run 3042 Delayed Coking Products
Direct Delayed Coking Wilsonville Feed

Gas (Composite Sample)	
	Mol% of Gas
Hydrogen	74.45
Carbon Monoxide	0.52
Carbon Dioxide	1.17
Hydrogen Sulfide	ND
Methane	13.08
Ethane	4.99
Ethylene	0.44
Propane	1.98
Propylene	0.82
Isobutane	0.17
n-Butane	0.81
Propadiene	—
Butene-1	0.19
Isobutene	0.09
trans-Butene-2	0.08
cis-Butene-2	0.06
Butadiene	—
Isopentane	0.12
n-Pentane	0.27
Pentene-1	0.10
cis/trans-pentene-2	0.08
2-Methyl butene-2	0.05
n-hexane	0.17
Unknown C ₈ 's	0.36

— none detected
ND Not Determined

**TABLE 82 Direct Delayed Coking Amoco Atmospheric Residue
From Black Thunder Subbituminous Coal**

Feedstock No.	22779A		
FWDC Run No.	3054		
Operating Conditions			
Coke Drum Pressure, psig	5		
Throughput Ratio (Total feed/Fresh feed)	1.0		
Steam/Feed Ratio, w/w	0.081		
Maximum Drum Temperature, °F (Avg.)	880		
Material Balance			
Product Distribution-Wt%			
	As Measured	Normalized	Normalized Solids-Free Feed ⁽¹⁾
Gas	2.4	2.4	2.6
Distillate Oil	65.9	66.5	71.3
Coke	30.8	31.1	26.1
Recovery	99.1	100.0	100.0

(1) Feedstock solids defined as Quinoline Insolubles (6.7 wt%).
Solids-free basis calculated by subtracting solids from coke product.

TABLE 83 Inspection of Run 3054 Delayed Coking Products
Direct Delayed Coking Amoco Feed

Distillate Oil			
API Gravity @ 60°F		10.4	
Carbon, wt%		90.13	
Hydrogen, wt%		8.70	
Sulfur, wt%		0.07	
Nitrogen, wt%		0.80	
Ash, wt%		0.005	
Metals, ppm (w)			
Iron		38	
Nickel		2	
Vanadium		0.4	
Copper		0.4	
Sodium		2	
ASTM Distillation, °F		D86/D1160	
IBP		290	
2 Vol%		524	
5		614	
10		656	
20		708	
30		742	
40		771	
50		799	
60		823	
70		862	
80		884	
90		928	
95		972	
EP		1018	
Coke			
Proximate Analysis, wt%		Ultimate Analysis, wt%	
Fixed Carbon	88.70	Carbon	88.57
Volatile Matter	6.52	Hydrogen	3.69
Ash	4.72	Oxygen	0.01
Moisture	0.06	Nitrogen	2.05
Total	100.0	Sulfur	0.90
		Ash	4.72
		Moisture	0.06
		Total	100.0

TABLE 83 (cont) Inspection of Run 3054 Delayed Coking Products
Direct Delayed Coking Amoco Feed

Gas (Composite Sample)	
	Mol% of Gas
Hydrogen	36.63
Carbon Monoxide	1.43
Carbon Dioxide	0.88
Hydrogen Sulfide	0.11
Methane	40.52
Ethane	10.88
Ethylene	1.00
Propane	3.45
Propylene	1.53
Isobutane	0.26
n-Butane	1.09
Propadiene	—
Butene-1	0.39
Isobutene	0.16
trans-Butene-2	0.14
cis-Butene-2	0.11
Butadiene	—
Isopentane	0.19
n-Pentane	0.48
Pentene-1	0.21
cis/trans-pentene-2	0.12
2-Methyl butene-2	0.14
n-hexane	0.16
Unknown C ₅ 's	0.12

— none detected

TABLE 84 Comparison of Yields from Atmospheric Residue, wt%

	Process			
	Wilsonville Run 262 Vac Tower + ROSE	Direct Delayed Coking	ASCOT	
			3047	3048
Products				
Gas	—	2.8	1.4	2.4
Oil				
Distillate	27.2	50.0	23.1	21.3
Deasphalted Oil	—	—	40.2	40.2
Resid	31.4	*	*	*
Solids/Coke	41.4	47.2	35.3	36.1
Total	100.0	100.0	100.0	100.0

- Included in oil product. The tail end of the ASCOT™ product oil would provide about three-quarters, and direct delayed coking about two-thirds the amount of Resid as the ROSE Process (Resid fraction defined as > 850°F).

TABLE 85

SUMMARY OF TEST DATA FOR ECONOMIC ASSESSMENT
COAL SOURCE: BLACK THUNDER SUBBITUMINOUS

Overall Liquid Yield, Wt%		
(Based on atm Residue Feedstock)		
Process	ASCOT SM	Direct Coking
Solvent Deasphalting	40.2	--
Coking Asphalt (Avg)	22.2	--
Coking atm Residue	--	<u>50.0</u>
Total Liquid Yield	62.4	50.0

357
TABLE 86 **Atmospheric Residue from Liquefied Coal**

Specific Gravity @ 60/60	1.187
°API	-12.29
Conradson Carbon, wt%	38.1
Sulfur, wt%	1.40
Nitrogen, wt%	1.12
Metals, wppm	
Fe	16200
Ni	36
V	43
Cu	46
Na	426
ASTM D1160 Distillation @ 1 atm	
LV% Distilled	Temperature, °F
IBP	592
2	677
5	721
10	764
20	812
30	846
40	883
50	931

TABLE 87 **Asphalt Feed to Coker Section of ASCOT™ Unit (50 wt% DAO Yield)**

Specific Gravity @ 60/60	1.440
°API	-33.24
Conradson Carbon, wt%	69.7
Sulfur, wt%	2.75
Nitrogen, wt%	1.51
Metals, wppm	
Ni	72
V	86

TABLE 88

Table 23 Overall Theoretical Material Balance

CASE 1 - ASCOT™ Unit				
SDA Section				
Product	Yield (Wt%) on Fresh Feed	Lbs/Hr	°API	BPSD
DAO	50.0	394,543	8.65	26,811
Asphalt	50.0	394,543	-33.24	18,793
Fresh Feed	100.0	789,086	-12.29	45,604
CASE 1 - ASCOT™ Unit				
Delayed Coking Section				
Product	Yield (Wt%) on Fresh Feed	Lbs/Hr	°API	BPSD
Gas	1.71	6,747		
Distillates	24.20	95,479	-6.80	5,772
Coke	74.09	292,317		
Fresh Feed	100.00	394,543		
CASE 2 - Delayed Coking Unit				
Product	Yield (Wt%) on Fresh Feed	Lbs/Hr	°API	BPSD
Gas	3.15	24,868		
Distillates	46.57	367,452	10.09	25,227
Coke	50.28	396,766		
Fresh Feed	100.0	789,086		

TABLE 89 Estimated Product Characteristics From FW USA Models

CASE 1 - ASCOT™ Unit	
Deasphalted Oil (DAO), 50 wt% Yield	
Specific Gravity @ 60/60	1.010
°API	8.65
Conradson Carbon, wt%	6.5
Sulfur, wt%	0.05
Nitrogen, wt%	0.73
Metals, wppm	
Ni	0.19
V	0.09
Coker Gas (Dry)	
Molecular Weight	11.7
H ₂ S, wt%	0.832 (On asphalt feed)
Distillate Liquids	
TBP, °F	C ₅ -972
°API	-6.80
Sulfur, wt%	0.54
Nitrogen, wt%	0.09
Green Coke	
VCM, wt%	10-12
Moisture	10
Sulfur, wt%	2.48
Nitrogen, wt%	2.01
CASE 2 - Delayed Coking Unit	
Coker Gas (Dry)	
Molecular Weight	7.9
H ₂ S, wt%	0.328 (On Atm Residue)
Distillate Liquids	
TBP, °F	C ₅ -972
°API	10.09
Sulfur, wt%	0.52
Nitrogen, wt%	0.22
Green Coke	
VCM, wt%	10-12
Moisture	10
Sulfur, wt%	1.69
Nitrogen, wt%	2.02

360
TABLE 90 Utility Summary

Case 1 - ASCOT™ Unit	
Continuous Utilities	
Utility	Amount
Fuel Consumed, MM BTU/Hr ⁽¹⁾	216
Power Consumed, KW	7,360
Steam Consumed, (150 psi sat) Lbs/Hr	103,300
BFW Consumed, Lbs/Hr	28,400
Cooling Water, GPM ($\Delta T = 25^{\circ}F$)	100
Raw Water Consumed, GPD	255,000
Recovered Water, GPD	126,000
Net Raw Water Consumed, GPD	129,000
Intermittent Utilities	
Utility	Amount
Power Consumed, KW	1,800
Steam Consumed, (150 psi sat) Lbs/Day	242,000
Cooling Water, GPD	375
Case 2 - Delayed Coking Unit	
Continuous Utilities	
Utility	Amount
Fuel Consumed, MM BTU/Hr ⁽¹⁾	270
Power Consumed, KW	6,900
Steam Produced, (150 psi sat) Lbs/Hr	33,300
BFW Consumed, Lbs/Hr	69,000
Cooling Water, GPM ($\Delta T = 25^{\circ}F$)	230
Raw Water Consumed, GPD	340,000
Recovered Water, GPD	168,000
Net Raw Water Consumed, GPD	172,000
Intermittent Utilities	
Utility	Amount
Power Consumed, KW	2,400
Steam Consumed, (150 psi sat) Lbs/Day	322,000
Cooling Water, GPD	500

"Fuel Consumed" refers to fuel fired by the heater(s). It corresponds to the "Fuel Absorbed," divided by the heater efficiency.

TABLE 91

Comparison of Low Rank Coal Baseline, Coker and ASCOT Cases

	Low Rank Baseline	Coker Case	ASCOT Case
ROM Coal Feed Rate, MTSD (MF)	24.951	26.593	27.303
Slag Production Rate, MTSD (MF)	1.664	1.773	1.821
Natural Gas Rate, MMBTU/SD	109.783	123.499	126.149
Raw Water Make-up, MMGSD	12.641	13.472	13.832
Naphtha Production, MBSD	12.916	13.609	13.197
Light Dist. Production, MBSD	6.633	6.896	6.673
Heavy Dist. Production, MBSD	24.078	25.35	25.125
Gas Oil Production, MBSD	21.358	23.485	26.751
Liquid Propane Production, MBSD	4.182	4.208	4.224
Mixed Butanes Production, MBSD	2.246	2.268	2.274
Ammonia Production, MTSD	0.167	0.172	0.176
Mixed Phenol Production, MTSD	0.045	0.045	0.045
Sulfur Production, MTSD	0.124	0.131	0.132
Number of Operators and Boardmen	430	494	532
Total Installed Capital, \$MM(E-YR)	3692.1	4038.3	4075.8
Catalyst and Chemicals, \$MM(B-YR)	80.00	80.00	80.00
Total C4+ Product, MBSD	67.231	71.607	74.020
Liquefaction Bottoms Processing	ROSE-SR Unit	Delayed Coker	SDA & Coker
Feed, Mlbs/hr	522.774	491.612	491.612
Products, Mlbs/hr			
Fuel gas	0	3.167	0.860
Naphtha	0	7.252	1.860
Gas Oil*	2.990	242.575	282.849
Resid (1000+ F)*	219.790	36.984	0
Coke	299.994	201.634	206.043
Total	522.774	491.612	491.612
Gasifier Feed*	299.994	238.618	206.043
as percent of unit feed	57.4	48.5	41.90
Utilities Consumptions			
Power, KWatts	2496	6409	6313
150 psig Steam, Mlbs/hr	15	199	238
Plant Fuel, MMBTUs/hr	121.0	186.1	148.9
Cooling Water, Mgal/hr	0	9.50	4.12
Process Water, Mgal/hr	0	81.31	60.98
Total Number of Plant Operators	8	24	52
Plant ISBL Field Cost, MM\$	33.4	160.4	166.4
Crude Oil Equivalent Price, \$/bbl	32.75	33.50	32.85

* In the ROSE unit case, the gas oil and resid are recycled back to the coal liquefaction plant instead of going to product; whereas, in the Coker case, some of the resid (1000+ F material) production is included in the gas oil stream.

TABLE 92

LOTUS Spreadsheet Economics Model Summary for the Low Rank
Rank Coal Baseline Case at a 15 Percent Return on Investment

DIRECT LIQUEFACTION ECONOMICS MODEL		INPUT	
Low Rank Coal Baseline		FROM:	NOTES:
ROM COAL FEED RATE, MTSD (MF)	24.951	MODEL	SHORT TNS
COAL CLEANING REFUSE RATE, MTSD (MF)	0.000	MODEL	SHORT TNS
SLAG PRODUCTION RATE, MTSD (MF)	1.664	MODEL	SHORT TNS
NATURAL GAS RATE, MMMBTU/SD	109.783	MODEL	
ELECTRICITY PURCHASE, MEGA-WH/SD	0.000	MODEL	
RAW WATER MAKE-UP, MMGSD	12.641	MODEL	M = 1000x
NAPHTHA PRODUCTION, MBSD	12.916	MODEL	MM=1000xM
LT. DIST. PRODUCTION, MBSD	6.633	MODEL	MMM=ETC.
HYY. DIST. PRODUCTION, MBSD	24.078	MODEL	
GAS OIL PRODUCTION, MBSD	21.358	MODEL	
LIQUID PROPANE PRODUCTION, MBSD	4.182	MODEL	
MIXED BUTANES PRODUCTION, MBSD	2.246	MODEL	
AMMONIA PRODUCTION, MTSD	0.167	MODEL	SHORT TNS
MIXED PHENOL PRODUCTION, MTSD	0.045	MODEL	SHORT TNS
SULFUR PRODUCTION, MTSD	0.124	MODEL	SHORT TNS
NUMBER OF OPERATORS AND BOARDMEN	430	MODEL	
TOTAL INSTALLED CAPITAL, \$MM(E-YR)	3692.10	MODEL	4TH QTR 1993 \$
CATALYST AND CHEMICALS, \$MM(B-YR)	80.00	MODEL	AT FULL PRODUCTION
TOT. INST. CAP., \$MM (BASE YEAR)	3719.5	CCI ESC.	ERROR FLAG, 1=OK
OPERATING FACTOR, PERCENT	88.4	DEFAULT	1
PERCENT PLANT OPERATIONAL, 1ST YR	100.0	DEFAULT	1
PERCENT PLANT OPERATIONAL, 2ND YR	100.0	DEFAULT	1
PERCENT PLANT OPERATIONAL, 3RD YR	100.0	DEFAULT	1
REFUSE DISP. COST, \$/S-TON (B-YR)	2.00	DEFAULT	
SLAG DISPOSAL COST, \$/S-TON (B-YR)	5.00	DEFAULT	
CAT. & CHEM., f(PROD), \$MM/MBSD(B-YR)	1.23	DEFAULT	CALCULATED VALUE
OPERATING SUPPLIES, % INITIAL CAP.	0.00	DEFAULT	
ROLLING STOCK, % INITIAL CAPITAL	0.00	DEFAULT	
OPERATOR'S PAY RATE, \$/HR (B-YR)	18.50	DEFAULT	BASIS = 2496 HR/YR
OVERHEAD FACTOR (BENEFITS, ETC.)	1.40	DEFAULT	
OTHER LABOR COSTS, \$MM/YR (B-YR)	14.27	DEFAULT	
MAINT., TAXES & INS., % INIT. CAP.	1.00	DEFAULT	
SALES, ADMIN., RES., \$MM/YR (B-YR)	0.0	DEFAULT	
PERCENT CAP. 1ST YEAR CONSTRUCTION	20.0	DEFAULT	1
PERCENT CAP. 2ND YEAR CONSTRUCTION	30.0	DEFAULT	1
PERCENT CAP. 3RD YEAR CONSTRUCTION	30.0	DEFAULT	1
PERCENT CAP. 4TH YEAR CONSTRUCTION	20.0	DEFAULT	1
TOTAL PERCENT INIT. CAPITAL SPENT	100.0	TEST	
WORKING CAPITAL, PERCENT REVENUE	10.0	DEFAULT	1
WORKING CAPITAL, PERCENT LIQUID	50.0	DEFAULT	1
SUSTAINING CAPITAL, %/YR(YRS 2-20)	0.00	DEFAULT	1
OWNER'S COST, % INIT. CAP., 1ST YR OP	5.00	DEFAULT	1

TABLE 92 (cont)

LOTUS Spreadsheet Economics Model Summary for the Low Rank
Rank Coal Baseline Case at 15 a Percent Return on Investment

REF. CRUDE (PADD II), \$/BBL (BASE YR)	32.74	USER	PROJECT SUMMARY:	
ROM COAL PRICE, \$/S-TON (BASE YR)	6.16	USER	BASE YEAR	1994
NAT. GAS PRICE, \$/MMBTU (BASE YEAR)	2.00	USER	TOTCAP\$MM	3719.5
ELECTRICITY PRICE, \$/KWH (BASE YEAR)	0.050	USER*	COE, \$/BBL	32.74
RAW WATER, \$/MGAL (BASE YEAR)	2.50	USER	SC PREM.#	1.07
GENERAL INFLATION RATE, %/YR	3.00	USER	SC, \$/BBL#	34.91
CONSTR. COST INDEX (CCI), %/YR	3.00	USER	COAL, \$/T	6.16
COAL ESC. (1=%, 2=INPUT STRING)	1	USER	NG\$/MMBTU	2.00
COAL ESCALATION+, %/YR	3.00	USER	DISC. IRR%	15.0
CRUDE OIL ESC. (1=%, 2=INPUT STRING)	1	USER	NPV15D\$MM	0.02
CRUDE OIL ESCALATION+, %/YR	3.00	USER	CONT. IRR%	14.0
NAT. GAS ESC. (1=%, 2=INPUT STRING)	1	USER	NPV15C\$MM	-98.1
NAT. GAS ESCALATION+, %/YR	3.00	USER		
NAPHTHA PRICE CODE @ (SEE KEY)	1	USER	KEY:	
NAPHTHA PRICE ENTRY	1.07	USER	* CALCULATED VALUE	
NAPHTHA PRICE, \$/BBL (B-YR)	35.00	CALC'D	+ INFLATION INCLUDED	
LT. DIST. PRICE CODE @ (SEE KEY)	1	USER	@ PRICE CODES	
LT. DIST. PRICE ENTRY	1.04	USER	0 = PRICE, \$/BBL	
LT. DIST. PRICE, \$/BBL (B-YR)	34.15	CALC'D	1 = RATIO TO CRUDE	
HVY. DIST. PRICE CODE @ (SEE KEY)	1	USER	2 = DELTA FROM CRUDE	
HVY. DIST. PRICE ENTRY	1.09	USER	# IN BASE YEAR PRICES	
HVY. DIST. PRICE, \$/BBL (B-YR)	35.75	CALC'D		
GAS OIL PRICE CODE @ (SEE KEY)	1	USER		
GAS OIL PRODUCT B PRICE ENTRY	1.04	USER		
GAS OIL PRICE, \$/BBL (B-YR)	34.15	CALC'D		
LIQUID PROPANE PRICE CODE @ (SEE KE	0	USER		
LIQUID PROPANE PRICE ENTRY	12.29	USER		
LIQ. PROPANE PRICE, \$/BBL (BASE YR)	12.29	CALC'D		
MIXED BUTANE PRICE CODE @ (SEE KEY)	0	USER		
MIXED BUTANE PRICE ENTRY	13.86	USER		
MIXED BUTANE PRICE, \$/BBL (BASE YR)	13.86	CALC'D		
AMMONIA PRICE, \$/S-TON (BASE YR)	200.00	USER		
MIXED PHENOL PRICE, \$/S-TON (BASE YR)	625.00	USER		
SULFUR PRICE, \$/SHORT-TON (BASE-YR)	47.30	USER	ERROR FLAG, 1=OK	
CONSTRUCTION START=JAN.1, BASE YEAR	1994	USER	1	
PERCENT EQUITY	25	USER	1	
BANK INTEREST RATE, %/YR	8.00	USER	1	
IMPUTED INTEREST RATE, %/YR	0.00	USER	1	
FEDERAL INCOME TAX RATE, %/YR	34.0	USER	1	
STATE INCOME TAX RATE, %/YR	0.0	USER	1	
FIXED COST, % INIT. CAP. (0=NOT USED)	0.00	USER	1	
TERM OF LOAN, YEARS (FIXED)	10	USER		
YEARS OF CONSTRUCTION (FIXED)	4	USER		
YEARS OF OPERATION (FIXED)	25	USER		
DEPRECIATION, YEARS (FIXED)	10	USER		

TABLE 93

Material Balance for the Coal Grinding and
SO₂ Cleaning Operations in Plants 1 and 1.4

Stream No. Description	<----- INPUT ----->			<----- OUTPUT ----->		
	5 SO ₂	1 Coal	Total	7 Cleaned Coal	16 Fines & Refuse	Total
Flow, Mlbs/hr	69.976	1956.548	2026.524	1643.500	383.024	2026.524
Percent of entering coal	3.58	100.00	103.58	84.00	19.58	103.58
Ultimate Analysis						
Carbon	0.00	68.50		70.33	48.12	
Hydrogen	0.00	4.80		4.93	3.37	
Nitrogen	0.00	1.00		1.03	0.70	
Sulfur	50.05	0.50		0.80	8.27	
Oxygen	49.95	18.90		19.41	22.40	
Ash	0.00	6.30		3.50	17.14	
Total	100.000	100.000		100.000	100.000	

NOTE: All of the above flows and compositions are on a dry basis.

Cost and Utilities Requirements for the SO₂
Coal Cleaning and Drying Steps in Plant 1.4

Number of Duplicate Trains	4
Train Capacity, Mlbs/hr of dry clean coal	373.5
Power Consumption, Kwatts	2256
Plant Fuel, MMBTU/hr	805
Cooling Water, Mgal/hr	42.8
Nitrogen, MMSCF/hr	46.5
Total Plant Operators per Day	25
Total Plant ISBL Field Cost, MM\$ (fourth quarter 1993)	70.6

TABLE 94

Comparison of Low Rank Coal Baseline and SO₂ Coal Cleaning Cases

	Low Rank	<-- SO ₂ Cleaning -->	
	Baseline	Case A	Case B
ROM Coal Feed Rate, MTSD (MF)	24.951	26.560	29.216
Slag Production Rate, MTSD (MF)	1.664	1.771	1.948
Natural Gas Rate, MMMBTU/SD	109.783	116.739	128.414
Raw Water Make-up, MMGSD	12.641	13.728	15.101
Naphtha Production, MBSD	12.916	13.286	14.615
Light Dist. Production, MBSD	6.633	6.822	7.504
Heavy Dist. Production, MBSD	24.078	24.761	27.237
Gas Oil Production, MBSD	21.358	21.962	24.158
Liquid Propane Production, MBSD	4.182	4.299	4.729
Mixed Butanes Production, MBSD	2.246	2.309	2.540
Ammonia Production, MTSD	0.167	0.172	0.190
Mixed Phenol Production, MTSD	0.045	0.046	0.051
Sulfur Production, MTSD	0.124	0.111	0.122
Number of Operators and Boardmen	430	492	508
Total Installed Capital, \$MM(E-YR)	3692.1	3895.9	4183.1
Catalyst and Chemicals, \$MM(B-YR)	80.0	82.3	90.5
Total C4+ Product, MBSD	67.231	69.140	76.054
Total Installed Capital per barrel of C4+ product, M\$/bbl	54.9	56.3	55.0
Coal Liquefaction Plant			
Dry Coal Feed Rate, Mlbs/hr	1494.1	1494.1	1643.5
Ultimate Analysis, wt%			
Carbon	68.50	70.34	70.34
Hydrogen	4.80	4.93	4.93
Nitrogen	1.00	1.03	1.03
Sulfur	0.50	0.80	0.80
Oxygen	18.90	19.40	19.40
Ash	6.30	3.50	3.50
Total	100.00	100.00	100.00
ISBL Field Cost, MM\$	792.4	796.7	814.7
ROSE-SR Solvent Deashing Plant			
Feed Rate, Mlbs/hr	522.77	495.95	545.54
Deashed Residum Rate, Mlbs/hr	222.78	230.91	254.00
Ash Concentrate Rate, Mlbs/hr	299.99	265.04	291.54
ISBL Field Cost, MM\$	33.4	32.2	34.4
Hydrogen production from Plant 9, MMSCF/hr	18.5	19.0	20.9
Crude Oil Equivalent Price, \$/bbl	32.75	33.70	33.00

TABLE 95

LOTUS Spreadsheet Economics Model Summary for SO₂
Coal Cleaning Case A at a 15 Percent Return on Investment

DIRECT LIQUEFACTION ECONOMICS MODEL		INPUT	
SO ₂ Cleaning - Case A - Same Rx Rate		FROM:	NOTES:
ROM COAL FEED RATE, MTSD (MF)	26.560	MODEL	SHORT TNS
COAL CLEANING REFUSE RATE, MTSD (MF)	0.000	MODEL	SHORT TNS
SLAG PRODUCTION RATE, MTSD (MF)	1.771	MODEL	SHORT TNS
NATURAL GAS RATE, MMMBTU/SD	116.739	MODEL	
ELECTRICITY PURCHASE, MEGA-WH/SD	0.000	MODEL	
RAW WATER MAKE-UP, MMGSD	13.728	MODEL	M = 1000x
NAPHTHA PRODUCTION, MBSD	13.286	MODEL	MM=1000xM
LT. DIST. PRODUCTION, MBSD	6.822	MODEL	MMM=ETC.
HYY. DIST. PRODUCTION, MBSD	24.761	MODEL	
GAS OIL PRODUCTION, MBSD	21.962	MODEL	
LIQUID PROPANE PRODUCTION, MBSD	4.299	MODEL	
MIXED BUTANES PRODUCTION, MBSD	2.309	MODEL	
AMMONIA PRODUCTION, MTSD	0.172	MODEL	SHORT TNS
MIXED PHENOL PRODUCTION, MTSD	0.046	MODEL	SHORT TNS
SULFUR PRODUCTION, MTSD	0.111	MODEL	SHORT TNS
NUMBER OF OPERATORS AND BOARDMEN	492	MODEL	
TOTAL INSTALLED CAPITAL, \$MM(E-YR)	3895.93	MODEL	4TH QTR 1993 \$
CATALYST AND CHEMICALS, \$MM(B-YR)	82.27	MODEL	AT FULL PRODUCTION
TOT. INST. CAP., \$MM (BASE YEAR)	3924.8	CCI ESC.	ERROR FLAG, 1=OK
OPERATING FACTOR, PERCENT	88.4	DEFAULT	1
PERCENT PLANT OPERATIONAL, 1ST YR	100.0	DEFAULT	1
PERCENT PLANT OPERATIONAL, 2ND YR	100.0	DEFAULT	1
PERCENT PLANT OPERATIONAL, 3RD YR	100.0	DEFAULT	1
REFUSE DISP. COST, \$/S-TON (B-YR)	2.00	DEFAULT	
SLAG DISPOSAL COST, \$/S-TON (B-YR)	5.00	DEFAULT	
CAT. & CHEM., f(PROD), \$MM/MBSD(B-YR)	1.23	DEFAULT	CALCULATED VALUE
OPERATING SUPPLIES, % INITIAL CAP.	0.00	DEFAULT	
ROLLING STOCK, % INITIAL CAPITAL	0.00	DEFAULT	
OPERATOR'S PAY RATE, \$/HR (B-YR)	18.50	DEFAULT	BASIS = 2496 HR/YR
OVERHEAD FACTOR (BENEFITS, ETC.)	1.40	DEFAULT	
OTHER LABOR COSTS, \$MM/YR (B-YR)	14.27	DEFAULT	
MAINT., TAXES & INS., % INIT. CAP.	1.00	DEFAULT	
SALES, ADMIN., RES., \$MM/YR (B-YR)	0.0	DEFAULT	
PERCENT CAP. 1ST YEAR CONSTRUCTION	20.0	DEFAULT	1
PERCENT CAP. 2ND YEAR CONSTRUCTION	30.0	DEFAULT	1
PERCENT CAP. 3RD YEAR CONSTRUCTION	30.0	DEFAULT	1
PERCENT CAP. 4TH YEAR CONSTRUCTION	20.0	DEFAULT	1
TOTAL PERCENT INIT. CAPITAL SPENT	100.0	TEST	
WORKING CAPITAL, PERCENT REVENUE	10.0	DEFAULT	1
WORKING CAPITAL, PERCENT LIQUID	50.0	DEFAULT	1
SUSTAINING CAPITAL, %/YR(YRS 2-20)	0.00	DEFAULT	1
OWNER'S COST, % INIT. CAP., 1ST YR OP	5.00	DEFAULT	1

TABLE 95 (cont)

REF. CRUDE (PADD II), \$/BBL (BASE YR)	33.72	USER	PROJECT SUMMARY:
ROM COAL PRICE, \$/S-TON (BASE YR)	6.16	USER	BASE YEAR 1994
NAT. GAS PRICE, \$/MMBTU (BASE YEAR)	2.00	USER	TOTCAP\$MM 3924.8
ELECTRICITY PRICE, \$/KWH (BASE YEAR)	0.050	USER*	COE, \$/BBL 33.72
RAW WATER, \$/MGAL (BASE YEAR)	2.50	USER	SC PREM.# 1.07
GENERAL INFLATION RATE, %/YR	3.00	USER	SC, \$/BBL# 35.96
CONSTR. COST INDEX (CCI), %/YR	3.00	USER	COAL, \$/T 6.16
COAL ESC. (1=%, 2=INPUT STRING)	1	USER	NG\$/MMBTU 2.00
COAL ESCALATION+, %/YR	3.00	USER	DISC. IRR% 15.0
CRUDE OIL ESC. (1=%, 2=INPUT STRING)	1	USER	NPV15D\$MM 0.36
CRUDE OIL ESCALATION+, %/YR	3.00	USER	CONT. IRR% 14.0
NAT. GAS ESC. (1=%, 2=INPUT STRING)	1	USER	NPV15C\$MM -103.2
NAT. GAS ESCALATION+, %/YR	3.00	USER	
NAPHTHA PRICE CODE @ (SEE KEY)	1	USER	
NAPHTHA PRICE ENTRY	1.07	USER	
NAPHTHA PRICE, \$/BBL (B-YR)	36.05	CALC'D	KEY:
LT. DIST. PRICE CODE @ (SEE KEY)	1	USER	* CALCULATED VALUE
LT. DIST. PRICE ENTRY	1.04	USER	+ INFLATION INCLUDED
LT. DIST. PRICE, \$/BBL (B-YR)	35.17	CALC'D	@ PRICE CODES
HVY. DIST. PRICE CODE @ (SEE KEY)	1	USER	0 = PRICE, \$/BBL
HVY. DIST. PRICE ENTRY	1.09	USER	1 = RATIO TO CRUDE
HVY. DIST. PRICE, \$/BBL (B-YR)	36.82	CALC'D	2 = DELTA FROM CRUDE
GAS OIL PRICE CODE @ (SEE KEY)	1	USER	# IN BASE YEAR PRICES
GAS OIL PRODUCT B PRICE ENTRY	1.04	USER	
GAS OIL PRICE, \$/BBL (B-YR)	35.17	CALC'D	
LIQUID PROPANE PRICE CODE @ (SEE KE	0	USER	
LIQUID PROPANE PRICE ENTRY	12.29	USER	
LIQ. PROPANE PRICE, \$/BBL (BASE YR)	12.29	CALC'D	
MIXED BUTANE PRICE CODE @ (SEE KEY)	0	USER	
MIXED BUTANE PRICE ENTRY	13.86	USER	
MIXED BUTANE PRICE, \$/BBL (BASE YR)	13.86	CALC'D	
AMMONIA PRICE, \$/S-TON (BASE YR)	200.00	USER	
MIXED PHENOL PRICE, \$/S-TON (BASE YR)	625.00	USER	
SULFUR PRICE, \$/SHORT-TON (BASE-YR)	47.30	USER	
CONSTRUCTION START=JAN.1, BASE YEAR	1994	USER	ERROR FLAG, 1=OK
PERCENT EQUITY	25	USER	1
BANK INTEREST RATE, %/YR	8.00	USER	1
IMPUTED INTEREST RATE, %/YR	0.00	USER	1
FEDERAL INCOME TAX RATE, %/YR	34.0	USER	1
STATE INCOME TAX RATE, %/YR	0.0	USER	1
FIXED COST, % INIT. CAP. (0=NOT USED)	0.00	USER	1
TERM OF LOAN, YEARS (FIXED)	10	USER	
YEARS OF CONSTRUCTION (FIXED)	4	USER	
YEARS OF OPERATION (FIXED)	25	USER	
DEPRECIATION, YEARS (FIXED)	10	USER	