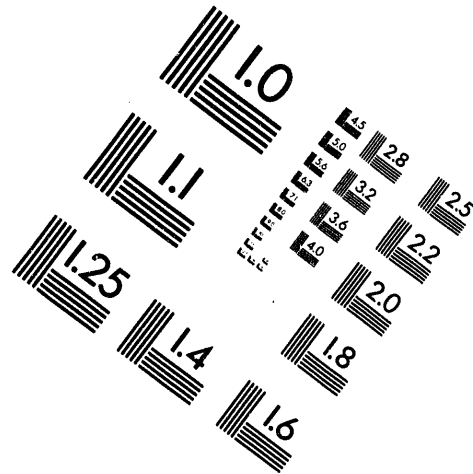
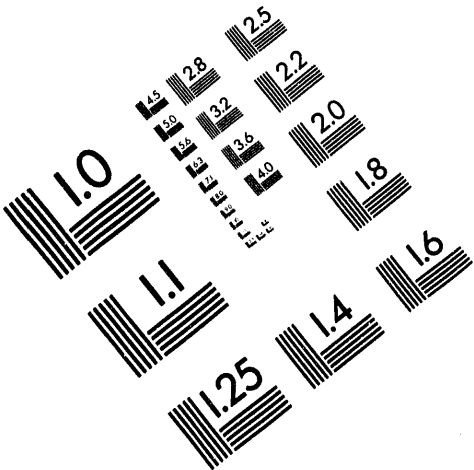




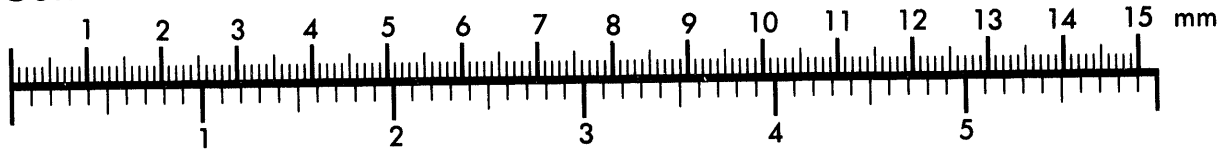
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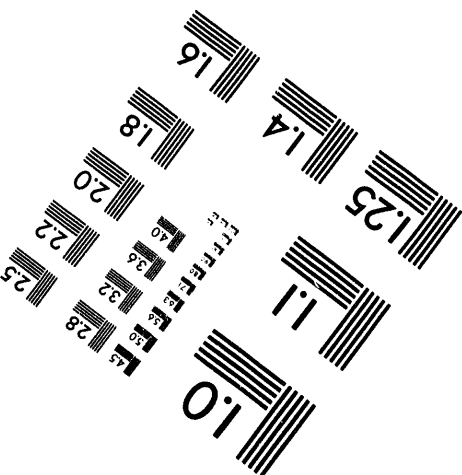
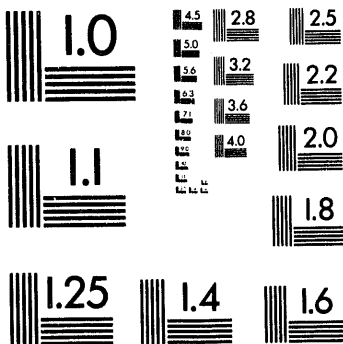
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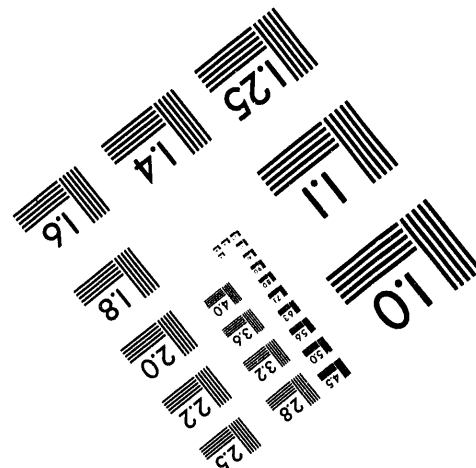
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ADVANCED LIQUEFACTION USING COAL SWELLING
AND CATALYST DISPERSION TECHNIQUES

Report Number Q-07
Quarterly Technical Progress Report
for
April-June 1993

Project Manager: D. C. Cronauer

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

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

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OKD Pete
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Amoco Oil Company

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June 22, 1994

Ms. S. Kornfeld
U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

DOE CONTRACT NUMBER DE-AC22-91PC91051

Attached please find the draft of our quarterly technical progress report covering April-June 1993 which incorporates the corrections you noted in your letter of June 13 (typo on the bottom of page 21 and the top of page 22, where two line of text are repeated.) We hope that with the incorporation of these corrections, the report is approved for publication.

If you have any questions or comments, please call.

Sincerely,

D. C. Cronauer (jw)
Mail Station D-4
708/420-5777

RJT/jlw/9401

Attachment

Ms. Robyn Knapek (DOE/PETC)
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DOE/PETC Office of Technology Transfer (DOE/PETC)



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May 31, 1994

Ms. S. Kornfeld
Mr. James W. Huenmrich
Ms. Joanne Wastek
U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

DOE CONTRACT NUMBER DE-AC22-91PC91051

Attached please find the draft of our quarterly technical progress report covering April-June 1993. Based on past discussions, it is understood that if we don't receive changes from you in the next twenty days, we will consider this draft to be approved to be issued as a final report.

If you have any questions or comments please call.

Sincerely,

D.C. Cronauer / jlt
D. C. Cronauer
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cc: DOE/PETC Office of Technology Transfer



Amoco Oil Company

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May 31, 1994

Robert Hamilton
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19901 Germantown Rd.
Germantown, Maryland 20585

Dear Mr. Hamilton:

Attached please find the draft of our quarterly technical progress report covering April-June, 1993. A copy of this draft also has been submitted to appropriate DOE/PETC personnel for approval. Based on past discussions, it is understood that if we do not receive changes from you in the next twenty days, we will consider this draft approved to be issued as a final report.

If you have any questions or comments please call.

Sincerely,

D C Cronauer /jts
D. C. Cronauer
Mail Station D-4
Phone 708/420-5777
Naperville

RJT/jlw/9401

Attachment

ADVANCED LIQUEFACTION USING COAL SWELLING
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Report Number Q-07
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Work Performed Under Contract No. DE-AC22-91PC91051

For

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

By

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TECHNICAL STATUS

This technical report is being transmitted in advance of DOE review, and no further dissemination or publication will be made of the report without prior approval of the DOE Project/Program Manager.

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Prepared by
Amoco Oil Company (Amoco Corporation)
Naperville, Illinois

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EXECUTIVE SUMMARY

The overall objective of this project is 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 integrates coal selection, pretreatment, coal swelling with catalyst impregnation, liquefaction, product recovery with characterization, alternate bottoms processing, and carrying out a technical assessment including an economic evaluation. The project is being carried out under contract to the United States Department of Energy. The primary contractor is Amoco Oil Company, and the subcontractors are Foster Wheeler Development Company, Auburn University, Pennsylvania State University, and Hazen Research, Inc.

The primary coal of this program, Black Thunder subbituminous coal, can be effectively beneficiated to about 4 wt% ash using aqueous sulfurous acid pretreatment. This treated coal can be further beneficiated to about 2 wt% ash using commercially available procedures. All three coals used in this study (Black Thunder, Burning Star bituminous, and Martin Lake lignite) are effectively swelled by a number of solvents. The most effective solvents are those having hetero-functionality. In addition, a synergistic effect has been demonstrated, in which solvent blends are more effective for coal swelling than the pure solvents alone. Therefore, it will be necessary to use only low levels of swelling agents and yet promote the impregnation of catalyst precursors. The rate of the impregnation of catalyst precursors into swollen coal increases greatly as the effectiveness of the solvent to swell the coal increases. This effect is also demonstrated by improved catalyst precursor impregnation with increased contact temperature.

Laboratory- and bench-scale liquefaction experimentation is underway using swelled and catalyst impregnated coal samples. Higher coal conversions were observed for the SO₂-treated coal than the raw coal, regardless of catalyst type. Conversions of swelled coal were highest when Molyvan-L, molybdenum naphthenate, and nickel octoate, respectively, were added to the liquefaction solvent. The initial laboratory and continuous flow unit (AU-51) experiments have indicated that the expected increase in coal conversion and product up-grading did not occur when the catalyst precursor, Molyvan-L, was impregnated into the swelled coal. The study of a possible interaction between catalyst precursors and the swelling solvents is underway.

The study of bottoms processing consists of combining the ASCOT process which consists of coupling solvent deasphalting with delayed coking to maximize the production of coal-derived liquids while rejecting solids within the coke drum. The asphalt production phase has been completed with the production of representative product for subsequent experimentation. Studies of the direct delayed coking of Wilsonville atmospheric bottoms are also complete. The data indicates that vaporization and steam stripping inside the coke drum produced more than half of the liquid product.

PROGRAM OBJECTIVES

The objective of this project is 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 are:

1. Task 1: Laboratory-Scale Experimentation--The goals are 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 are 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 includes observing pumping characteristics, deasphalting, and coking.
3. Task 3: Technical Assessment--The goals are to analyze the data, develop descriptive models, and carry out an economic evaluation.

The research is being carried out in cooperation with the following subcontractors: Foster Wheeler Development Corporation (FWDC), Auburn University (AU), Pennsylvania State University (PSU), and Hazen Research Inc. Appropriate meetings and correspondence are being maintained to ensure effective completion of the project.

PROGRAM MILESTONES

The current milestones are those shown in Figures 1a and 1b. The first milestone was to obtain the appropriate feed stocks for the experiments, and the second was preparing the beneficiated bulk samples of coal for subsequent experiments. The feedstocks have been obtained, and the beneficiation of a single sample of Martin Lake lignite and two samples of Black Thunder subbituminous coal have been done by Hazen Research Inc. A sample of froth floated, sulfurous acid-treated Black Thunder coal has been prepared. The laboratory-scale coal swelling and catalyst screening program is underway. The initial bench-scale liquefaction experiments with Black Thunder coal were carried out. However coal conversion was not adequate, so additional runs are planned. The batch deasphalting experiments and delayed coking experiments have been completed. The current program calls for program completion on May 31, 1994. (A request for a no-cost extension to September 1994 has been proposed.)

SUMMARY OF RESULTS AND ACTIVITY

The objective of this project is 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 are included with emphasis upon coal pretreatment, coal swelling with catalyst impregnation, and alternate bottoms processing. Research is under way at Amoco Oil Company, Foster Wheeler Development Company, Auburn University, Pennsylvania State University, and Hazen Research, Inc. In addition, results and samples are being exchanged with Karl Vorres of Argonne Laboratories. His program involves the preparation of coals containing potentially catalytic metals that are placed in the coals using ion exchange. A copy of his Annual Report (June 1993) is attached as Appendix A.

Black Thunder subbituminous coal, can be effectively beneficiated to about 4 wt% ash using aqueous sulfurous acid pretreatment, and it can be further beneficiated to about 2 wt% ash using commercially available procedures. The three coals used in this study are effectively swelled by a number of solvents, the most effective of which are those having hetero-functionality. The rate of the impregnation of catalyst precursors into swollen coal increases greatly as the effectiveness of the solvent to swell the coal increases; this also includes increasing the temperature of the contacting process.

Laboratory- and bench-scale liquefaction experimentation is underway using swelled and catalyst impregnated coal samples. Higher coal conversions were observed for the SO₂-treated coal than the raw coal, regardless of catalyst type. Conversions of swelled coal were highest when Molyvan-L, molybdenum naphthenate, and nickel octoate, respectively, were added to the liquefaction solvent. The initial laboratory and continuous flow unit (AU-51) experiments have indicated that the expected increase in coal conversion and product up-grading did not occur when the catalyst precursor, Molyvan-L, was impregnated into the swelled coal. The study of a possible interaction between catalyst precursors and the swelling solvents is underway.

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DISCUSSION OF RESULTS AND ACTIVITIES BY TASK

Project Documentation

The Milestone Schedule and budget was modified as shown in Figures 1a and 1b.

Task 1.0: Laboratory-Scale Experimentation

Subtask 1.1: Laboratory Support

The feedstocks are on hand; their analyses were reported in previous quarterlies. An additional 10-drum sample of Black Thunder coal (Thunder Basin Coal Co./ARCO Coal Co.) was obtained to provide a fresh sample for sulfurous acid treatment followed by froth flotation tests. At this time, experimentation is underway at Hazen Research, Inc.

Task 2.0: Laboratory-Scale Operation

Subtask 2.1: Coal Pretreatment

Bulk samples of both Martin Lake Texas lignite and Black Thunder subbituminous coal were pretreated to provide beneficiated coal for subsequent experiments. The treatment included crushing, sizing, contacting the coarse fraction with aqueous SO_2 to remove alkali and alkaline metals, and subsequent gravity separation to recover a fraction having particularly low ash content. Two 55-gallon drums of Martin Lake lignite and three drums of Black Thunder subbituminous coal were processed at Hazen Research, Inc. The SO_2 -treated subbituminous coal was 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 about 80 wt%. Therefore, the bulk samples of raw and SO_2 -treated coals were characterized and used as-prepared.

An extensive research program has been underway at Pennsylvania State University. It is directed at beneficiating coal by a combination of chemical treatment and physical separation methods. A procedure has been developed for producing a low ash coal from SO_2 -treated Black Thunder subbituminous coal. The procedure involved a combination of flotation and agglomeration methods to generate a clean coal product of about 2% ash. This was described in the previous Quarterly Report (Q-06). A manuscript expanding upon these results will be included in the next quarterly along with data being generated in the bench-scale experiments of Hazen Research, Inc.

Subtask 2.2: Catalyst and Swelling Studies

Summary of Coal Swelling Results:

The results of the initial set of the coal swelling experiments were reported in Quarterly Report Number Q-04 (July-September, 1992), and the literature concerning coal swelling, both alone and in combination with coal liquefaction, was reported in Quarterly Report Number Q-03 (April-June, 1992).

These above runs and additional laboratory-scale experiments on simultaneous swelling of coal and catalyst impregnation with soluble precursors were performed to determine the effects on catalyst uptake of the swelling/impregnating solution, impregnation conditions, coal properties, and catalyst. A compilation of the coal swelling/catalyst impregnation results are presented in this quarterly report to close out this portion of the research program. However, a characterization of the Mo dispersion in these simultaneously swollen and impregnated coal particles by electron microscopy as well as the results of using these materials for liquefaction will be reported in a subsequent quarterly report.

Catalyst uptake by coal was enhanced by the use of effective swelling solvents, increased impregnation temperature, and finer coal particles. The rate and extent of uptake correlated with the ability of the solvent to swell coal (e.g., DMSO >> THF-IPA). Increased impregnation temperature has the strongest effect on catalyst uptake. The uptake of Molyvan-L was higher than molybdenum octoate's for IPA-swollen coal. Impregnation with molybdenum octoate using THF and DMSO resulted in formation of a precipitate, indicating a possible interaction between the swelling solvent and the catalyst precursor. Partial saturation of deposition sites was a possibility at high initial precursor concentrations. This simultaneous swelling and impregnation treatment can be done during feed slurry preparation.

Introduction:

Reports in the open literature⁽¹⁻⁶⁾ have shown that solvent swelling of coal improves liquefaction conversions and yields. It was proposed that further improvements may be possible with catalyst impregnation of solvent-swollen coal if conducting these treatments simultaneously enhanced catalyst dispersion and/or coal-catalyst contact. The objective of this specific task was to find the optimum treatment conditions for improved catalyst penetration into the coal. In previous experiments (Quarterly Report Number Q-04 (July-September, 1992), swelling ratios were determined with a wide variety of solvents and solvent blends using pulverized (325 mesh) samples of Black Thunder subbituminous, Illinois No. 6 bituminous, and Martin Lake lignite. Experiments were also conducted with 8 x 60 mesh Black Thunder treated with sulphurous acid (SO₂) to remove mineral matter. Only marginal levels of swelling were observed for the hydrocarbon solvents (e.g., hexane, cyclohexane, single-ring aromatics (BTX), and tetralin). Hetero-functionality in the solvent enhanced swelling ratios. Oxygenates (alcohols, ketones, acetate, tetrahydrofuran [THF]) gave equilibrium (3-day) swelling ratios (Q) in the range of 1.15 to 1.6, with THF as the most effective solvent. The nitrogen-containing solvents tetrabutyl ammonium hydroxide (TBAH) and aniline, and dimethylsulfoxide (DMSO) were generally more effective, with Q ranging 1.6 to 2.7.

SO₂-treatment removed the alkali and alkaline earth ions from subbituminous Black Thunder and enhanced coal swelling. The effects of coal type may be attributed to the interaction of the solvent with the ionic or hydrogen bonds present in the coal. A highly-basic solvent, such as TBAH, interacts readily with the ionic and hydrogen bonds in low-rank coals, such as Martin Lake lignite, thereby swelling it to a greater

extent than the other coals. On the other hand, THF disrupts charge transfer complexes which are predominant in higher-rank coals, such as Illinois No. 6, thereby resulting in an opposite swelling trend. This solvent-coal interaction can also explain the enhancing effect of SO₂-treatment. Experiments with blends of highly-swelling solvents with either water or tetralin resulted in swelling ratios much greater than those expected from a linear combination of the two solvents. The greatest synergisms were observed with Black Thunder and Illinois No. 6. This suggests that relatively low levels of swelling agent may be effective in treating coal feed slurries.

Catalyst Precursor Impregnation - Experimental:

Simultaneous swelling and catalyst impregnation experiments with SO₂-treated Black Thunder coal were performed using Molyvan L and molybdenum octoate as catalyst precursors. Table 1 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 solvent, 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. The filtrate was analyzed for Mo by either X-ray fluorescence or inductively coupled plasma (ICP) spectroscopy to estimate the extent of catalyst uptake by the coal. In some cases, the treated coal was filtered and analyzed by ICP to confirm the liquid ICP results.

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. Appendix B is a summary of experimental conditions and 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 C describes the corrections, which were generally within experimental error. Table 2 and Figure 1 give indications of the magnitudes of the corrections and the experimental error.

Table 2 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 1 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.⁽¹²⁾ 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 3 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 2a and 2b 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 2a). Catalyst uptake by coal swollen by the more polar DMSO was greater than that achieved with either the IPA- or THF-swollen coal (Figure 2b).

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 2c 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. The effects of impregnation temperature are discussed further in the next section.

Effect of Impregnation Temperature:

Figure 3 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 4a and 4b 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 4b). 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 5, 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 6a compares catalyst uptake for 8x60 mesh IPA-swollen coal for ambient impregnation with Molyvan-L and molybdenum octoate. Penetration was similar at short times (<6 hr) but became better for Molyvan-L as time increased. The uptake of molybdenum octoate at 150°F is also shown.

Similar uptake experiments were conducted with molybdenum octoate as precursor for DMSO and THF as swelling solvents (Figures 6b and 6c, respectively). As with IPA-swollen coal, the uptake of Molyvan-L was greater than that of molybdenum octoate for DMSO-swollen coal (Figure 6b). The results also suggested that the use of high impregnation temperatures decreased the difference in uptakes between Molyvan-L and molybdenum octoate. [Note in this figure that the molybdenum octoate uptake was calculated as $(1 - Mo_1/Mo_0)$ instead of using the sampling corrections. This was because of the large scatter in the molybdenum content data, particularly at the early impregnation times; the sampling corrections require that molybdenum content monotonically decrease with time. (Appendix C explains how the corrections were handled when the molybdenum content did not decrease with time.)]

Figure 6c suggests that molybdenum 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 molybdenum octoate may be an artifact due to an instability observed with molybdenum 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 molybdenum 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 molybdenum octoate.

Although this instability of molybdenum octoate was also observed with DMSO/toluene, the results for the DMSO-swollen coal suggested Molyvan-L uptake was higher than that for molybdenum octoate. This indicates that the precipitate formed with DMSO may not contain molybdenum. No instability was observed for molybdenum 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 molybdenum octoate. However, the instability of molybdenum octoate (at typical Mo loadings) with some swelling solvents could result in an inactive catalyst form.

The introduction of Molyvan-L with a small amount of swelling solvent such as THF or IPA in the feed slurry tank ($T > 120^{\circ}\text{F}$) could be a practical way of implementing this improved catalyst impregnation method for coal liquefaction. Whether it also improves liquefaction performance is currently being studied.

Subtask 2.3: Reactivity of Swelled Coals with Dispersed Catalysts

Laboratory-scale research performed during the April to June 1993 quarter evaluated the effect of adding catalyst to the preswelling solvent and subsequently absorbing the catalyst into the coal. Liquefaction experiments were then performed on these preswelled coals with absorbed catalyst. Coal conversion was compared to that achieved when the catalyst was added directly to the reactor. Three preswelling solvents were used: tetrahydrofuran (THF), methanol, and isopropanol. Two coals were tested: untreated Black Thunder coal and SO_2 treated Black Thunder coal. Three catalysts were tried: slurry-phase Molyvan-L, molybdenum naphthenate (reacted without sulfur), and nickel octoate.

In addition, thermal reactions of three Argonne coals were carried out in three reaction solvents. The Argonne coals were Wyodak, Illinois No. 6, and North Dakota. The liquefaction reactions with the Argonne coals were performed thermally with the reaction solvents: 1-methylnaphthalene (1-MN), 9,10-dihydroanthracene (DHA), and V1074, a Wilsonville coal-derived solvent nominally boiling in the range of $650\text{-}1000^{\circ}\text{F}$.

Experimental:

Liquefaction reactions were performed using untreated and SO_2 -treated Black Thunder coals. The swelling solvents, THF, methanol, and isopropanol, were obtained from Fisher and were used as received. The liquefaction reaction solvents used were 1-MN (98% purity) and DHA, which were obtained from Aldrich, and V1074.

Untreated and SO_2 -treated Black Thunder coals were swelled by introducing coal (equivalent to 1.33 g maf) to the swelling tube and then adding 7 g of solvent (Table 4). Molyvan L, Mo naphthenate, and Ni octoate catalysts were charged to the swelling solvent at 1.05 times the amount which had been previously used (600 to 800 ppm of active metal on maf coal) when the catalyst was added directly to the liquefaction reactions. The coal was then allowed to sit unagitated in the swelling solvent for 96 hr. These experiments were designated with a "N" on the tables. Several experiments were performed in which the coal and swelling solvent were agitated during the 96 hr preswelling period. These experiments are designated with an "A" on the tables. Molyvan-L was also added to the swelling solvent at 2.0 times the amount that had previously been used when the catalyst was added directly to the liquefaction reactions. These experiments are designated with a "D" on the tables. Several experiments were performed with Molyvan-L, in which the swelling time with the catalyst present was varied: 6, 16, and 28 hr. The exact mass of catalyst added to each preswelling solvent is given in Table 5. The amount of catalyst uptake is given for those reactions where the analysis was reported.

The reaction conditions are given in Table 1. These reactions were carried out using untreated Black Thunder at 410 °C for 30, 20, and 10 min. The liquefaction reactions for SO₂-treated Black Thunder coal were conducted for 30 min. Each reaction contained the equivalent of 1.33 g of maf coal, 2 g of 1-MN as solvent, 0.67 g of pyrene (added as probe hydrogenation species) and residual swelling solvent that remained in the swelled coal. The amount of solvent absorbed in the coal for the different preswelling and reaction conditions is presented in Table 5. Hydrogen gas was introduced at 1250 psig at ambient temperature. The reactor was well-agitated at 450 rpm.

The products from the liquefaction reactions were removed from the reactor with THF, and the conversion of the coal to THF solubles was determined. For the reactions where analysis of catalyst uptake was performed, the values for the weight percent of coal added are given. The weight percent of the coal added in the other reactions are indicated as NYD but were in the range of 30 to 31%. The amount of pyrene hydrogenation to hydrogenated products was obtained by gas chromatographic analyses using a Varian Model 3400, a J&W DB-5 column and flame ionization detection. Pyrene hydrogenation is 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 the most hydrogenated product, perhydropyrene.

Liquefaction of Untreated Black Thunder Coal:

When THF was used as the swelling solvent, the largest coal conversion achieved from untreated coal with Molyvan-L at the lower catalyst loading occurred with a reaction time of 30 min and no agitation. The average coal conversion obtained using 1-MN as the reaction solvent was 81.9% and pyrene (PYR) conversion was 15.1%. Agitating the sample decreased the coal conversion to 73.6% on the average, while PYR conversion was essentially unchanged at 14.7%. The results are shown in Table 6 for the untreated coal, and in Table 7 for the SO₂-treated coal.

Reactions using the three different catalysts and THF as swelling solvent were performed at shorter reaction times of 20 and 10 min (Table 6). In each case, coal and PYR conversions decreased substantially. Hence, longer reaction time was required for Molyvan-L to obtain good coal liquefaction. Table 5 shows the amount of solvent incorporated in each reaction. It ranged from 1.3 to 1.8 g.

Untreated coal preswelled with Molyvan-L and Ni octoate in methanol was also reacted for 30 and 20 min using 1-MN as the reaction solvent (Table 6). With Molyvan-L as the catalyst, only 68.4% coal conversion was achieved after 30 min of reaction (67.6% after 20 min.) By contrast, when untreated coal preswelled with methanol was reacted with Molyvan-L introduced directly into the reactor, -88% coal conversion was achieved. Likewise, with Molyvan-L introduced to methanol as the swelling solvent -3% PYR conversion occurred for both 20 and 30 min reactions. When Molyvan-L was introduced directly into the reactor with coal preswelled with methanol, then -24% PYR conversion occurred. Hence, Molyvan-L catalyst introduction with methanol was detrimental for both coal and PYR conversions. When methanol was used as the preswelling solvent, little

effect of reaction time was observed. One possible explanation was that Molyvan-L was deactivated by methanol.

Reactions using Ni octoate preswelled with methanol also resulted in decreased coal and pyrene conversions compared to adding the catalyst directly to the reactor. Somewhat higher coal conversions were obtained after 30 min of reaction than after 20 min. Pyrene conversions were very similar for the two reaction times.

Reactions were performed with untreated coal preswelled with isopropanol with either Molyvan-L or Ni octoate introduced with the swelling solvent. Reactions with both catalysts yielded reasonable (~80%) conversion at 30 min. Pyrene conversion was dependent upon reaction time with Molyvan-L but PYR conversions were not changed in the case of Ni octoate.

Molyvan-L catalyst loading was doubled in some experiments as shown in Table 6. Resulting coal conversion increased. This increase occurred in all three swelling solvents with methanol having the greatest effect. Pyrene conversion was affected substantially by doubling the catalyst loading, although PYR was added directly to the reactor and not to the preswelling solvent. The amount of PYR conversion ranged from 23.8 to 30.3%.

Molyvan-L was added to THF, the preswelling solvent, for contact times of 6, 16, and 28 hr. The amount of coal swelling obtained at these three times was similar to that obtained at 96 hr. The amount of coal conversion obtained for these reactions ranged from 73.3 to 81.7% and did not seem to be affected by the preswelling time. A nominally higher coal conversion (82.5%) was obtained at 96 hr swelling. Hence, the effect of preswelling time was minimal.

Results of the Liquefaction of SO₂-Treated Black Thunder Coal:

SO₂-treated Black Thunder coal was preswelled with THF, methanol and isopropanol with Molyvan-L and Ni octoate present with contact times of 96 hr. Liquefaction reactions with 1-MN as solvent were then carried out with a 30 min reaction time. The results of the completed reactions are given in Table 7. They will be discussed next quarter.

In summary, coal conversion decreased when the catalyst was present during preswelling compared to reactions when the catalyst was added directly to the reactor. The amount of decrease ranged from -0.3 to -5.1%. By contrast, the amount of PYR conversion during the liquefaction reaction increased for most of the systems. This indicates that hydrogenation activity has remained good. The percentage increase ranged from +2.2 to +6.0%. Only one system, Molyvan-L preswelled in methanol, showed a small decrease in PYR conversion (-1.3%).

Evaluation of Different Methods of Catalyst Introduction:

Tables 8 and 9 give a comparison of coal and PYR conversions with untreated and SO₂- treated Black Thunder coals, respectively, using two methods of catalyst introduction: (1) adding catalyst to the preswelling solvent and (2) adding the catalyst directly to the reactor after the coal

has been preswelled. With equivalent catalyst loading, coal conversion was generally better in the latter case.

In the case of runs made with untreated coal, pyrene conversion was generally lower for reactions when the Molyvan-L catalyst was introduced into the preswelling solvent compared to direct catalyst addition to the reactor. The exception was when catalyst loading was doubled; here, pyrene conversion was higher when the catalyst was introduced with the swelling solvent (Table 8). On the other hand, pyrene conversion with Ni octoate introduced to the preswelling solvent was increased compared to adding the catalyst directly to the reactor. For SO₂-treated coal, introduction of catalyst with swelling solvent generally increased pyrene conversion compared to direct catalyst addition to the reactor. (See Table 9).

Evaluation of V1074 as the Preswelling and Reaction Solvent:

V1074 was used as both the preswelling solvent and the reaction solvent to determine if the type of preswelling solvent used strongly affected coal conversion. In these experiments, the coal was preswelled directly in the reactor, because of difficulty in handling V1074 in the swelling tubes. Since 2 ml of V1074 were normally used for reaction and 7 ml of solvent for preswelling, a compromise of 4 ml as both the preswelling and reaction solvents was chosen. Because of the increased amount of solvent, the weight percent of coal present in the reactor decreased to approximately 21%. The mass of coal and PYR introduced into the reactor remained the same as in all previous reactions. The results are given in Table 10.

Coal conversions in the thermal reactions after preswelling with V1074 averaged 70.7%. However, the pyrene conversion was only 5.8%. When Molyvan-L was added, either directly to the reactor after preswelling or during preswelling, coal conversion increased compared to the thermal case. Pyrene conversion also increased substantially. Little effect of the type of catalyst introduction was observed.

Pyrene Product Distributions:

The pyrene product distributions obtained during the reactions with untreated and SO₂-treated Black Thunder coals are presented in Tables 11 and 12, respectively. The 30-min reactions using Molyvan-L, Mo naphthenate and Ni octoate achieved the most conversion of PYR and yielded hydrogenation products dihydropyrene (DHP), tetrahydropyrene (THP), and hexahydropyrene (HHP). The 20- and 10-min reactions yielded less PYR conversion than did the 30 min reaction. Agitation during preswelling did not have any apparent effect on pyrene conversion. However, doubling the catalyst loading had a substantial effect on PYR conversion.

The amount of PYR hydrogenation which occurred during the varied time preswelling experiments with Molyvan-L and untreated coal was inconsistent. The amounts ranged from 2.9 to 10.1%. Higher hydrogenation values correlated with higher coal conversion. Therefore, possibly the manner in which the catalyst was incorporated into the coal during the shortened preswelling time affected both reactions. For SO₂-treated coal, pyrene hydrogenation was substantially higher with Molyvan-L than with Ni

octoate when the treated coal was preswelled with catalyst in methanol and isopropanol (Table 12). For all of the experimental conditions, the primary product from PYR was DHP. THP was formed when there was a higher percent hydrogenation. Trace amounts of HEP were observed in most reactions.

Pyrene hydrogenation was substantially higher in the reactions with Molyvan-L compared to the thermal reactions, when V1074 was used as both the swelling and reaction solvents, (Table 13). The primary product was DHP for all reaction conditions. The PYR product distribution was not affected by the catalyst introduction method.

Comparison of Catalyst Introduction Methods:

The two methods of catalyst introduction are compared in Tables 14 and 15 for untreated and SO₂- treated Black Thunder coals, respectively. Conversion of untreated Black Thunder coal reacted in 1-MN was always less with Molyvan-L being added to the preswelling solvent, regardless of the type of solvent used. Pyrene conversion was also less for all of the Molyvan-L systems. The system which showed the lowest conversion of both coal and pyrene was the methanol/Molyvan-L system.

The systems with Ni octoate added to the preswelling solvent also showed less coal conversion when the catalyst was added to preswelling solvent. The exception was the THF/Ni octoate system. These latter runs will be repeated. The methanol/Ni octoate system showed more difference between the two methods than did the other two solvents. Again, an effect of the type of preswelling solvent on both coal and PYR conversion was evident.

Table 15 presents the comparison of the two methods for SO₂-treated Black Thunder coal. The THF system showed less coal conversion when the catalyst was added to the preswelling solvent than when the catalyst was added directly to the reactor. However, PYR conversion showed the opposite trend. Pyrene conversion increased frequently when the catalyst was absorbed into the coal from the preswelling solvent, although some negative values were obtained.

Argonne Coals:

Liquefaction reactions were also performed using Wyodak, Illinois No. 6, and North Dakota coals received from Karl Vorres of Argonne National Laboratories. Coal was received in both a dry and a wet state after acid washing. Only the coals received in the dry state have been tested. The reactions were performed thermally without swelling using as reaction solvents: 1-MN, coal-derived V1074, and DHA. Pyrene was introduced into the reactor as a probe hydrogenation species. The results are given in Tables 16-21. Both Illinois No. 6 and Wyodak coals gave similar coal conversions for all the solvents except for Wyodak and 1-MN. Higher PYR conversion was observed with Illinois No. 6 coal, indicating indigenous catalysis by some of the mineral matter present in the coal. The highest PYR conversion was achieved with the Illinois No. 6/V1074 system.

Reactions were also performed with North Dakota coal in the reaction solvents of DHA, V1074 and 1-MN. The average coal conversion was affected

only slightly by the reaction solvent, yielding 76.7% for DHA, 74.1% for V1074 and 73.5% for 1-MN. These coal conversions were less than those of Illinois No. 6 for all three solvents. North Dakota coal yielded less coal conversion with DHA and V-1074 than Wyodak but similar conversion with 1-MN. The PYR hydrogenation was also similar for all three reactions but slightly more PYR was hydrogenated with DHA as the reaction solvent than with V1074.

Future Work:

Planned experiments include performing reactions with coal that has been preswelled in the reaction solvents. 1-Methylnaphthalene will be used as a preswelling solvent followed by reactions in 1-MN. The liquefaction reactions using SO₂-treated coal will also be completed. Also, reactions using untreated Black Thunder coal preswelled with THF with Ni octoate present will be performed to determine the validity of the currently reported value. Several experiments will be performed to evaluate the effect of the preswelling solvent on the catalyst. The use of other catalysts in the preswelling solvent will be tested.

Subtask 2.4: Bench-Scale Studies

The objectives of this subtask are (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. The initial series of runs were made with 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, as reported in the last quarterly (Quarterly Report Number Q-06 (January-March, 1993) 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.)

Because additional Black Thunder coal would need to be prepared and the AU-51L unit was scheduled for other runs, the decision was made to progress to carrying out flow experiments with Illinois No. 6 coal in the AU-44L flow unit. During this quarter, the coal samples were generated (sampled, screened, etc.), and initial flow runs were made with a start-up solvent, V-1074, to insure smooth operation and to check for leaks.

Subtask 2.5: Solids Separation/Alternative Bottoms Processing

The overall project objective is "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." FWDC's effort covers solids separation and alternative bottoms processing through direct delayed coking and the ASCOT process. The ASCOT process couples solvent deasphalting with delayed coking to maximize the production of coal-derived liquids while rejecting troublesome solids within the coke drum.

These results will then be integrated into the overall improved coal liquefaction concept proposed in this program.

A preliminary economics assessment of the battery limits for solvent deasphalting units, delayed coking units, or both, as incorporated in an integrated processing scheme, will be completed. The assessment will be for two case studies.

The asphalt production phase of this sub-task has been completed. The material balance and ash determinations are reported in Table 22. The solvent blend was adjusted, increasing the percentage pentane to 40 vol%, to consistently achieve the target 40 wt% DAO yield over the multiple batch extractions needed to produce the required amount of asphalt.

The Direct Delayed Coking of Wilsonville Atmospheric Residue (Subtask 2.5.4) test has also been completed. The operating conditions and material balance are reported in Table 23 and product inspections are reported in Table 24. The residue feedstock from the liquefaction of Black Thunder coal at Wilsonville is very high in Quinoline Insolubles (QI) and ash content. This presents more of a challenge than coking liquefaction product from Illinois No. 6 coal which was also processed at Wilsonville. The yield data was calculated "as measured" and on a solids-free basis, solids being defined as the Quinoline Insolubles.

The data indicate that vaporization and steam stripping inside the coke drum produced more than half of the liquid product. Only about 10 vol% of the liquid is lower boiling than the feedstock (an indication of thermal cracking product). Vaporizing and steam stripping a 634° (IBP) - 900°F fraction of the feed provided about 30 vol%, leaving thermal cracking and stripping as the source of another 10% of the liquid product that is heavier than 900°F. This scenario is in agreement with our distillate oil yield of 50 wt%. If the 50 wt% yield could not be improved upon, direct delayed coking of this particular feedstock would not produce as much liquid product as deep solvent deasphalting.

The resulting coke had a relatively high volatile matter content (15.2 wt%), which could be a source of additional liquid product. This could be promoted by more thermal cracking and deeper vaporization and steam stripping. This would include raising coking temperatures and modifying the schedule used to steam-out the coke drum for additional liquid product. The practical limitation is the ability to raise the temperature of a high-solids-containing feed without plugging the preheat coil to the drum.

The gas yield was desirably low and it consisted of hydrogen and methane with some ethane and propane. Other hydrocarbons were present in relatively small concentrations. This is consistent with past results from processing other liquefaction feedstocks.

The products from solvent deasphalting production runs that produced candidate asphalts for transport tests and delayed coking are reported in Table 25.

The asphalt that will be coked was produced in sequential production Runs 3039 and 3040, which were blended to generate the needed quantities. The

asphalt from Runs 3034 and 3035 were rejected candidates for coking after evaluating the transport tests. These contain higher solids loadings and prohibitive softening points and did not pass the transport test criteria. Examining the data on toluene and quinoline insolubles, ash and softening point confirms the reason for the difficulty in handling these asphalts. If the integrated coal liquefaction process delivered lower-solids-containing material, the ASCOT process would provide more options as to how deeply to top the feedstock via solvent deasphalting prior to coking.

The pilot plant was modified to operate the feed system at high pressure (~ 350 psig), a requirement imposed by the vapor pressure of the solvent/asphalt blend that was formulated in the pressurized blending/feeding vessel.

Table 26 reports the inspection of DAO from deep deasphalting (80.6% yield) with xylene (Run 3017) to compare with the lower DAO yields of Table 25. The reduction in quality, as measured by Conradson carbon residue, ash and heptane insolubles, is evident and could be a negative factor if the material were further processed in a refinery mode rather than recycled to the front end of the liquefaction process.

Table 22: Asphalt Production for Delayed Coking

Solvent	S/F Ratio (V/V at 60°F)	Temp. (°F)	Yields (wt%)			Ash (wt%)	
			Oil	Asphalt	Recov.	Oil	Asphalt
60%C ₄ , 40%C ₅	4	290	40.2	59.8	100.0	0.010	19.09

CONCLUSIONS AND FUTURE WORK

Experimentation is confirming some aspects of the overall process concept, but it is also raising problem areas. Black Thunder subbituminous coal can be effectively beneficiated to about 4 wt% ash using aqueous sulfurous acid pretreatment. This treated coal can be further beneficiated to about 2 wt% ash using commercially available procedures. All three coals (Black Thunder subbituminous, Burning Star bituminous, and Martin Lake lignite) are effectively swelled by a number of solvents. The most effective solvents are those having hetero-functionality. In addition, a synergistic effect has been demonstrated, in which solvent blends are more effective than the pure solvents alone. Therefore, it will be necessary to use only low levels of swelling agents and yet promote the impregnation of catalyst precursors. The rate of the impregnation of catalyst precursors into swollen coal increases greatly as the effectiveness of the solvent to swell the coal increases. The initial laboratory and continuous flow unit (AU-51L) experiments have indicated that the expected increase in coal conversion and product up-grading did not occur with the selected swelling solvents and catalyst precursor. There may be an

interaction between the Molyvan-L catalyst precursor and swelling solvent that effects coal liquefaction. It is also noted that the most effective swelling solvent, dimethyl sulfoxide, was detrimental to subsequent liquefaction. Therefore, more extensive research is needed to develop an effective process. With respect to solids separation and recovery, the solvent system for the deasphalting process has been established. An asphalt stream containing 21% ash has been handled successfully in the transport tests, and delayed coking tests are underway using this stream.

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TABLE 1. ANALYSIS OF SO₂-TREATED BLACK THUNDER COAL

	Proximate Analysis	
	As received	Dry basis
% Moisture	9.88	
% Ash	3.08	3.42
% Volatile	41.74	46.32
% Fixed Carbon	45.30	50.26
TOTAL	100.00	100.0
BTU/lb maf BTU	10,993	12,198 12,630
	Ultimate Analysis	
	As received	Dry basis
% Moisture	9.88	
% Carbon	63.57	70.54
% Hydrogen	4.46	4.95
% Nitrogen	0.80	0.89
% Sulfur	0.73	0.81
% Ash	3.08	3.42
% Oxygen (diff.)	17.48	19.39

TABLE 2. 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_{coal} = 100 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 3. 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 4. Reaction Conditions for Untreated and SO₂ Treated Black Thunder Coals Preswelled with Catalyst

Reaction Conditions	
Coals	Untreated and SO ₂ treated Black Thunder
Temperature	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, V1076
Catalyst Loading	~ 600-800 or 1200-1600 ppm based on maf coal
Reaction Time	30, 20, 10 min
Conditions for Preswelling	
Solvents for Preswelling	Methanol, THF, isopropanol
Amount of Preswelling Solvent	7 g
Catalyst	Mo Naphthenate, Ni Octoate, Molyvan L
Catalyst Charge to Swelling Solvent	Case 1: 1.05 x 600 to 800 ppm of active metal Case 2: 2.0 x 600 to 800 ppm of active metal
Swelling Time	Varied: 6, 16, 28, 96 hr
Analysis	1. Coal conversion to THF solubles 2. Pyrene conversion to hydrogenated products 3. Catalyst loading (analysis by Amoco)

Table 5. Solvent Uptake by Coal During Swelling

Catalyst	Conditions ^a	Coal Mass (g)	Solvent Mass Absorbed (g)	Catalyst Mass (g)	ID Number
Coal: untreated Reaction Time: 30 min Swelling Solvent: THF					
Mo Naphthenate	A	1.6492	1.2374	0.0523	1C
Mo Naphthenate	A	1.6486	1.5141	0.0523	2C
Molyvan L	N	1.6486	1.6040	0.0398	3A
Molyvan L	N	1.6496	1.6048	0.0373	2A
Molyvan L	A	1.6488	1.7701	0.0347	3C
Molyvan L	A	1.6492	1.7366	0.0427	5C
Molyvan L	D	1.6509	1.6187	0.0702	1D
Molyvan L	D	1.6505	1.5540	0.0738	5D
Molyvan L	28h	1.6492	1.6275	0.0353	1H
Molyvan L	28h	1.6505	1.3392	0.0381	3H
Molyvan L	16h	1.6522	1.4365	0.0390	2H
Molyvan L	16h	1.6492	1.3081	0.0406	5H
Molyvan L	6h	1.6502	1.4754	0.0399	4H
Molyvan L	6h	1.6487	1.3771	0.0352	6H
Ni Octoate	N	1.6474	1.5776	0.0268	1A
Coal: untreated Reaction Time: 20 min Swelling Solvent: THF					
Mo Naphthenate	A	1.6470	1.2326	0.0476	4C
Mo Naphthenate	A	1.6474	1.7495	0.0500	6C
Molyvan L	N	1.6499	1.7082	0.0352	1E
Molyvan L	N	1.6484	1.5902	0.0358	3E
Ni Octoate	N	1.6532	1.2222	0.0278	3B
Ni Octoate	N	1.6506	1.2391	0.0257	5B
Coal: untreated Reaction Time: 10 min Swelling Solvent: THF					
Molyvan L	N	1.6497	1.4850	0.0362	4A
Molyvan L	N	1.6487	1.4663	0.0349	5A

^a A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling.

Table 5. Solvent Uptake by Coal During Swelling (Continued)

Catalyst	Conditions ^a	Coal Mass (g)	Solvent Mass Absorbed (g)	Catalyst Mass (g)	ID Number
Coal: untreated Reaction Time: 30 min Swelling Solvent: Methanol					
Molyvan L	N	1.6474	1.0783	0.0409	1B
Molyvan L	N	1.6470	1.1374	0.0367	2B
Molyvan L	D	1.6457	1.3570	0.0709	4E
Molyvan L	D	1.6487	1.1967	0.0757	5E
Ni Octoate	N	1.6490	0.9481	0.0251	1F
Ni Octoate	N	1.6463	1.0915	0.0242	4F
Coal: untreated Reaction Time: 20 min Swelling Solvent: Methanol					
Molyvan L	N	1.6416	1.0018	0.0394	4B
Molyvan L	N	1.6506	0.9803	0.0362	6B
Ni Octoate	N	1.6481	0.8815	0.0228	5F
Ni Octoate	N	1.6450	1.0572	0.0255	6F
Coal: untreated Reaction Time: 30 min Swelling Solvent: Isopropanol					
Molyvan L	N	1.6456	1.2749	0.0392	3D
Molyvan L	N	1.6424	1.2210	0.0408	4D
Molyvan L	D	1.6442	1.1892	0.0710	2D
Molyvan L	D	1.6413	1.2599	0.0791	6D
Ni Octoate	N	1.6435	1.0631	0.0265	2F
Ni Octoate	N	1.6388	1.0936	0.0228	3F
Coal: untreated Reaction Time: 20 min Swelling Solvent: Isopropanol					
Molyvan L	N	1.6437	1.1480	0.0352	2E
Molyvan L	N	1.6431	1.1281	0.0353	6E
Ni Octoate	N	1.6461	1.1089	0.0254	1G
Ni Octoate	N	1.6415	1.0320	0.0258	3G

^a A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling.

Table 5. Solvent Uptake by Coal During Swelling (Continued)

Catalyst	Conditions ^a	Coal Mass (g)	Solvent Mass Absorbed (g)	Catalyst Mass (g)	ID Number
Coal: SO₂ treated Reaction Time: 30 min Swelling Solvent: Isopropanol					
Molyvan L	N	1.5314	2.1159	0.0344	2G
Molyvan L	N	1.5283	1.8332	0.0356	4G
Ni Octoate	N	1.5305	2.0377	0.0235	5G
Ni Octoate	N	1.5303	1.5671	0.0232	6G
Coal: SO₂ treated Reaction Time: 30 min Swelling Solvent: Methanol					
Molyvan L	N	1.5272	1.1793	0.0389	6I
Ni Octoate	N	1.5243	1.2622	0.0263	2I
Ni Octoate	N	1.5267	1.2300	0.0263	3I
Coal: SO₂ treated Reaction Time: 30 min Swelling Solvent: Isopropanol					
Molyvan L	N	1.5231	1.4260	0.0362	4I
Molyvan L	N	1.5278	1.5494	0.0374	5I

^a A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling.

Table 6. Coal and Pyrene Conversion for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling

Catalyst Type	Catalyst Loading (ppm) ^a	Condi-tions ^b	Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [% R]	ID Number
			%A ^c	(g)	wt% ^c				
Reaction Time: 30 min Swelling Solvent: THF									
Mo Naphthenate	NYD	A	31.8	1.6492	NYD	3.3	62.7	NYD	1C
Mo Naphthenate	683	A	38.1	1.6486	30.5	3.6	61.8	4.7470(108.6)	2C
Molyvan L	NYD	N	41.7	1.6486	NYD	13.8	80.8	NYD	3A
Molyvan L	544	N	39.1	1.6496	30.7	16.4	83.0	4.8742(112.0)	2A
Molyvan L	NYD	A	50.0	1.6488	NYD	11.1	75.7	NYD	3C
Molyvan L	NYD	A	54.5	1.6492	NYD	18.2	71.4	NYD	5C
Molyvan L	1143	D	39.1	1.6509	30.5	26.8	84.0	5.2166(119.0)	1D
Molyvan L	NYD	D	42.9	1.6505	NYD	30.3	85.6	NYD	5D
Molyvan L	NYD	28 h	45.5	1.6492	NYD	10.4	74.9	NYD	1H
Molyvan L	NYD	28 h	36.4	1.6505	NYD	7.2	73.3	NYD	3H
Molyvan L	NYD	16 h	42.9	1.6522	NYD	10.8	74.6	NYD	2H
Molyvan L	NYD	16 h	30.1	1.6492	NYD	25.3	81.7	NYD	5H
Molyvan L	NYD	6 h	42.9	1.6502	NYD	20.1	79.6	NYD	4H
Molyvan L	NYD	6 h	40.9	1.6487	NYD	10.3	74.0	NYD	6H
Ni Octoate	569	N	34.8	1.6474	30.7	18.8	83.9	5.1322(118.2)	1A
Reaction Time: 20 min Swelling Solvent: THF									
Mo Naphthenate	601	A	28.6	1.6470	30.5	3.0	50.7	4.6187(105.8)	4C
Mo Naphthenate	614	A	45.5	1.6474	30.5	2.3	55.4	5.0585(115.8)	6C
Molyvan L	NYD	N	40.9	1.6499	NYD	7.2	71.3	NYD	1E
Molyvan L	NYD	N	36.4	1.6484	NYD	2.3	63.7	NYD	3E
Ni Octoate	NYD	N	36.4	1.6532	NYD	2.2	58.5	NYD	3B
Ni Octoate	599	N	31.8	1.6506	30.7	2.6	63.0	4.9287(113.4)	5B

^a NYD = Not yet determined.

^b A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h 16 h 6 h = hours of catalyst solvent contact during preswelling.

^c Coal percentages should be near 31%.

Table 6. Coal and Pyrene Conversion for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling (Continued)

Catalyst Type	Catalyst Loading (ppm) ^a	Condi-tions ^b	Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [% R]	ID No.
			%ΔV	(g)	wt% ^c				
Reaction Time: 10 minutes			Swelling Solvent: THF						
Molyvan L	NYD	N	40.9	1.6497	NYD	5.4	46.7	NYD	4A
Molyvan L	NYD	N	45.5	1.6487	NYD	6.7	52.0	NYD	5A
Reaction Time: 30 min			Swelling Solvent: Methanol						
Molyvan L	NYD	N	21.7	1.6474	NYD	2.4	68.4	NYD	1B
Molyvan L	644	N	28.6	1.6470	30.6	3.6	68.4	4.9238(113.2)	2B
Molyvan L	1261	D	28.6	1.6457	30.3	23.8	89.1	5.2578(119.8)	4E
Molyvan L	NYD	D	23.8	1.6487	NYD	27.6	88.4	NYD	5E
Ni Octoate	NYD	N	22.7	1.6490	NYD	3.2	70.9	NYD	1F
Ni Octoate	653	N	23.8	1.6463	30.7	3.7	69.3	5.0006(115.3)	4F
Reaction Time: 20 min			Swelling Solvent: Methanol						
Molyvan L	NYD	N	19.0	1.6416	NYD	3.4	67.6	NYD	4B
Molyvan L	637	N	31.8	1.6506	30.6	2.2	67.5	5.2988(121.6)	6B
Ni Octoate	608	N	23.8	1.6481	30.7	2.6	64.1	4.5322(104.4)	5F
Ni Octoate	617	N	17.4	1.6450	30.7	2.0	64.7	4.8101(110.8)	6F
Reaction Time: 30 min			Swelling Solvent: Isopropanol						
Molyvan L	626	N	17.4	1.6456	30.6	15.2	80.5	4.5367(104.2)	3D
Molyvan L	663	N	19.0	1.6424	30.5	18.5	79.3	5.0069(115.0)	4D
Molyvan L	NYD	D	23.8	1.6442	NYD	27.9	83.1	NYD	2D
Molyvan L	NYD	D	21.7	1.6413	NYD	28.4	80.6	NYD	6D
Ni Octoate	716	N	18.2	1.6435	30.6	4.3	75.8	4.7073(108.4)	2F
Ni Octoate	617	N	13.0	1.6388	30.6	3.4	74.6	4.4727(103.2)	3F

^a NYD = Not yet determined.

^b A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling.

^c Coal percentages should be near 31%.

Table 6. Coal and Pyrene Conversion for Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling (Continued)

Catalyst Type	Catalyst Loading (ppm) ^a	Condi-tions ^b	Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [% R]	ID No.
			% Δ V	(g)	wt% ^c				
			Reaction Time: 20 minutes			Swelling Solvent: Isopropanol			
Molyvan L	NYD	N	19.0	1.6437	NYD	3.2	65.4	NYD	2E
Molyvan L	572	N	18.2	1.6431	30.6	5.8	71.0	5.3159(122.2)	6E
Ni Octoate	699	N	13.0	1.6461	30.6	4.0	67.4	4.8985(112.7)	1G
Ni Octoate	NYD	N	18.2	1.6415	NYD	4.6	62.2	NYD	3G

^a NYD = Not yet determined.

^b A = agitated; Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling.

^c Coal percentages should be near 31%.

Table 7. Coal and Pyrene Conversion for SO₂ Treated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling

Catalyst Type	Catalyst Loading (ppm) ^a	Condi-tions ^b	Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [% R]	ID No.
			% Δ V	(g)	wt% ^c				
			Reaction Time: 30 min			Swelling Solvent: THF			
Molyvan L	NYD	N	88.9	1.5314	NYD	30.8	87.5	NYD	2G
Molyvan L	638	N	63.2	1.5283	31.3	31.9	84.4	4.4536(105.3)	4G
Ni Octoate	659	N	77.8	1.5305	31.4	7.7	74.3	4.9130(116.3)	5G
Ni Octoate	NYD	N	40.0	1.5303	NYD	6.0	68.5	NYD	6G
			Reaction Time: 30 min			Swelling Solvent: Methanol			
Molyvan L	NYD	N	40.0	1.5272	NYD	28.7	89.1	NYD	6I
Ni Octoate	NYD	N	36.8	1.5243	NYD	6.7	78.5	NYD	2I
Ni Octoate	NYD	N	30.0	1.5267	NYD	7.4	78.2	NYD	3I
			Reaction Time: 30 min			Swelling Solvent Isopropanol			
Molyvan L	NYD	N	33.3	1.5231	NYD	25.8	86.9	NYD	4I
Molyvan L	NYD	N	31.6	1.5278	NYD	26.1	88.3	NYD	5I

^a NYD = Not yet determined.

^b A = Agitated during preswelling; N = not agitated.

^c Coal percentage should be near 31%.

Table 8. Comparison of Coal and Pyrene Conversions With Untreated Black Thunder Coal With Different Catalyst Introduction Methods

Catalyst	Agitated (A) Not Agitated (N) Double Catalyst (D)	% Change in Coal Conversion ^a (weight %)	% Change in Pyrene Conversion ^a (mole %)	Swelling Index (%ΔV)
Coal: untreated Swelling Solvent: THF				
Molyvan L	N	-6.5	-4.8	41.7
Molyvan L	N	-4.3	-2.2	39.1
Molyvan L	A	-11.6	-7.5	50.0
Molyvan L	A	-15.9	-0.4	54.5
Molyvan L	D	-3.3	+8.2	39.1
Molyvan L	D	-1.7	+11.7	42.9
Molyvan L	28h	-12.4	-8.2	45.5
Molyvan L	28h	-14.0	-11.4	36.4
Molyvan L	16h	-12.7	-7.8	42.9
Molyvan L	16h	-5.6	+6.7	30.1
Molyvan L	6h	-7.7	+1.5	42.9
Molyvan L	6h	-13.3	-8.3	40.9
Ni Octoate	N	+6.9	+16.4	34.8
Coal: untreated Swelling Solvent: Methanol				
Molyvan L	N	-19.6	-21.9	21.7
Molyvan L	N	-19.6	-20.7	28.6
Molyvan L	D	+1.1	-0.5	28.6
Molyvan L	D	+0.4	+3.3	23.8
Ni Octoate	N	-14.6	-7.7	22.7
Ni Octoate	N	-16.2	-7.2	23.8

^a% change in conversion is the difference between the percentage of conversion when the catalyst was added directly to the reactor and the percentage conversion when the catalyst was added to the preswelling solvent.

Table 8 Comparison of Coal and Pyrene Conversions With Untreated Black Thunder Coal With Different Catalyst Introduction Methods (Continued)

Catalyst	Agitated (A) Not Agitated (N) Double Catalyst (D)	% Change in Coal Conversion ^a (weight %)	% Change in Pyrene Conversion ^a (mole %)	Swelling Index (%ΔV)
Coal: untreated Swelling Solvent: Isopropanol				
Molyvan L	N	-7.6	-3.5	17.4
Molyvan L	N	-8.8	-0.2	19.0
Molyvan L	D	-5.0	+9.2	23.8
Molyvan L	D	-7.5	+9.7	21.7
Ni Octoate	N	-1.8	+2.1	18.2
Ni Octoate	N	-3.0	+1.2	13.0

^a% change in conversion is the difference between the percentage of conversion when the catalyst was added directly to the reactor and the percentage conversion when the catalyst was added to the preswelling solvent.

Table 9. Comparison of Coal and Pyrene Conversions With SO₂ Treated Black Thunder Coal With Different Catalyst Introduction Methods

Catalyst	Agitated (A) Not Agitated (N) Double Catalyst (D)	% Change in Coal Conversion (weight %)	% Change in Pyrene Conversion (mole %)	Swelling Index (%ΔV)
Coal: SO₂ Treated Swelling Solvent: THF				
Molyvan L	N	-3.6	+5.4	88.9
Molyvan L	N	-6.7	+6.5	63.2
Ni Octoate	N	+1.8	+5.5	77.8
Ni Octoate	N	-4.0	+3.8	40.0
Coal: SO₂ Treated Swelling Solvent: Methanol				
Molyvan L	N	-0.9	-1.3	40.0
Molyvan L	N	-0.2	+1.8	36.8
Ni Octoate	N	-0.5	+2.5	30.0
Coal: SO₂ Treated Swelling Solvent: Isopropanol				
Molyvan L	N	-4.4	+4.5	33.3
Molyvan L	N	-3.0	+4.8	31.6

Table 10. Coal and Pyrene Conversion for Untreated Black Thunder Coal Using V1074 as a Swelling and Reaction Solvent

Catalyst Type	Catalyst Loading (ppm)	Condi- tions	Added Coal			Pyrene Conversion (mol %)	Coal Conversion (wt %)	Total Recovery (g) [% R]	ID No.
			%ΔV	(g)	wt% ^c				
Reaction Time: 30 min Swelling Solvent: Methanol V1074									
Thermal	None	N ^b	NA ^a	1.6444	21.0	5.1	69.7	7.2651(114.6)	NA
Thermal	None	N ^b	NA	1.6413	21.1	6.4	71.6	6.7985(108.0)	NA
Molyvan L	684	NoPS ^c	NA	1.6409	20.6	24.2	75.1	7.0453(109.2)	NA
Molyvan L	606	NoPS ^c	NA	1.6412	20.8	27.6	78.4	7.0550(110.5)	NA
Molyvan L	678	N ^d	NA	1.6431	20.8	26.6	78.1	7.2753(113.7)	NA
Molyvan L	631	N ^d	NA	1.6417	20.8	27.9	77.6	7.0208(109.7)	NA

^a NA = Not applicable.

^b N = not agitated during preswelling.

^c NoPS = No preswelling; catalysts added directly to the reactor.

^d Catalyst added to preswelling solvent.

Table 11 Pyrene Product Distribution Using Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling

Catalyst Type	Catalyst Loading (ppm) ^a	Conditions ^b	% HYD ^c (% Coal) ^d	Product Distribution (mole %)				ID No.	% Catalyst Absorbed
				PYR	DHP	THP	HHP		
Reaction Time: 30 min Swelling Solvent: THF									
Mo Naphthenate	NYD	A	1.5 (NYD)	96.7	2.7	0	0.6	1C	NYD
Mo Naphthenate	683	A	2.0 (30.5)	96.4	2.3	0	1.3	2C	95.2
Molyvan L	NYD	N	5.4 (NYD)	86.2	12.4	0.3	1.1	3A	NYD
Molyvan L	544	N	5.9 (30.7)	83.6	15.6	0.3	0.5	2A	79.4
Molyvan L	NYD	A	4.3 (NYD)	88.9	10.0	0.3	0.8	3C	NYD
Molyvan L	NYD	A	7.0 (NYD)	81.8	16.5	0.7	1.0	5C	NYD
Molyvan L	1143	D	10.1(30.5)	73.2	24.2	1.8	0.8	1D	89.2
Molyvan L	NYD	D	11.8(NYD)	69.7	26.3	2.8	1.2	5D	NYD
Molyvan L	NYD	28h	4.3(NYD)	89.6	9.1	0.3	1.0	1H	NYD
Molyvan L	NYD	28h	2.9(NYD)	92.8	6.5	0	0.7	3H	NYD
Molyvan L	NYD	16h	4.2(NYD)	89.2	9.8	0.3	0.7	2H	NYD
Molyvan L	NYD	16h	10.1(NYD)	74.7	21.8	2.1	1.4	5H	NYD
Molyvan L	NYD	6h	7.7(NYD)	79.9	18.0	1.1	1.0	4H	NYD
Molyvan L	NYD	6h	4.1(NYD)	89.7	9.2	0.2	0.9	6H	NYD
Ni Octoate	569	N	7.6 (30.7)	81.2	16.4	0.9	1.5	1A	76.8
Reaction Time: 20 min Swelling Solvent: THF									
Mo Naphthenate	601	A	1.8 (30.5)	97.0	1.8	0	1.2	4C	91.8
Mo Naphthenate	614	A	1.5 (30.5)	97.7	1.3	0	1.0	6C	89.4
Molyvan L	NYD	N	3.0(NYD)	92.8	6.2	0.1	0.9	1E	NYD
Molyvan L	NYD	N	1.1(NYD)	97.7	1.7	0.0	0.6	3E	NYD
Ni Octoate	NYD	N	1.2 (NYD)	97.8	1.5	0	0.7	3B	NYD
Ni Octoate	599	N	1.4 (30.7)	97.4	1.8	0	0.8	5B	84.3
Reaction Time: 10 minutes Swelling Solvent: THF									
Molyvan L	NYD	N	2.4 (NYD)	94.6	4.5	0	0.9	4A	NYD
Molyvan L	NYD	N	2.7 (NYD)	93.3	6.0	0	0.7	5A	NYD

^a NYD = Not yet determined.

^b A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst loading; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling.

^c % HYD = % hydrogenation.

^d Coal percentages should be near 31%.

Table 11 Pyrene Product Distribution Using Untreated Black Thunder Coal Reacted in 1-Methylnaphthalene with Catalyst Introduced During Preswelling (Continued)

Catalyst Type	Catalyst Loading (ppm) ^b	Conditions ^b	% HYD ^c (% Coal) ^d	Product Distribution (mole %)				ID No.	Catalyst Absorbed
				PYR	DHP	THP	HHP		
Reaction Time: 30 min Swelling Solvent: Methanol									
Molyvan L	NYD ^a	N	1.3 (NYD)	97.6	1.6	0	0.8	1B	NYD
Molyvan L	644	N	2.0 (30.6)	96.4	2.3	0	1.3	2B	95.3
Molyvan L	1261	D	9.0 (30.3)	76.2	21.6	1.3	0.9	4E	97.7
Molyvan L	NYD	D	10.8 (NYD)	72.4	24.2	1.9	1.5	5E	NYD
Ni Octoate	NYD	N	1.8 (NYD)	96.8	2.1	0.0	1.1	1F	NYD
Ni Octoate	653	N	2.0 (30.7)	96.3	2.5	0.0	1.2	4F	97.5
Reaction Time: 20 min Swelling Solvent: Methanol									
Molyvan L	NYD	N	1.8 (NYD)	96.6	2.5	0	0.9	4B	NYD
Molyvan L	637	N	2.0 (30.6)	97.8	1.2	0	1.0	6B	96.0
Ni Octoate	608	N	1.6 (30.7)	97.4	1.5	0.0	1.1	5F	96.6
Ni Octoate	617	N	1.2 (30.7)	98.0	1.2	0.0	0.8	6F	87.3
Time: 30 min Swelling Solvent: Isopropanol									
Molyvan L	626	N	5.9 (30.6)	84.8	13.6	0.5	1.1	3D	87.0
Molyvan L	663	N	7.1 (30.5)	81.5	16.8	0.6	1.1	4D	88.6
Molyvan L	NYD	D	10.7 (NYD)	72.1	24.5	2.4	0.9	2D	NYD
Molyvan L	NYD	D	11.1 (NYD)	71.6	24.8	2.4	1.2	6D	NYD
Ni Octoate	716	N	2.1 (30.6)	95.7	3.3	0	1.0	2F	97.8
Ni Octoate	617	N	1.7 (30.6)	96.6	2.5	0	0.9	3F	97.7
Time: 20 min Swelling Solvent: Isopropanol									
Molyvan L	NYD	N	1.4 (NYD)	96.8	2.7	0	0.5	2E	NYD
Molyvan L	572	N	2.4 (30.6)	94.2	5.2	0.1	0.5	6E	88.1
Ni Octoate	699	N	2.1 (30.6)	96.0	2.8	0	1.2	1G	99.5
Ni Octoate	NYD	N	2.2 (NYD)	95.4	3.6	0	1.0	3G	NYD

^a NYD = Not yet determined.

^b A = agitated: Samples were agitated with catalyst for 96 hr during preswelling; N = not agitated for 96 hr during preswelling; D = double catalyst; 28 h, 16 h, 6 h = hours of catalyst solvent contact during preswelling.

^c % HYD = % hydrogenation.

^d Coal percentages should be near 31%.

Table 12 Pyrene Product Distribution Using SO₂ Treated Black Thunder Coal Reacted in 1-Methylnaphthalene With Catalyst Introduced During Preswelling

Catalyst	Catalyst Loading (ppm)	% H (% Coal)	Product Distribution (mole %)				ID No.	% Catalyst Absorbed
			PYR	DHP	THP	HHP		
Time: 30 min Swelling Solvent: THF								
Molyvan L	NYD	12.2 (NYD)	69.2	26.5	2.7	1.6	2G	NYD
Molyvan L	638	12.8 (31.3)	68.1	27.3	2.9	1.7	4G	94.7
Ni Octoate	659	3.3 (31.4)	92.3	6.6	0.0	1.1	5G	98.5
Ni Octoate	NYD	2.8 (NYD)	94.0	4.8	0.0	1.2	6G	NYD
Time: 30 min Swelling Solvent: Methanol								
Molyvan L	NYD	12.2(NYD)	71.3	23.2	3.2	2.3	6I	NYD
Ni Octoate	NYD	3.0(NYD)	93.3	5.6	0	1.1	2I	NYD
Ni Octoate	NYD	3.1(NYD)	92.6	6.4	0	1.0	3I	NYD
Time: 30 min Swelling Solvent: Isopropanol								
Molyvan L	NYD	10.3(NYD)	74.2	22.1	2.3	1.4	4I	NYD
Molyvan L	NYD	10.4(NYD)	73.9	22.5	2.2	1.4	5I	NYD

Table 13. Pyrene Product Distribution for Untreated Black Thunder Coal Using V1074 as a Swelling and Reaction Solvent

Catalyst	Catalyst Loading (ppm)	Conditions	% H (% Coal)	Product Distribution (mole %)				ID No.	% Catalyst Absorbed
				PYR	DHP	THP	HHP		
Time: 30 min Swelling Solvent: V1074									
Thermal	None	N ^a	2.7(21.0)	94.9	3.3	0.6	1.2	NA*	NA
Thermal	None	N ^a	3.3(21.1)	93.6	4.3	0.6	1.5	NA	NA
Molyvan L	684	NoPS ^b	9.8(20.6)	75.8	20.9	1.5	1.8	NA	NA
Molyvan L	606	NoPS ^b	11.6(20.8)	72.4	23.0	2.1	2.5	NA	NA
Molyvan L	678	N ^c	11.2(20.8)	73.4	22.2	2.0	2.4	NA	NA
Molyvan L	631	N ^c	11.9(20.8)	72.1	22.9	2.1	2.9	NA	NA

* NA = Not applicable.

^a N = not agitated during preswelling.

^b NoPS = No preswelling; catalyst added directly to the reactor.

^c Catalyst added to the preswelling solvent.

Table 14. Comparison of Preswelling Untreated Black Thunder Coal With Catalyst Being Added Directly to Reactor After Preswelling

Swelling Solvent (Catalyst)	Method 1 Coal Conversion Averages ^a	Method 2 Coal Conversion Averages ^b	Difference (Method 2 - Method 1)	Method 1 Pyrene Conversion Averages	Method 2 Pyrene Conversion Averages	Difference (Method 2 - Method 1)
THF (Molyvan L)	87.3	81.9	-5.4	18.6	15.1	-3.5
THF ^c (Ni Octoate)	77.0	83.9	+6.9	2.4	18.8	+16.4
Methanol (Molyvan L)	88.0	68.4	-19.6	24.3	3.0	-21.3
Methanol (Ni Octoate)	85.5	70.1	-15.4	10.9	3.5	-7.4
Isopropanol (Molyvan L)	88.1	79.9	-8.2	18.7	16.9	-1.8
Isopropanol (Ni Octoate)	77.6	75.2	-2.4	2.2	3.9	+1.7

^a Method 1 describes the catalyst being introduced into the reactor after swelling of the coal.

^b Method 2 describes the swelling of coal with catalyst.

^c Only 1 run was successfully completed before this report was written.

Table 15. Comparison of Preswelling SO₂ Treated Black Thunder Coal With Catalyst Being Added Directly to Reactor After Preswelling

Swelling Solvent (Catalyst)	Method 1 Coal Conversion Averages ^a	Method 2 Coal Conversion Averages ^b	Difference (Method 2 - Method 1)	Method 1 Pyrene Conversion Averages	Method 2 Pyrene Conversion Averages	Difference (Method 2 - Method 1)
THF (Molyvan L)	91.1	86.0	-5.1	25.4	31.4	+6.0
THF (Ni Octoate)	72.5	71.4	-1.1	2.2	6.8	+4.6
Methanol ^c (Molyvan L)	90.0	89.1	-0.9	30.0	28.7	-1.3
Methanol (Ni Octoate)	78.7	78.4	-0.3	4.9	7.1	+2.2
Isopropanol (Molyvan L)	91.3	87.6	-3.7	21.3	26.0	+4.7

^a Method 1 describes the catalyst being introduced into the reactor after swelling of the coal.

^b Method 2 describes the swelling of coal with catalyst.

^c Only 1 run was successfully completed before this report was written.

Table 16. Coal and Pyrene Conversions for Thermal Reactions of Illinois No. 6 Coal With Three Different Solvents^a

Catalyst (ppm)	Added Coal		Pyrene Conversion (mol %)	Coal Conversion (%)	Total Recovery (g) [%R]
	(g)	wt %			
Solvent: 9,10-Dihydroanthracene					
None	1.7199	30.4	9.2	84.6	5.5567 [126.5]
None	1.7185	30.4	10.7	88.3	5.8684 [133.7]
Solvent: V1074					
None	1.7195	30.4	14.5	86.0	5.3063 [120.7]
None	1.7182	30.2	21.2	87.1	5.4136 [122.4]
Solvent: 1-Methylnaphthalene					
None	1.7204	30.4	10.0	86.6	5.0116 [114.1]
None	1.7226	30.4	7.9	86.3	4.9572 [112.8]

^a Reaction Conditions: 410°C; 30 min; no catalyst; 1250 psig H₂ introduced at ambient temperature.

Table 17. Pyrene Product Distributions from Thermal Reactions of Illinois No. 6 Coal in Three Solvents

Catalyst (ppm)	% H (% Coal)	Product Distribution (mol %)			
		PYR ^a	DHP	THP	HHP
Solvent: 9,10-Dihydroanthracene					
None	4.1 (30.4)	90.8	7.6	0.3	1.3
None	4.6 (30.4)	89.3	9.1	0.3	1.3
Solvent: V1074					
None	6.1 (30.4)	85.5	12.2	0.8	1.5
None	8.6 (30.2)	78.8	18.5	0.8	1.9
Solvent: 1-Methylnaphthalene					
None	4.2 (30.4)	90.0	8.6	0.3	1.1
None	3.6 (30.4)	92.1	6.4	0.2	1.3

^a PYR = pyrene; DHP = dihydropyrene; THP = tetrahydropyrene; HHP = hexahydropyrene

Table 18. Pyrene and Coal Conversions for Thermal Reactions of Wyodak Coal With Three Different Solvents^a

Catalyst (ppm)	Added Coal		Pyrene Conversion (mol %)	Coal Conversion (%)	Total Recovery (g) [%R]
	(g)	wt %			
Solvent: 9,10-Dihydroanthracene					
None	2.0297	28.3	4.4	85.6	6.7280 [143.0]
None	2.0287	28.3	4.4	88.3	6.3865 [135.8]
Solvent: V1074					
None	2.0287	28.1	4.0	84.4	5.3686 [113.3]
None	3.0009	34.7	2.9	87.5	6.3743 [112.2]
Solvent: 1-Methylnaphthalene					
None	2.0286	28.3	2.3	71.4	4.9975 [106.3]
None	2.0277	28.3	1.8	71.5	4.9101 [104.6]

^a Reaction Conditions: 410°C; 30 min; no catalyst; 1250 psig H₂ introduced at ambient temperature.

Table 19 Pyrene Product Distributions from Thermal Reactions of Wyodak Coal in Three Solvents

Catalyst (ppm)	% H (% Coal)	Product Distribution (mol %)			
		PYR ^a	DHP	THP	HHP
Solvent: 9,10-Dihydroanthracene					
None	2.4 (28.3)	95.6	2.7	0.7	1.0
None	2.6 (28.3)	95.6	2.3	0.7	1.4
Solvent: V1074					
None	1.9 (28.1)	96.0	2.9	0.3	0.8
None	1.4 (34.7)	97.1	2.2	0.2	0.5
Solvent: 1-Methylnaphthalene					
None	1.3 (28.3)	97.7	1.5	0	0.8
None	1.1 (28.3)	98.2	1.0	0	0.8

^a PYR = pyrene; DHP = dihydropyrene; THP = tetrahydropyrene; HHP = hexahydropyrene

Table 20. Coal and Pyrene Conversions for Thermal Reactions of North Dakota Coal with Three Different Solvents^a

Catalyst (ppm)	Added Coal		Pyrene Conversion (mole %)	Coal Conversion (%)	Total Recovery (g)[%R]
	(g)	wt %			
Solvent: 9,10 Dihydroanthracene					
None	2.1206	27.1	5.6	80.3	5.2459(109.4)
None	2.1221	27.1	6.3	73.1	5.6131(117.1)
Solvent: V1074					
None	2.1212	27.0	6.3	69.7	5.1910(108.0)
None	2.1205	26.9	5.9	78.5	5.3826(111.6)
Solvent: 1-Methylnaphthalene					
None	2.1169	27.0	4.1	70.7	4.8791(101.8)
None	2.1213	27.1	5.3	76.3	5.2497(109.5)

^a Reaction Conditions: 410 °C, 30 min, no catalyst, 1250 psig H₂ introduced at ambient temperature.

Table 21. Pyrene Product Distributions from Thermal Reactions of North Dakota Coal With Three Solvents

Catalyst (ppm)	% H (% Coal)	Product Distribution (mole %)			
		PYR ^a	DHP	THP	HHP
Solvent: 9,10 Dihydroanthracene					
None	3.1(27.1)	94.4	3.3	1.1	1.2
None	3.8(27.1)	93.7	3.1	1.5	1.7
Solvent: V1074					
None	2.8(27.0)	93.7	5.2	0.2	0.9
None	2.9(26.9)	94.1	4.4	0.3	1.2
Solvent: 1-Methylnaphthalene					
None	2.0(27.0)	95.9	3.1	0	1.0
None	2.4(27.1)	94.7	4.4	0	0.9

^a PYR = pyrene; DHP = dihydroxyrene; THP = tetrahydroxyrene; HHP = hexahydroxyrene

TABLES OF SUBTASK 2.5

**Table 23 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%

	<u>As Measured</u>	<u>Normalized</u>	<u>Normalized Solids-Free Feed⁽¹⁾</u>
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.

Table 24 Inspection of Run 3042 Delayed Coking Products

Distillate Oil

API Gravity @ 60°F	10.4	
Carbon, wt%	87.95	
Hydrogen, wt%	9.99	
Sulfur, wt%	0.05	
Nitrogen, wt%	0.79	
Metals, ppm (w)		
Iron	22	
Nickel	< 1	
Vanadium	< 1	
Copper	1	
Sodium	3	
ASTM Distillation, °F	<u>D86</u>	<u>D1160</u>
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

CokeProximate Analysis, wt%

Fixed Carbon	59.04
Volatile Matter	15.21
Ash	25.33
Moisture	<u>0.42</u>
Total	100.0

Ultimate Analysis, wt%

Carbon	67.49
Hydrogen	3.04
Oxygen	(-0.28)
Nitrogen	1.21
Sulfur	2.79
Ash	25.33
Moisture	<u>0.42</u>
Total	100.0

**Table 25 Inspection of Products from Solvent Deasphalting
(Asphalt Considered a Candidate Feed to Delayed Coking)**

Run No.	<u>3039/3040</u> <u>Blend</u>	<u>3034</u>	<u>3035</u>
<u>Deasphalted Oil (DAO)</u>			
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
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 25 (Cont) Inspection of Products from Solvent Deasphalting
(Asphalt considered a Candidate Feed to Delayed Coking)**

Run No.	3039/3040 ⁽¹⁾ <u>Blend</u>	<u>3034</u>	<u>3035</u>
<u>Asphalt</u>			
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 Insolubles, 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

NA - Not applicable. Sample decomposed before melting.
(1) - Selected Feedstock for Delayed Coking.

**Table 26 Inspection of Products from Solvent Deasphalting
Deasphalted Oil (DAO) from Deep Solvent Deasphalting**

Run No.	3017
DAO Yield, wt%	80.6
API Gravity @ 60°F	4.4
Conradson Carbon Residue, wt%	24.07
Heptane Insolubles, wt%	24.42
Ash, wt%	2.27
Carbon, wt%	86.87
Hydrogen, wt%	8.56
Sulfur, wt%	0.25
Nitrogen, wt%	0.96
ASTM Distillation (D-1160), °F	
IBP	574
2 vol%	717
5	753
10	783
20	819
30	855
40	914
50	928

Figure 1a
U.S. DEPARTMENT OF ENERGY

MILESTONE SCHEDULE PLAN STATUS REPORT

FORM APPROVED
OMB NO. 1901-1400

DOE F 13373
111 (M)

1. TITLE Advanced Liquefaction Using Coal Swelling and Catalyst Dispersion Techniques		2. REPORTING PERIOD		3. IDENTIFICATION NUMBER DE-AC22-91PC91051																									
4. PARTICIPANT NAME AND ADDRESS Amoco Oil Company P. O. Box 3011 Naperville, IL 60566		5. START DATE October 1991 *		6. COMPLETION DATE May 31, 1994																									
7. ELEMENT CODE	8. IDENTIFYING ELEMENT	9. DURATION												FY	FY	10. PERCENT COMPLETE													
		FY 1992						FY 1993								Plan	Actual												
		O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S				
Task 1.1	Lab Support	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=	=				
Task 1.2	Lab Supp. FWD																												
Task 2.1	Pretreat																												
Task 2.2	Cat and Swelling																												
Task 2.3	Reactivity																												
Task 2.4	Bench-Scale																												
Task 2.5	Solids Separation																												
Task 2.6	Feedstock																												
Task 3.1	Tech Assessment																												
		NEPA APPROVAL ↑																											
		* The start of laboratory research was delayed to June 1992; a contract extension has been requested for project completion on May 31, 1994.																											
11. SIGNATURE OF PARTICIPANT'S PROJECT MANAGER AND DATE																													

Figure 1b
U.S. DEPARTMENT OF ENERGY

MILESTONE SCHEDULE PLAN STATUS REPORT

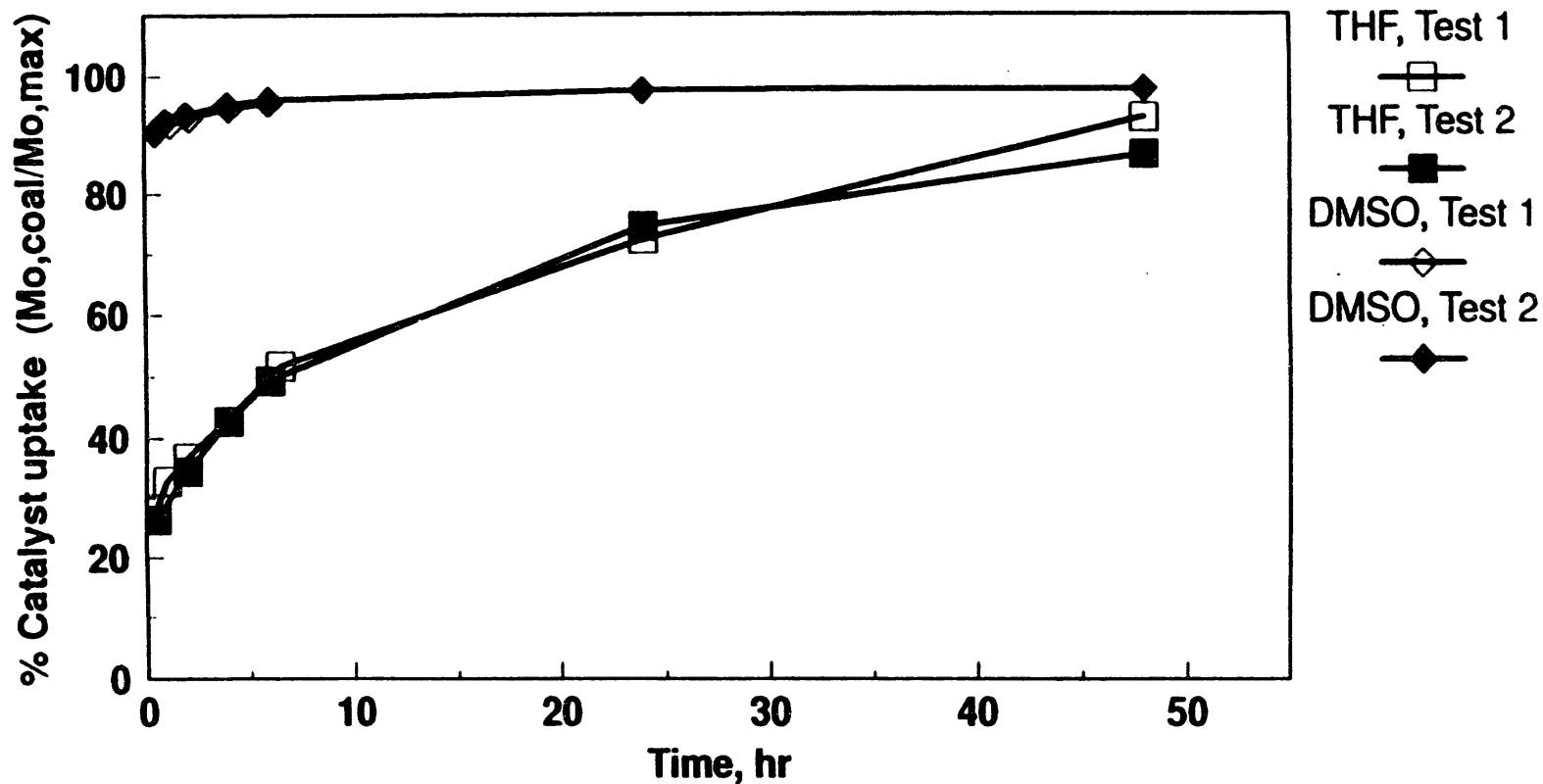
FORM APPROVED
OMB NO. 1901-1400

FORM 7 (3/373)
(11 M)

1. TITLE Advanced Liquefaction Using Coal Swelling and Catalyst Dispersion Techniques		2. REPORTING PERIOD Modified to reflect anticipated extension to May 31, 1994		3. IDENTIFICATION NUMBER DE-AC22-91PC91051															
4. PARTICIPANT NAME AND ADDRESS Amoco Oil Company P. O. Box 3011 Naperville, IL 60566		6. START DATE October 1991 ^A		8. COMPLETION DATE May 31, 1994															
7. ELEMENT CODE	8. DEFINITIVE ELEMENT	9. DURATION												FY	FY	10. PERCENT COMPLETE			
		FY 1994														Plan	Actual		
		O	N	D	J	F	M	A	M										
Task 1.1	Lab Support																		
Task 1.2	Lab Supp. FWDC																		
Task 2.1	Pretreat																		
Task 2.2	Cat and Swelling																		
Task 2.3	Reactivity																		
Task 2.4	Bench-Scale																		
Task 2.5	Solids Separation																		
Task 2.6	Feedstock																		
Task 3.1	Tech Assessment																		
		NEPA APPROVAL																	
		^A The start of laboratory research was delayed to June 1992; a contract extension has been requested for project completion on May 31, 1994.																	
11. SIGNATURE OF PARTICIPANT'S PROJECT MANAGER AND DATE																			

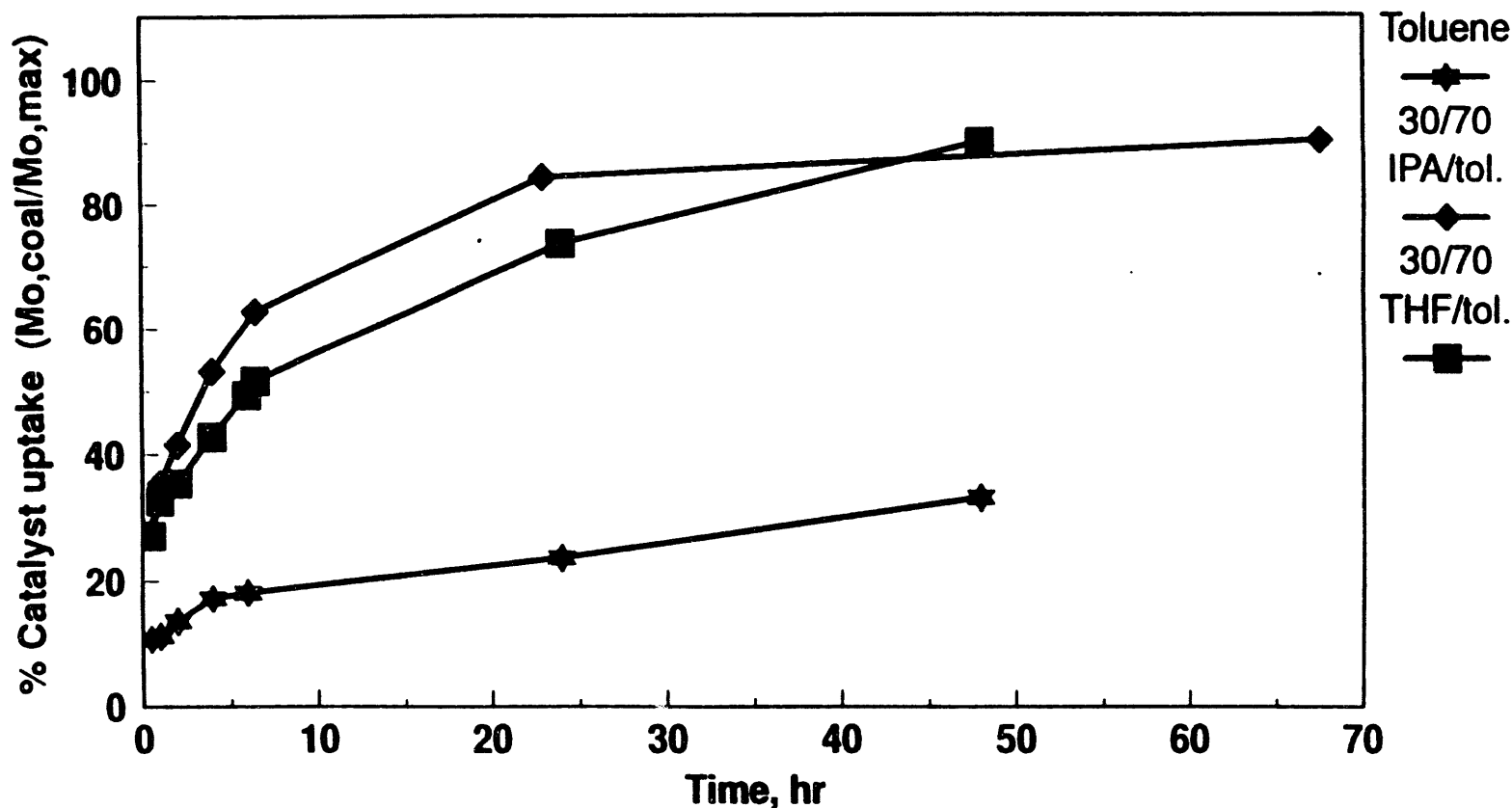
FIGURES SUBTASK 2.2

Figure 1 -- Reproducibility of experiments



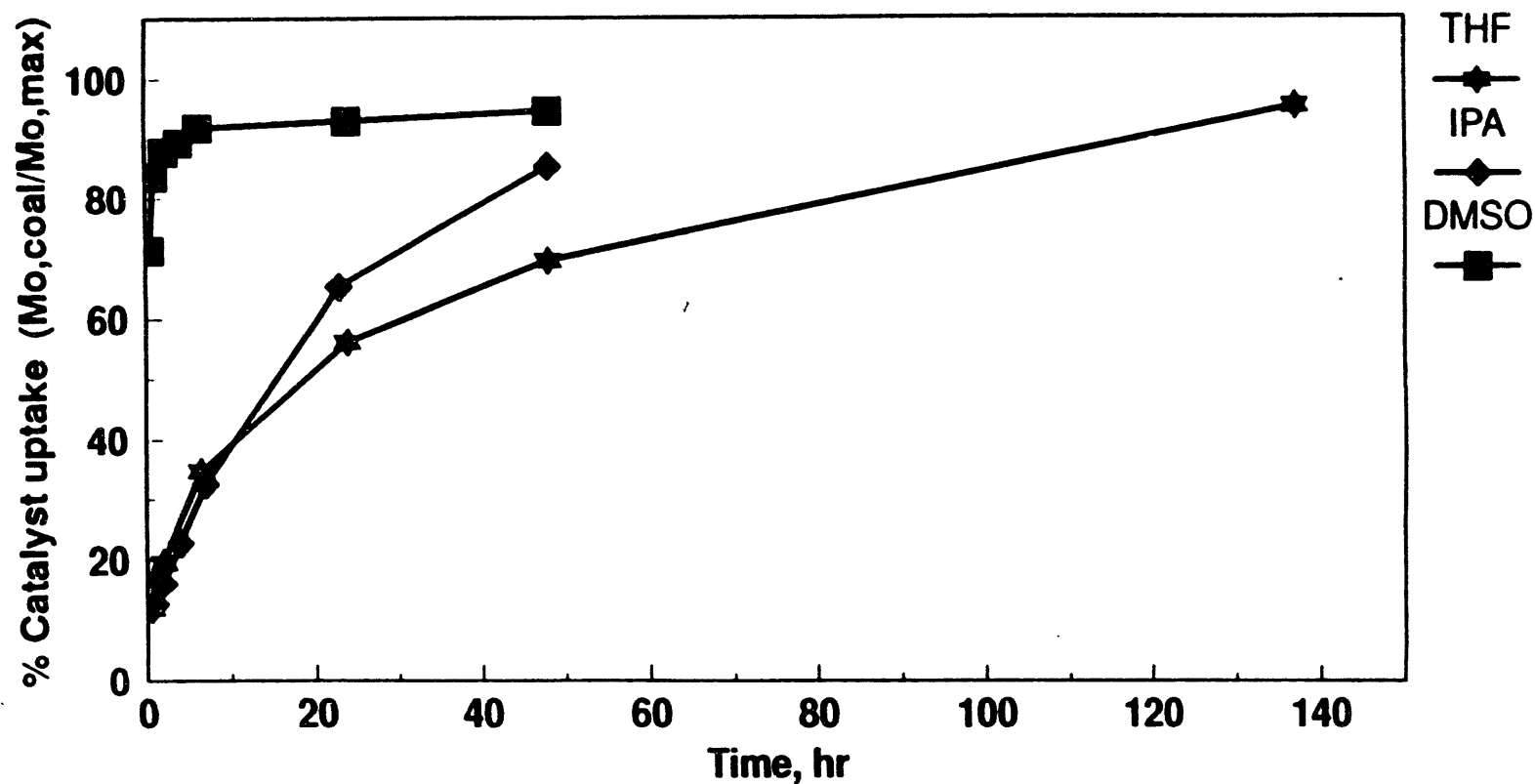
30/70 solvent/toluene blends, 100 ppm Mo initial
-70 mesh coal with THF, 70 F
8 x 60 mesh coal with DMSO, 150 F

**Figure 2a -- Effect of Solvent on Molyvan-L Uptake
(IPA, THF, and Toluene at Ambient)**



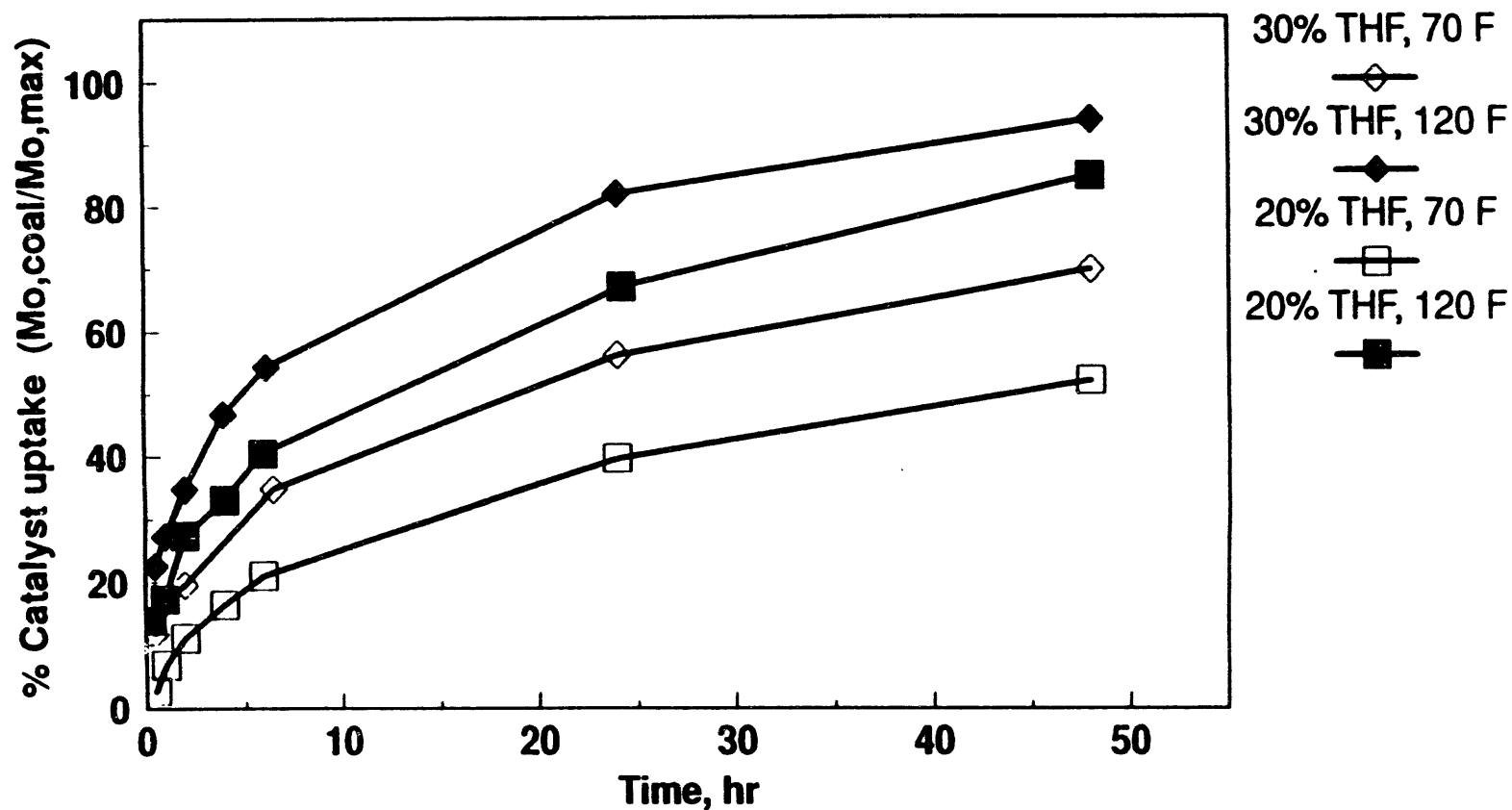
-70 mesh SO₂-treated Black Thunder
~ 100 ppm Mo initial, 70 F

**Figure 2b -- Effect of Solvent on Molyvan-L Uptake
(IPA, THF, and DMSO at Ambient)**



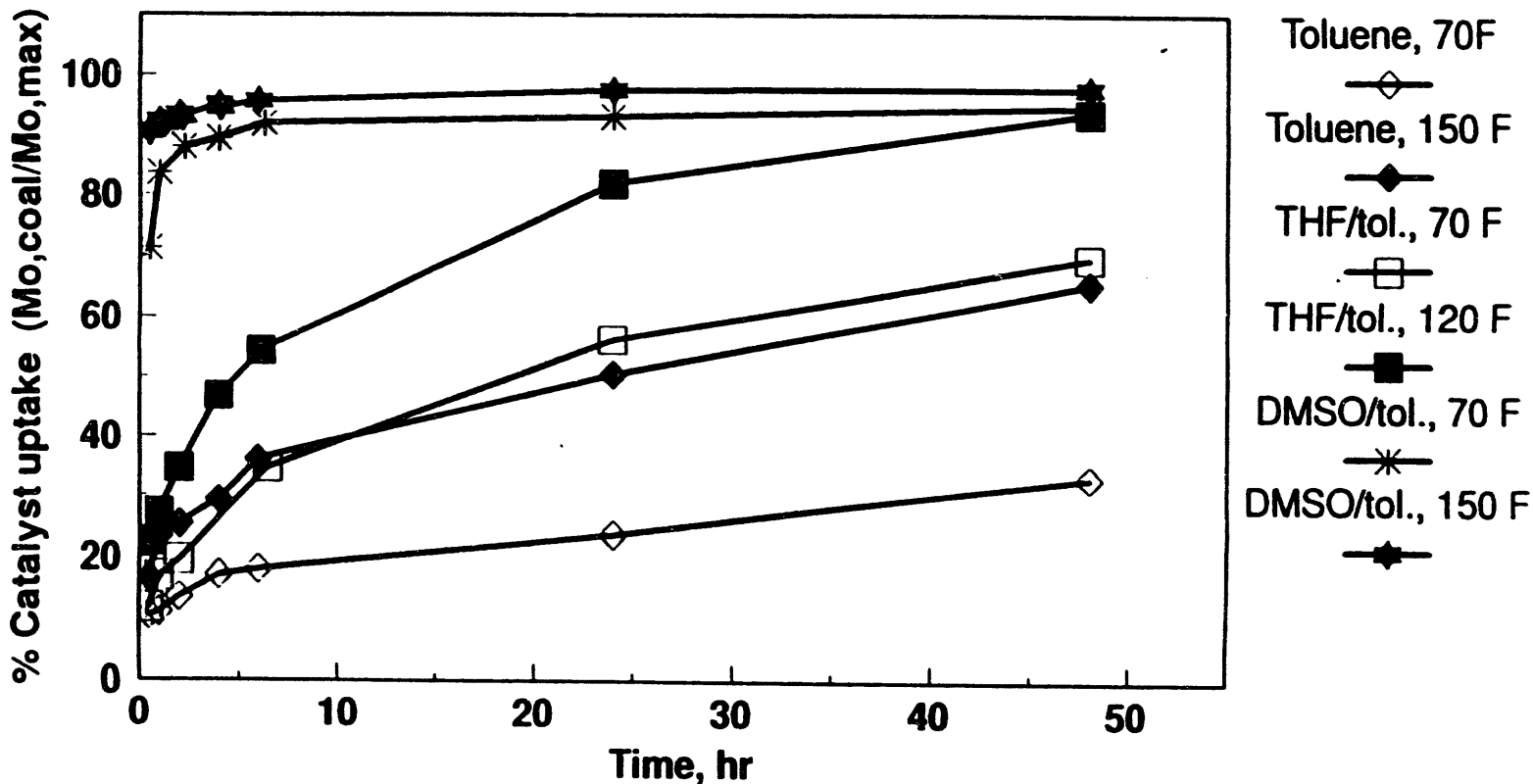
8 x 60 mesh SO₂-treated Black Thunder
~ 100 ppm Mo initial, 70 F
30/70 blends of swelling solvent with toluene

Figure 2c -- Effect of Swelling Solvent Concentration on Molyvan-L Uptake



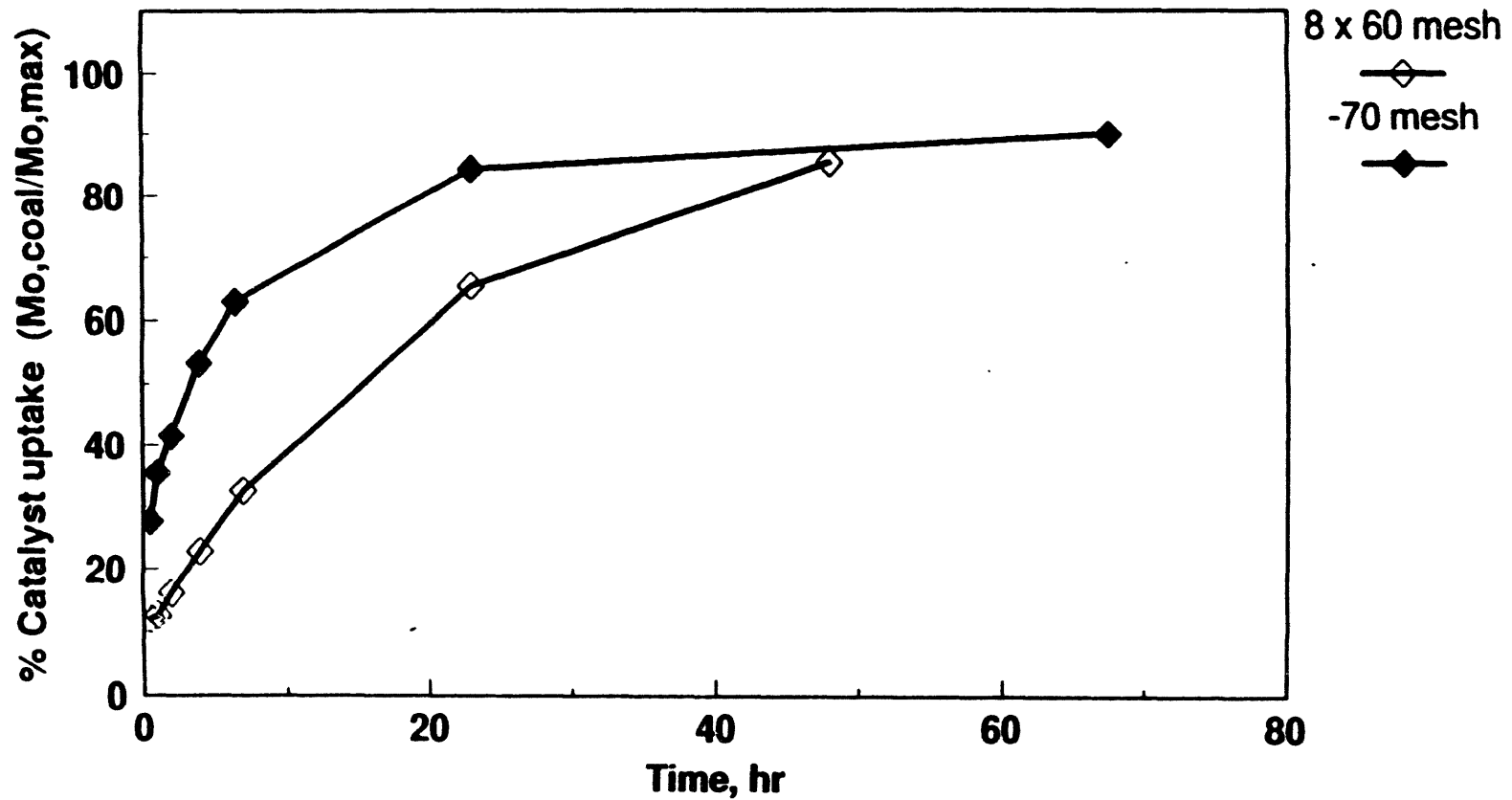
8 x 60 mesh SO₂-treated Black Thunder
~ 100 ppm Mo initial, THF/toluene blends

**Figure 3 -- Effect of Temperature on Molyvan-L Uptake
(Toluene, THF, and DMSO Solvents)**



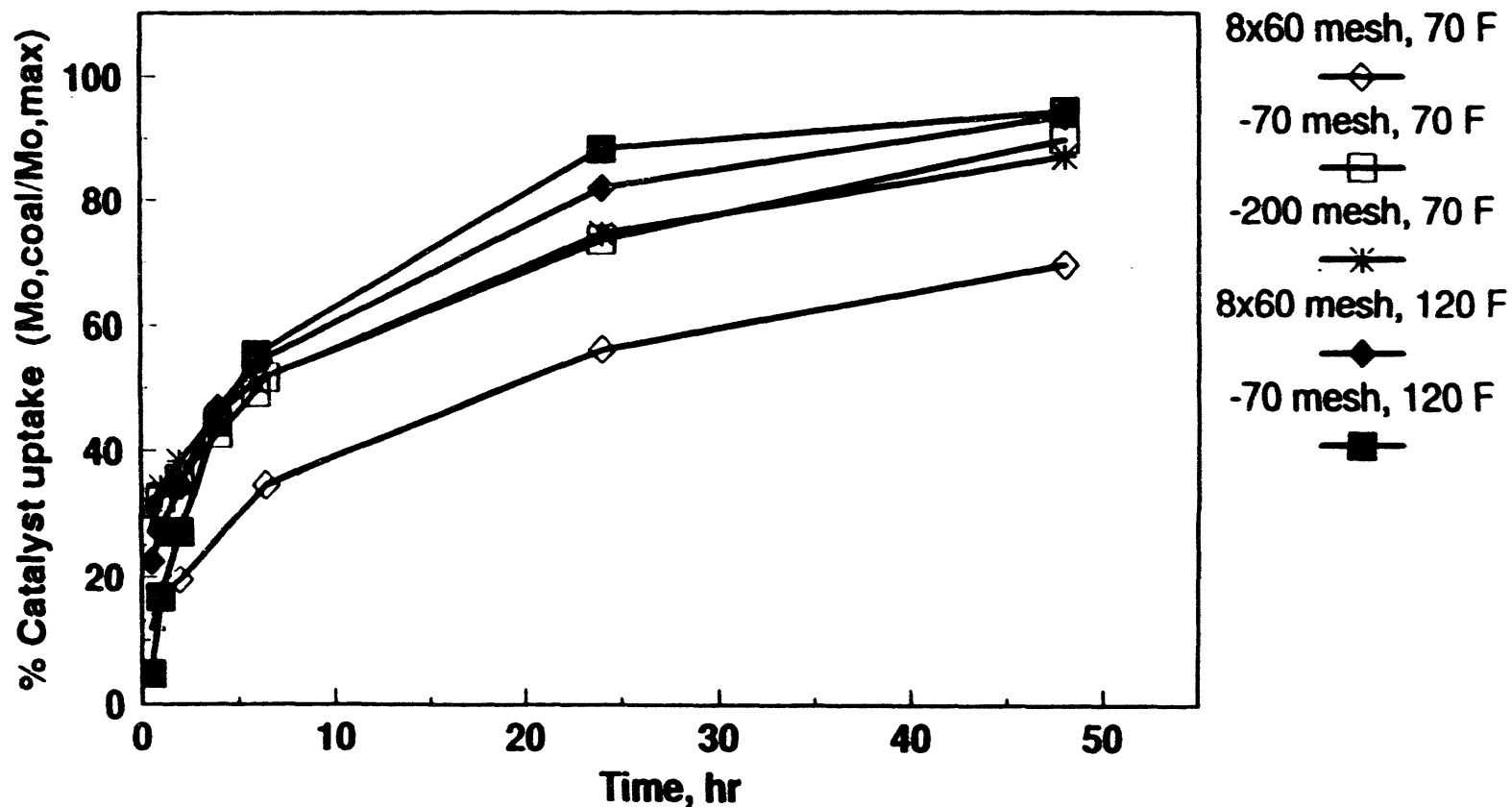
-70 mesh (toluene) or 8 x 60 mesh (THF, DMSO)
 ~ 100 ppm Mo initial
 30/70 solvent/toluene blends

**Figure 4a -- Effect of Coal Size on Molyvan-L Uptake
(IPA/Toluene at Ambient Temperature)**



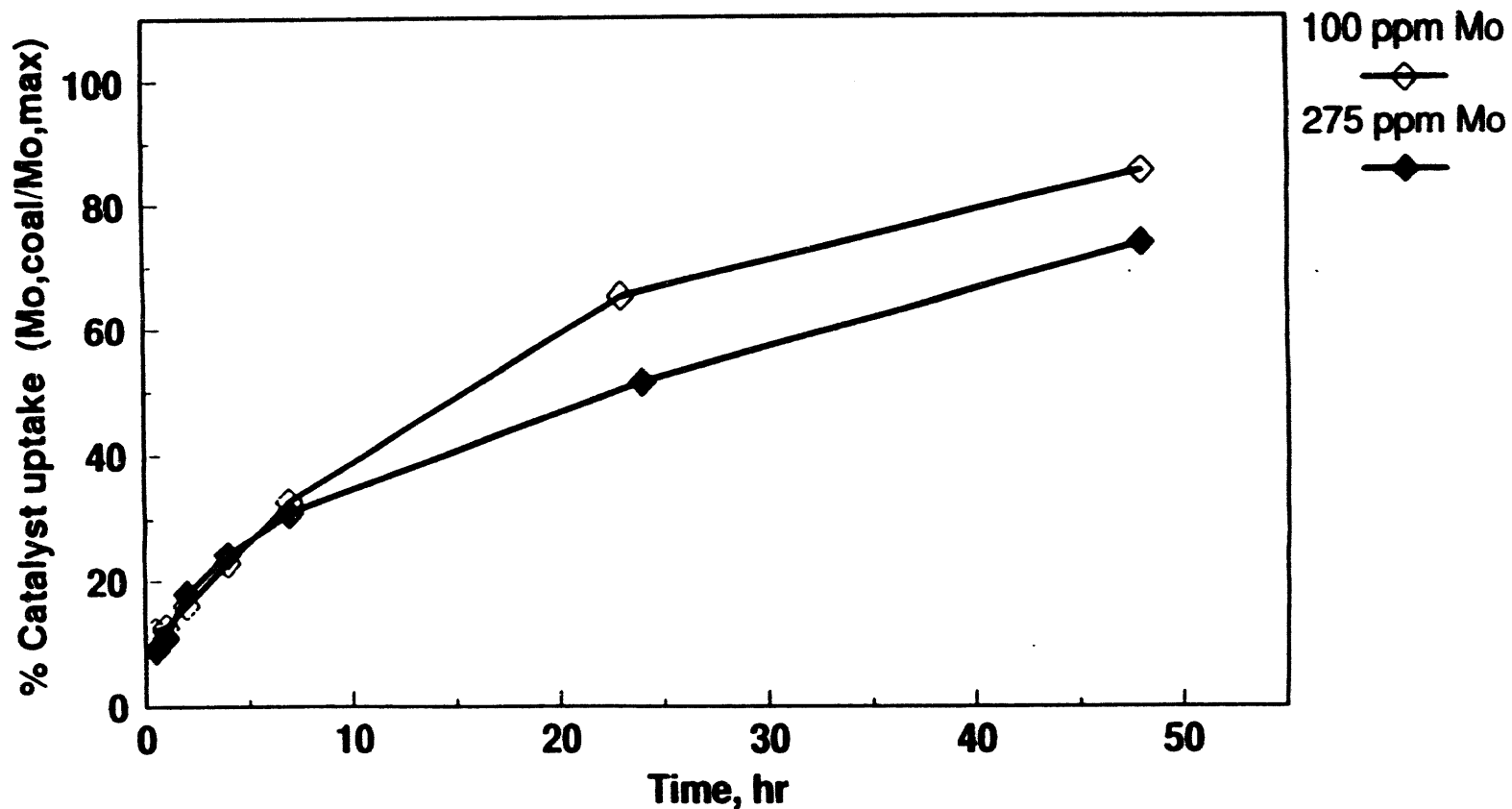
~ 100 ppm Mo initial, SO₂-treated Black Thunder
30/70 IPA/toluene blend

**Figure 4b -- Effect of Coal Size on Molyvan-L Uptake
(THF/Toluene at Ambient and Elevated Temperatures)**



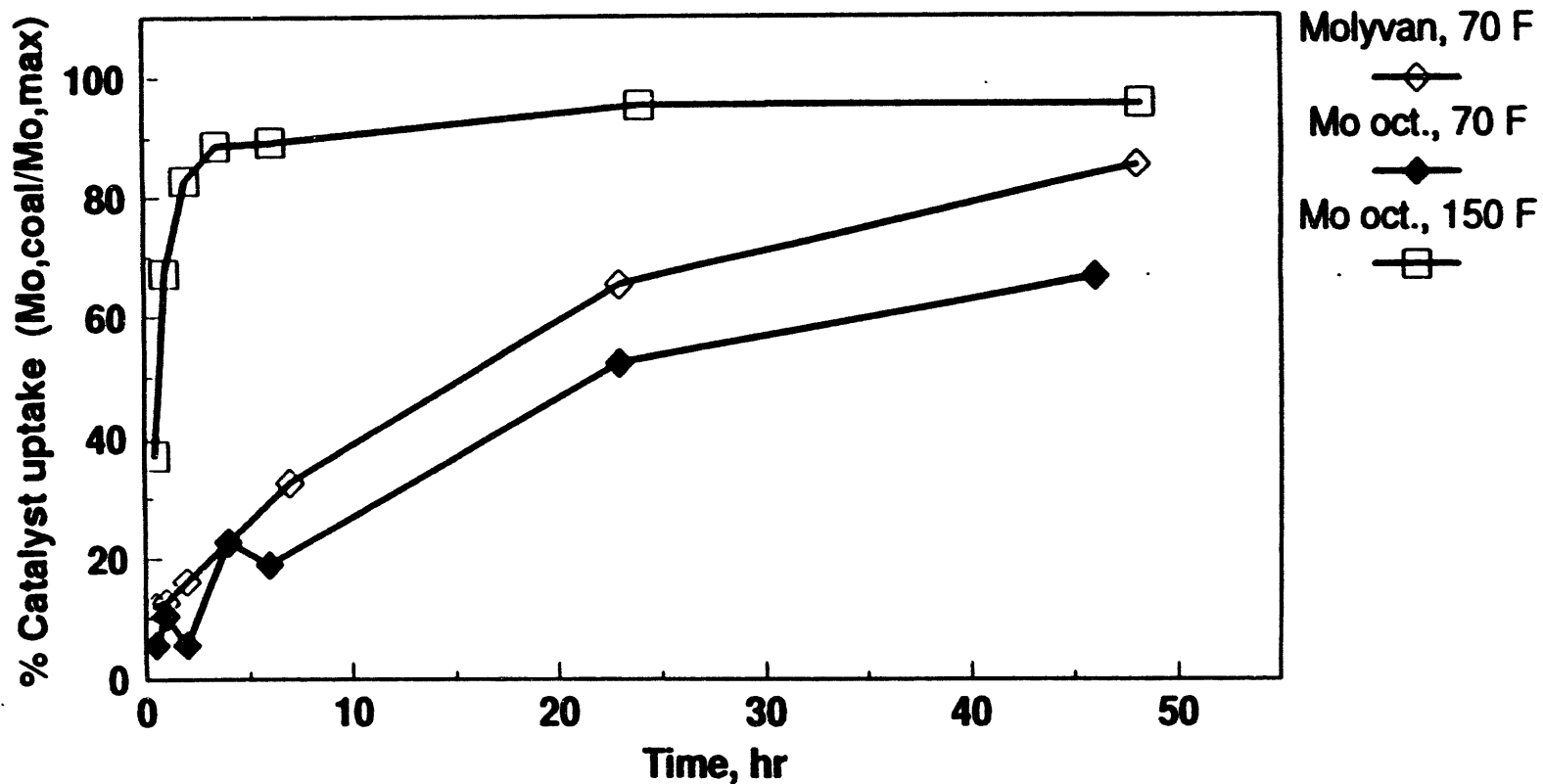
SO₂-treated Black Thunder, 30/70 THF/toluene
~ 100 ppm Mo initial

**Figure 5 -- Effect of Initial Catalyst Concentration on Molyvan-L Uptake
(IPA/Toluene at Ambient Temperature)**



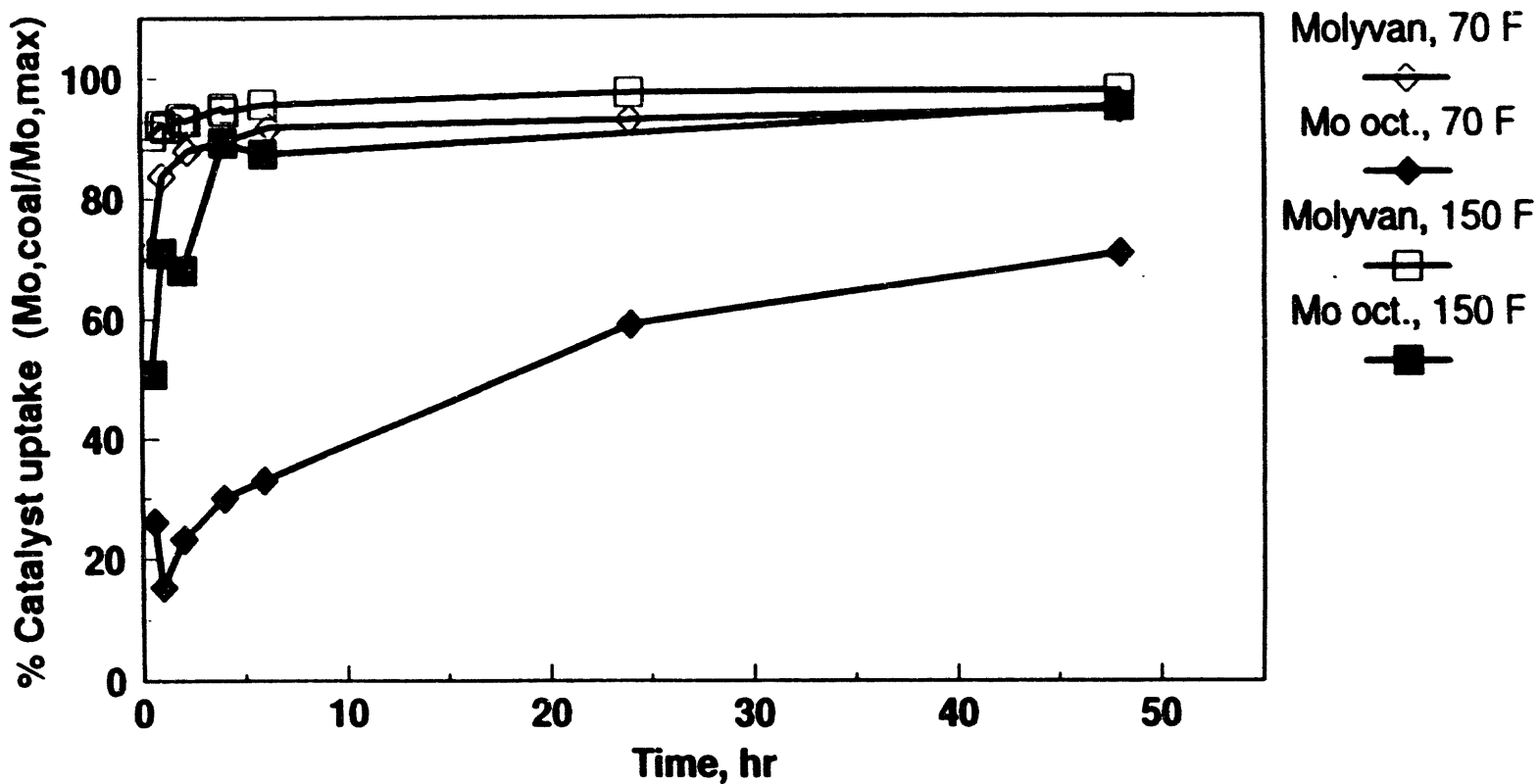
8x60 mesh SO₂-treated Black Thunder
30/70 IPA/toluene blend

**Figure 6a -- Effect of Catalyst Precursor on Uptake
(IPA/Toluene)**



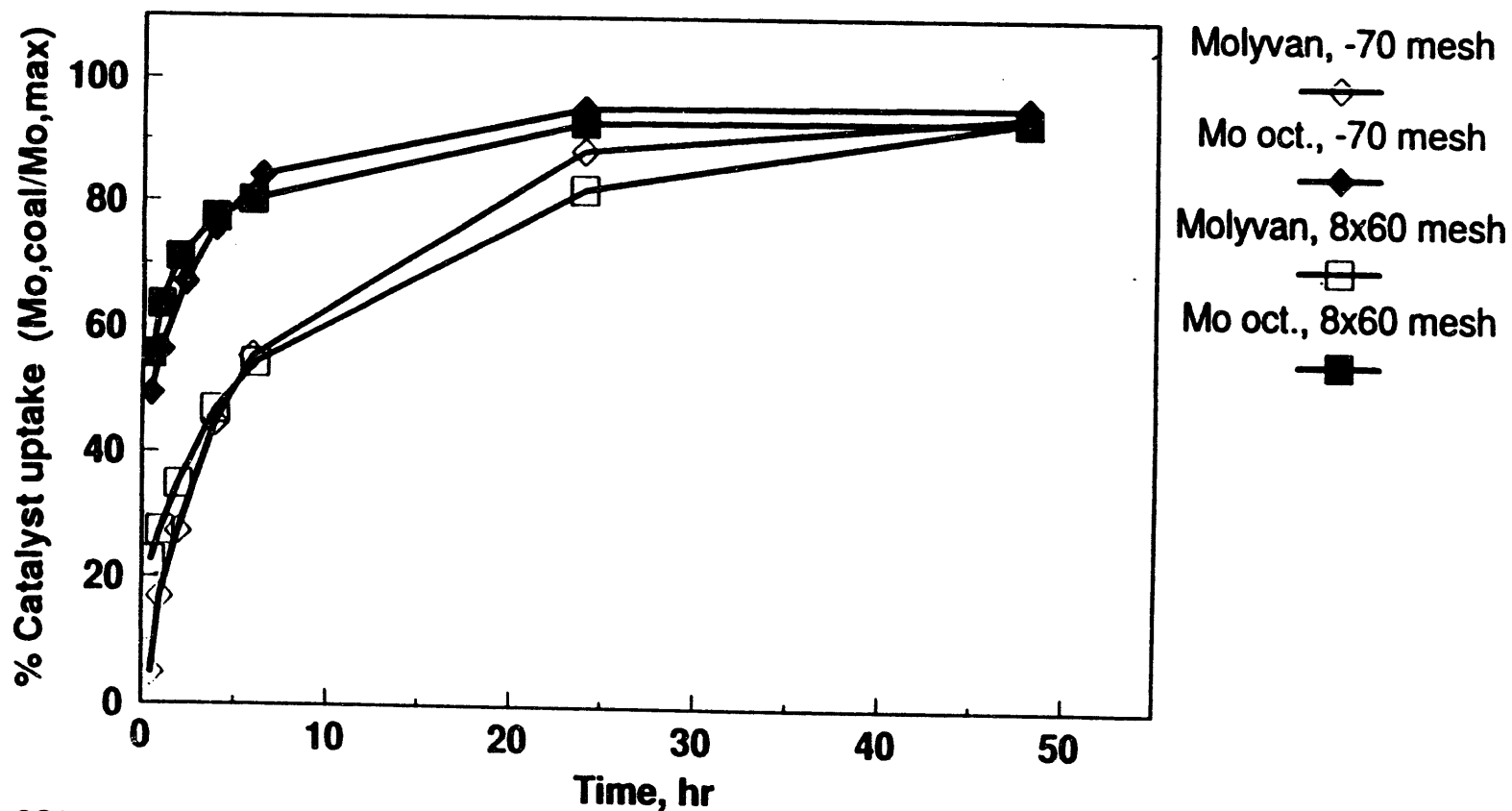
8x60 mesh SO₂-treated Black Thunder
 30/70 IPA/toluene blend, 100 ppm Mo initial
 Mo oct. uptake at 70 F calculated as $1 - \frac{\text{Mo}_i}{\text{Mo}_o}$

**Figure 6b -- 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 6c -- 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

APPENDIX A

Annual Report

June, 1993

"Ion Exchange and Adsorption on Low Rank Coals for Liquefaction"

by Karl S. Vorres,
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Argonne, IL 60439

1. OBJECTIVES:

The objectives of this program have been changed to study the catalysis of liquefaction of low rank coals. Ion exchange and adsorption techniques are being used or modified to incorporate catalytically active metals in relatively small (100-2000 ppm) quantities into coal samples. Relative oil yields will be determined by PETC, Amoco, Auburn University and/or other collaborators to establish the effectiveness of the catalyst incorporation techniques. It is hoped that these techniques will provide highly active forms of the catalyst in concentrations which are low enough that recovery of the metals may not be required.

2. INTRODUCTION:

The focus of this program is to develop a more economical means of converting the low rank coals to synthetic transportation fuels. Earlier efforts have examined the removal of moisture to limit energy losses and improve conversion. The current program is oriented to developing a catalytic approach to low rank coal conversion. This approach uses a two step preparation of the coal to (1) remove material which limits oil conversion, and (2) add catalytically active material which enhances the conversion of the coal matter to the oil fraction in the processing.

2.1. Removal of Exchangeable Cations

The initial step involves the removal of reactive or exchangeable cations. The western low rank coals of the US, such as the Wyodak subbituminous and Beulah-Zap lignite, contain considerable quantities of chemically combined oxygen in the form of carboxylate and phenolic groups. These groups, in turn, can form salts with the alkali or alkaline earth cations that may pass through the coal during the coalification process. As a result the content of calcium, sodium and potassium etc is much higher than eastern US coals. For some purposes the presence of these elements is beneficial, as for combustion or gasification, in that the alkali or alkaline materials accelerate the processes. However, for liquefaction, the calcium reduces the rate of conversion or the oil yield. The somewhat higher rank coals (high volatile bituminous) have a significantly lower carboxylate group content and less of the alkali and alkaline earths. The ion exchange technique's usefulness will depend on the capacity to exchange enough of the desired catalyst.

The deleterious effects of calcium and any other exchangeable cations in the coal can be overcome by removal of these species. A number of studies have indicated that low rank coals can be treated with acids to exchange the cation species with hydrogen ions (1-3). The cations can then be washed away from the coal to minimize their effect.

The initial acid treatment of the coal needs to be understood to ensure that the alkaline materials are adequately removed, and that sufficient exchange sites are available. The details of the ion exchange behavior of the coals have not yet been studied. A part of this study includes the monitoring of the release of the alkali and alkaline species as a function of the volume of acid added to establish the completeness of removal of the exchangeable cations.

The removal of the cations serves two purposes. Since calcium is believed to limit the oil yields on liquefaction, the removal should improve liquefaction performance. Also, the availability of exchange sites will be enhanced by removal of the cations which already occupy these sites.

Cations with a single charge can be attached to a single carboxylate group. Calcium may be present in either or both of two forms. In one case the doubly charged cation can be bound to one hydroxyl and one carboxylate group. This represents a more easily removed form. The second case involves simultaneous bonding to two nearby carboxylate groups. Removal of this calcium involves release from one carboxylate, and later from the second. This process is more difficult and would appear more slowly.

Several reasons have been given for the detrimental effects of calcium. Baldwin et al (4) indicate that retrogressive reactions to produce tetrahydrofuran (THF) insoluble materials are catalyzed by calcium. Mochida and coworkers (5) suggest that the effect of cations is to bridge between different groups in the coal structure which limits the access of solvent to the internal structure of the coal. Joseph and Forrai (6) indicate that the presence of the alkali and alkaline earth cations inhibits hydrogen transfer in the liquefaction reactions.

The economical and effective removal of the alkaline species has been the subject of other studies. The low rank coals have been considered for application as ion-exchange materials. In preparing the coals for removal of cations, the coals are first put into an acid form. An acid passed over the coals will liberate most of the alkaline ions, placing the coal in an acid form, similar to materials used for water softening treatment.

The choice of acid for commercial application is complicated by the effect of the anion on the materials of plant construction, the solubility of by-products of the coal treatment, and oxidation of the coal sample. Hydrochloric acid may leave a chloride residue in the coal which can lead to stress corrosion cracking of the stainless steel components in the processing equipment. Sulfuric acid may form insoluble calcium sulfate which would stay

in the feedstock and may lead to reduced oil conversion or deposition problems in the reactors. Nitric acid avoids these problems, but may lead to oxidation of the coal, which would reduce yields. The initial choice was to use the nitric acid.

Each coal exhibits a distinctive pH after being slurried with water and allowed to stand for a period of time. This pH partly reflects the carboxylate group content. The effect of the carboxylate groups led to evaluation of the slurry pH, and is used by the State Electricity Commission of Victoria as a standard means of comparison of brown coals (7). Since the inorganic and carboxylate components may affect the ion exchange results, a series of slurry pH measurements were made on the 8 Argonne Premium Coal Samples to provide a basis for comparison, and examine trends. These are discussed further in a later section.

2.2. Addition of Catalytically Active Metal Ions

Once the alkaline species have been removed from the coal the first step of preparation has been completed. The next step is to enhance the reactivity by adding a catalytically active metal to speed the conversion to oil products, and limit retrogressive reactions that lead to unconverted material. Metals such as Fe, Ni, Co and Mo are known to be useful in conversion to liquids. A number of techniques have been examined by other workers to place these metals onto the coal in an active form. The first three metals can be added to the coal by an ion exchange technique. This approach has advantages of using minimal quantities of material, such that the necessity of recovery of the metals for economic reasons will be minimized. An absorption technique for application of Mo has been developed with similar advantages.

The catalyst addition is not a very rapid process, requiring hours to achieve a useful loading. This is true of both the ion exchange and absorption steps. These steps are sensitive to the surface charges on the particle, which are in turn affected by the pH. For these reasons, as well as those mentioned earlier, an understanding of the slurry pH and change of pH with addition of acid is quite important.

A number of other efforts are being made to catalyze the coal liquefaction process. At the 1992 Liquefaction Contractors Review Conference (8), Swanson (8A) described the performance of commercial supported catalysts (Amocat) at the Wilsonville pilot plant. The effectiveness varies for different coals. Calcium deposition was observed on the catalyst for runs with the Black Thunder coal (similar to the Wyodak sample used here). It should be noted that successful operation with Illinois #6 was achieved in spite of high calcium content as calcite. The crucial difference in calcium content is likely to be the organic bonding to carboxylate in the subbituminous coal. Calcite does not seem to be as likely to form the undesirable deposits on the catalysts. She reported that a dispersed catalyst system of sulfated iron oxide plus molybdenum and a sulfiding agent is most effective for processing Black Thunder coal. It should also be noted that the

ion exchange technique could be combined with absorption techniques to provide mixed catalysts for improved performance from these ANL studies.

Vimalchand et al (8B) reported on the use of dispersed molybdenum catalyst tests at Wilsonville with Black Thunder coal. The Molyvan catalyst precursors permit adding molybdenum in an unsupported form in easily varied concentrations. A sulfiding agent (dimethyl disulfide, DMDS) was added with the Molyvan. They used 100 ppm of Mo. They also used 1-2% iron oxide with the DMDS sulfiding agent. They observed improved coal and resid conversion compared to supported catalysts, and eliminated deposit formation in the process lines. Hybrid systems (supported and unsupported catalysts) were better than either type alone. In combined Mo and Fe catalyst tests, the 1% Fe loadings gave better performance than 2%.

Cugini and coworkers (8C) reported on the liquefaction of Black Thunder coal with a highly dispersed iron catalyst. They used an incipient wetness impregnation technique followed by precipitation of hydrated iron oxide and in-situ activation (sulfiding) in a preliquefaction stage. The sulfiding was done by adding H₂S to the hydrogen stream for liquefaction. Iron loadings were typically about 2500 ppm. Molybdenum loadings of 1500 ppm were also used with sulfiding agents. The results were better with dispersed iron than physically added iron. Comparison of heptane and tetrahydrofuran (THF) solubles (measures of oil yield and total conversion) indicated 73% and 33% THF and heptane solubles with impregnated Fe, compared to 86 and 52% for the 1500 ppm Mo additions. They observed an optimum Fe catalyst performance with 1.5 wt% sulfur for the 2500 ppm Fe loading.

Lott and coworkers (8D) at Sandia National Laboratory described work with hydrous titanium oxide catalysts. Their approach uses titanium isopropoxide to form an intermediate which is used to coat coal particles. This coating then acts as an ion exchange membrane which can accept molybdenum. Cations such as nickel are added by incipient wetness impregnation. Multiple coatings can be used to increase loadings of Mo from 0.67% for one coat to 1.32% for 3 coats. Combined Ni and Mo loadings were more effective than Mo alone.

Eyring and coworkers (8E) at the University of Utah studied incipient wetness impregnation and ultrasound dispersion with 3 Argonne Premium Coal Samples (Wyodak, Pittsburgh and Blind Canyon). The two techniques of catalyst addition did not give very different yields of THF solubles.

Warzinski from PETC (8F) reported the use of supercritical fluid impregnation techniques. Comparisons of incipient wetness and supercritical fluid techniques showed no significant improvement of THF solubles for an Illinois #6 or Blind Canyon coal.

Stohl from Sandia National Laboratory (8G) described the development of a protocol for testing the use of ultra-fine non-supported catalysts.

The coal samples used in the effort described in this report include the raw materials from the Argonne Premium Coal Sample program, chosen because they represent a near pristine material, are well characterized, available in uniform lots and the same as or very similar to coals used by other investigators. The samples for liquefaction evaluation also include the prepared material, before and after acid treatment, and the samples with catalyst added.

3. EXPERIMENTAL:

The coal samples studied to date were the Argonne Premium Wyodak subbituminous and Illinois #6 high volatile bituminous (9). This Wyodak coal contains (dry basis) 8.7% mineral matter from low temperature ashing. The 8.7% is made up of: 2.0% quartz, 0.1% pyrite, 0.4% calcite and 6.2 % clays which may be kaolinite (10). The Illinois #6 coal contains 18.1% total mineral matter. The 18.1% is made up of 3.4% quartz, 5.5% pyrite, 1.9% calcite, and 7.3% clays including illite, kaolinite and expandable clays. A trace of marcasite is also present (10).

The -20 mesh samples were dry screened to -20+200 mesh. The later samples were shaken up to 15 minutes with a Gilson shaker. Weighed amounts (about 30 grams) of the screened samples were slurried with distilled or deionized water. Fines (still -200 mesh) were decanted away from the slurry using about 200-600 ml of water. The slurry was washed into a special 50 ml burette. The burette had been fitted with a coarse fritted glass disk at the 50 ml mark to retain the coal but allow solutions to pass. Fine coal particles (-200 mesh) had to be removed to avoid plugging of the frit. A peristaltic pump provided a uniform flow of standardized 0.100 N HNO_3 or distilled water to the sample. Acid or water flow rates were typically about 1-3 ml/minute and were set according to the ability of the solution to pass through the coal bed. Following the treatment with the acid, the samples were washed with distilled water fed by the peristaltic pump, and the record of pH and ion concentration was obtained.

The burette tip was fitted with tubing to connect a flow-through pH electrode from Cole-Parmer, or from Microelectrodes, Inc (Londonderry, NH). For the more recent experiments the pH electrodes were augmented with ion-selective electrodes for Ca^{+2} , Na^{+} and K^{+} . The electrodes were used with an Orion EA940 pH meter and model 607 switchbox. The pH meter in turn was connected to an IBM model AT computer for data acquisition. A schematic diagram of the equipment is given in Figure 1. A program was written which allowed data points to be acquired at specific intervals in the range of 10-18 seconds. The data files were then manipulated with Lotus 123 macros to permit plots to be drawn of the data. Workers contemplating building a similar system should be aware that the documentation of the interfacing is exceedingly brief and the quality of technical service for the instrumentation may cause considerable delays in setting up such a system.

The pH electrodes were calibrated with Cole Parmer standard buffers of pH 4.00 and 7.00. The ion selective electrodes were calibrated with standard solutions made up of a series of analyzed reagents salts diluted to give 0.10, 0.010 and 0.0010 M solutions for each of the cations. Calibrations were checked at the end of the runs. The response of the ion selective electrodes is dependent on the ionic strength of the solutions, which changes during the course of an experiment. The values given here are good for comparison purposes, but are not intended to serve as reference analytical numbers.

This arrangement does give a different approach to an endpoint than a simple titration since the exchanged cations are removed from the system.

Slurry pH measurements were made using a technique similar to that described by Brockway and Higgins (7). Five gram ampoules of -100 mesh coal were mixed with water using twice the weight of coal, stirred well and allowed to stand for 30 minutes before taking the pH with a pH electrode immersed in the slurry. Later measurements involved the 30 gram samples of Illinois coal mixed with twice the sample weight of water, magnetically stirred and with the pH recorded during the stirring. pH values were noted after 30 minutes, consistent with the cited method (7).

4. RESULTS AND DISCUSSION:

4.1. Acid Treatment Requirements

The acid treatment of the coal samples serves two purposes. One is to remove the unwanted cations such as calcium which interfere with the subsequent liquefaction of the coal. The other is to change enough exchangeable sites to the acid form so that it will be possible to adequately load the coal with the desired catalyst. Both goals may be achieved at the same time as in the removal of calcium bound to carboxylate sites. However significant amounts of calcium may be present in other forms, such as the mineral calcite.

In order to determine how many sites are being made available, and whether these will be sufficient for the desired catalyst loading, titration curves were carried out. These curves plot the change in pH as known amounts of acid are added to the coal sample. A typical curve involves a plateau or gently descending slope as the acid removes exchangeable cations from the coal and replaces them with hydrogen ions. These hydrogen ions can later be replaced by the catalytic metals (Fe or Co or Ni) in the ion exchange step.

Since the lower rank coals contain a substantial amount of alkali and alkaline earth cations attached to carboxylate groups, but not all of these alkalis are attached to organic groups, additional data were obtained with ion selective electrodes. These electrodes are available for calcium, sodium and potassium. The titration curves were then obtained for not only pH but the Ca, Na and K concentrations as well.

The atomic weight of calcium is 40 and the atomic weights of Fe, Co and Ni are 56, 59 and 59. In order to place 1000 ppm by weight of catalytic metal on the samples it is necessary to remove about 0.7 milligrams of exchangeable calcium or equivalent per gram of coal. This is about .175 ml of 0.100 N HNO₃ for singly bonded Ca or about .35 ml for doubly bonded Ca.

The amount of exchangeable calcium or other cations can be approximated from the titration curves. Several stages are seen in a typical case. Figure 2 illustrates a pH titration. Initially (the first 14 minutes or 28 ml of acid) the burette full of distilled water is displaced by the added standard nitric acid. During this time the pH will shift through values depending on the coal from near neutral to an alkaline state with pH values frequently about 8-9. The steepness of change of pH indicates the degree of mixing of acid with water during the displacement. In this first stage some alkaline species reacts with the acid. In the case of the Illinois coal some calcite reacts. In the second stage (after the first 12 minutes) the added acid reacts with exchangeable cations, and earlier reactions that did not go to completion will continue. For example, calcium bonded to carboxylate will exchange with the hydrogen ions from the acid, and incompletely reacted calcite will continue to react. The duration of this stage depends on the amount of carboxylate groups on the coal. The pH value, slightly above 6, indicates that 99.999% of the acid is utilized. This stage determines whether enough exchangeable cation was removed for the catalyst to be added in the desired amount. If other exchangeable materials are present, then additional features such as the approach to a plateau near pH 4 are seen. This may be due to clay materials in the coal. In the third stage (after 75 minutes) the pH of the eluent approaches that of the incoming acid and further reaction of the acid is not expected at any observable rate with this system.

For the purposes of this study, it is necessary that the number of exchangeable cations equal or preferably exceed the number of catalyst cations that are desired to add. The maximum amount of exchangeable cations is at most the amount indicated in the second stage described above. The maximum is reduced in practice by the amount of alternative reactions such as calcite decomposition which take place.

4.2. Acid Treatment of Wyodak Samples

The results for a Wyodak sample with the pH and sodium electrode are shown in Figure 3. A number of features are evident in the progression of the treatment. The pH changes for the Wyodak coal titrated with 0.100 N nitric acid indicate an initial period in which the water in contact with the coal was displaced by the acid (pH about 8 to 5.5). During this time no significant amount of sodium was evolved. This period was followed by an extensive period in which the pH was almost constant at about 6. During this time the other cations associated with carboxylate groups

were exchanging with hydrogen ions and being eluted. At the end of this phase a pair of inflections was exhibited before reaching the pH of the input acid.

The Na electrode indicated that the Na was eluted early in the exchange process, and tailed off slowly. The increase near the end of the acid addition is associated with a change in sensitivity with pH and is not associated with an increase in Na concentration. The most readily released species was released first. The pH remained high after the sodium release indicating that other species were reacting with the acid.

Figure 4 shows the effect of washing the coal with acid and monitoring the calcium ion concentration as well as the pH. A number of features can be seen. The initial pH for this solution is about the same as in Figure 3. The initial interaction yields an alkaline solution as the pH exceeds 7. As the water is displaced from the coal by the acid, the pH drops to about 6. During this period an initial calcium species is eluted. There is a slight increase to about pH 6.2 and a long period of very slow decrease to pH 6.1. During this period there is a rapid rise of the calcium concentration (dissolution of calcite is at least partially responsible) and then a slow and consistent increase to a maximum. Just before the maximum calcium concentration the pH drops from about 6.1 to about 4. During this period there is a rapid decrease in the calcium concentration. This is followed by an even more rapid decrease in pH to about 1.15, accompanied by a very rapid decrease in the calcium ion concentration. An instrumental problem caused the discontinuity in the pH curve. The scatter in values for the calcium values at higher concentrations is attributed to the release of carbon dioxide bubbles which affects the flow-through electrode stability.

4.3. Water Rinse of Wyodak Samples

Figure 5 shows the effects of rinsing the acid washed coal with distilled water. It should be noted that the coal changes character in the process and the rate of passage of the deionized water decreased. Initially the acid was washed out of the column at pH 1.15. A period followed during which the pH changed from 1.15 to about 1.9 with a nearly linear slope. The pH then changed somewhat more rapidly and then asymptotically approached a value of about 3.3. The initial linear portion is assumed to be due to the mixing of the acid in the space between the particles with the incoming water flow and discharge from the burette. The latter more parabolic shaped curve is believed to be due to diffusional processes from the pores of the particles.

One characteristic of the water washing step is the release of some calcium at about pH 1.5. This is seen in Figure 5 and is reproducible through several stages of acid washing and water rinsing. The shape of the curve is consistent through 3 wash and rinse sequences. In each case the calcium is rinsed out near the same pH. The calcium is also washed out in successive acid washes in a slightly higher pH range.

The cause of the release of calcium in both the acid wash and water rinse near the same pH is not yet clear. It may be that the physical structure or form of the external surface changes at a certain pH. If that were so, then any calcium which had been freed from internal linkages to carboxylate or other groups might be released in the rearrangement step during the transition between the structures. The release of the calcium at the initiation of the diffusional process may be due to hydrolysis of some organic bonding which involves a combination of hydrogen ions and release of the hydroxide ions from the hydrolyzing water molecule. These hydroxide ions change the former linear course of the plot of pH versus water added.

4.4. Other Analytical Observations

A small amount of cloudy material was seen in the supernatant water after the treated coal was removed from the burette. The cloudy material was decanted and allowed to settle. The clear supernatant was discarded. A grey solid was recovered and analyzed with FTIR.

FTIR indicated the presence of clay type minerals, as shown by peaks at lower wave numbers. The FTIR spectrum is shown in Figure 6. Apparently gradual changes in pH from neutral to acid and back again can release very finely divided clay material.

An analysis of the the acid eluent after passage over the coal in the burette for the experiment with the sodium electrode, and the rinse water, was made. The results are given in Table 1.

Table 1. Concentrations of Some Cationic Species in Wyodak Solutions
in ppm (ug/ml)

Cation	Acid Sol'n	Rinse	Cation	Acid Sol'n	Rinse
Al	56.6	6.80	Si	.55	<.3
B	1.04	<.10	Sr	16.5	.22
Ba	7.94	.37	Ti	.07	.04
Ca	908.	14.6	V	.13	<.1
Fe	35.7	4.73	Zn	.42	.05
Mg	212.	1.26	Na	49.8	.19
Mn	1.21	.04	K	4.91	.20
Ni	.21	<.05			

The estimated accuracy of the ICP AES analysis is +/- 10%.

Be, Cd, Co, Cr, Cu, Mo, Pb, Sn, and Zr were all below the limits of determination.

The calcium content is the highest observed as expected. Magnesium is second highest and should behave like the calcium. Aluminum is third highest. This aluminum concentration was not expected, and implies that there is a very active form of aluminum present, possibly derived from extremely fine clay par-

ticles. Sodium is the fourth highest, consistent with the high alkali content. Iron is the fifth highest, indicating that there is a substantial amount of soluble iron. The nature of this iron would be of interest since iron is going to be added in some experiments for catalytic purposes. Strontium and barium are sixth and seventh highest consistent with the high alkaline earth content of the coal. The rinse water after the acid treatment showed a somewhat different ranking of species. The calcium was highest again, but the aluminum content was second highest, again indicating some very active form of this element. The aluminum content is also interesting in light of the clay found at the end of the run. Iron was third highest indicating that there is a substantial amount and that it comes out consistently during the low pH conditions. The magnesium is fourth highest instead of second with the acid treatment, indicating that the aluminum and iron both tend to be continuously dissolved at a significant rate from the sample.

The catalytic metals Co, Ni and Mo were present at very low concentrations or below the limits of detection.

The release of clay during the acid washing and subsequent water rinsing may indicate that the clay is attracted to negative groups such as the carboxylate in the coal structure. The clay has a number of cations bound in its layer structure. The rinse water following the acid wash contained some additional calcium, indicating the release of this cation during the duration of the contact with the water. It is possible that the coal structure includes coal-matter-to-clay bonds. Acid washing can rupture some of these linkages, permitting the liberation of the clay. The structure of the coal particle would then be weakened. This weakening would limit the useful life of low rank coals for uses such as ion exchange resins.

Subsequent treatment with catalytic metals should result in placement of the metal on the exchange sites of the coal. However, the coal has about 6.3% mineral matter associated with it, and about 71% of the mineral matter is clay. The exact type of clay was not identified, but kaolinite is said to be present. As long as the clays can act as ion exchange materials, they will compete with the coal to accept the catalytic metals. If the acid treatment can reduce the clay content, this side benefit should enhance the ability to load the coal with catalyst. If the clay is not removed, then some of the catalytic metal may be exchanged onto the clay, giving two types of active catalyst - one exchanged on the coal - and the other in the form of a clay supported metal catalyst.

Samples of the coals sent to Anthony Cugini at PETC earlier have been analyzed. The ash content of the acid washed materials was notably less than the original sample. This is discussed further in the section on results of liquefaction studies.

The Wyodak samples have been taken from the titration and contacted with solutions containing the catalytic metals. Analysis of the solutions of catalyst described in the April report indi-

cated that the use of acidic samples did not result in the exchange of much metal. New catalyst standards were prepared to give solutions closer to neutral but with a pH low enough to avoid precipitation of hydroxide or oxyhydroxide species. Samples have been contacted with solutions containing Fe, Co and Ni for ion exchange. The procedure developed by Karl Schroeder at PETC for impregnation with Mo at pH 2 was followed with one of the samples. These 4 samples were augmented by a fresh acid washed sample for comparison. Samples of the solution used for the ion exchange and Mo adsorption experiments were submitted for analysis to establish the metal content on the coal. Samples have been sent to Anthony Cugini for testing of the oil liquefaction yield.

4.5. Successive Acid and Water Treatments - Wyodak

The evolution of calcium during the water rinse prompted a repetition of the acid and water rinse through two cycles to explore the potential for release of additional calcium or other species. This phenomenon was noted to persist through another acid treatment and rinse cycle for this particular sample. The calcium was released at about pH 2-2.5 in both the acid wash and the water rinse. Still another cycle was carried out, and again the calcium was released in a peak at about pH 2-2.5. Of course the height of the peaks diminished with the cycles. Figures 7 and 8 show the third acid wash and water rinse.

The significance of these observations seems to be that the coal particles are going through some pH sensitive structural change. This may be a form of chemical comminution, in which the presence of a solvent or other agent causes the propagation of cracks in the particles. The propagation is believed to be due to the accumulation of liquid in the tips of fine pores in the particles. It is also significant that clay particles seem to be released during the cycles of acid and water treatment.

Another possibility is that the external surfaces of the particles rearrange as the surface charges change in response to the pH change. There may be a major change in surface conformation at a critical pH as a result of these changes. The internal cations which may have been loosened during the earlier treatments may then be freed. Studies of coals of different ranks (IL#6, lignite) which may have different isoelectric points should clarify this possibility.

4.6. Preliminary Treatment of Illinois #6 Samples

Several runs were made to prepare enough material to add catalysts and for comparison without catalyst. The Illinois #6 coal samples were weighed (typically 30 grams per run), screened and the weight of -20+200 mesh sample was obtained. The initial acid titration indicated that a gas is released during the acid washing in the burette. The release of the gas bubbles effectively blocked the flow of the acid solution through the burette. In order to obtain similar data and avoid the problems, a change in the procedure used earlier with the Wyodak coal was made. The

pH of the initial slurry was measured for later reference and then 20.0 grams of 0.100 N nitric acid was added to about 30 grams of coal to consume some of the calcite in the sample. It was assumed that the gas was carbon dioxide which was produced from the reaction of the calcite and the nitric acid.

The initial data on the pH of the slurry over a 30 minute period involved magnetic stirring of the sample to compare with values of the pH of a slurry obtained by static measurements. It was observed that the pH varied slightly, decreasing about 0.2 units over 40 minutes in a linear fashion from an initial value of about 9.0. This value is higher than that of 8.51 obtained from the static measurements and indicates that some hydrolysis reaction is facilitated by the stirring.

The treatment of the sample with 20.0 grams of 0.100 N HNO₃ indicated a rapid drop in pH, and then an increase. The shape of the curve of pH as a function of time begins with a linear segment, followed by another steeper segment and ending with an asymptotic approach to a value around 6 in 2 hours. Figure 9 shows the change in pH through this step.

4.7. Acid Treatment of Illinois #6 Samples

Following the pretreatment of the Illinois #6 slurry in the magnetically stirred container, the coal slurry was transferred to the burette. The arrangement of peristaltic pump and computer were the same as for the Wyodak sample. Data were obtained for pH and concentrations of the Ca, Na and K ions. For this run the pH data were not as consistent as in the earlier runs. Figure 10 shows the change in pH, and Ca. The sodium electrode gives unreliable data for pH values below 4 because of interference from the hydrogen ions, so this data was eliminated. The data do show that there is a release of calcium as soon as the water is displaced by the dilute acid in the burette. The sample is 1.9% calcite, so a significant amount is expected. The possibility that some of the calcite may be present in small particles embedded within the coal particles would hinder access of the acid and cause a delayed release of the calcium. The release of carbon dioxide bubbles at this time caused significant variations in individual Ca electrode readings, as seen in the scatter of the points. The titration indicates a significant period during which the pH changes from about 7 to 5 in a nearly linear manner with time. This would indicate the existence of a series of organic acids of varying strength.

4.8. Water Rinse of Illinois #6 Samples

The results for a water rinse of the Illinois sample following a nitric acid wash are given in Figure 11. The pH increased to about 1.8 when a small evolution of calcium took place, similar to the Wyodak evolution at pH 2.5. The shape of the curve of pH versus time indicates an active mixing of residual acid on the column followed by a hydrolytic reaction, as was observed for the Wyodak sample.

4.9. Successive Acid and Water Treatments

Two additional cycles of acid wash and water rinse were carried out to evaluate the potential for release of additional calcium. It was observed that calcium and potassium are evolved each time that the coal passes through the pH range 1-3, whether from the acid-rich or water-rich side. This result is similar to that seen for the Wyodak coal and implies that there is a similar phenomenon in both subbituminous and high volatile bituminous coals. It was observed, however, that the concentration of potassium in the eluent was greater than calcium, indicating that the calcium was more thoroughly washed out, and that the potassium is released more slowly at this stage. At present it is speculated that these observations are associated with the clays present in each coal. Again, catalyst loading of clay bearing samples may produce two kinds of catalytic species - organically bound and clay-supported.

As acid is passed over the sample the Ca is released at about pH 2.8, while as water is passed over the acidic sample the Ca is released over a broad peak centered about pH 1.8. By the time of the third acid wash, the calcium has been so thoroughly washed out that more potassium is released at pH about 1.4. Figures 12 and 13 illustrate these steps.

4.10. pH of Slurries

The pH values of the 8 Argonne Premium Coal Samples were obtained by mixing about 5 grams of the -100 mesh coal with twice the coal weight of water, stirring and letting stand for 30 minutes. A calibrated pH electrode was then placed in the slurry to measure the pH. The values obtained are listed below:

Coal	pH
Upper Freeport	8.59
Wyodak	7.59
Illinois #6	8.51
Pittsburgh	9.23
Pocahontas	8.16
Blind Canyon	8.32
Lewiston-Stockton	7.74
Beulah-Zap	7.98

Another value was obtained by placing 10 grams of -20 mesh Illinois #6 coal with twice the weight of water in a beaker and constantly stirring with a magnetic stirrer. The initial pH value obtained was about 9.0 and declined about 0.2 units over a 40 minute period. Evidently constant stirring does have an effect. This will be used in future slurry pH measurements.

There are at least two noteworthy observations about these measurements. All of the pH values are above 7.00, indicating that some species are causing the system to be alkaline. The most alkaline are not the western coals, but rather the eastern ones. There are no known organic species that would cause the

system to be alkaline, implying that there must be an inorganic cause. The higher value for the stirred sample indicates that the release of the alkali material is enhanced.

The highest pH values in the set of 8 coals are for the Pittsburgh, Upper Freeport and Illinois #6 coals. These are all the higher rank coals, and do not have the higher concentrations of combined alkali and alkaline earth ions associated with the western US samples. Further they are not expected to have significant concentrations of carboxyl or organic acid groups. The pH values do not correlate with rank or carbon content of the coal or with total ash or mineral matter content. However the sequence Pittsburgh >Upper Freeport >Illinois #6 >Blind Canyon >Pocahontas >Beulah-Zap >Lewiston-Stockton >Wyodak approximates the order of the acidity of the mineral matter in the coal. The most acidic ashes or mineral matter have the highest SiO₂ content. The principal investigator has earlier suggested a scale for ranking the acidity of the mineral cations (12). An understanding of this phenomenon will require further study.

4.11. Ion Exchange and Absorption of Catalytic Metals

The acid washed and water rinsed coal samples were treated to incorporate catalytically active metals on the coal. The objective is to use the active acid sites to attach Fe or Ni or Co ions, and separately to use the technique developed by Schroeder to incorporate Mo on the coal. To date, no reference has been found which describes the ion exchange behavior of these coals well enough to permit the incorporation of Fe, Ni or Co with the certainty that the Schroeder method permits for Mo.

For the ion exchange technique to be effective the metal ions must be available in a positively charged form. If the pH is increased from an acidic value, ion pairs are expected to form (such as Fe(OH)⁺). These ion pairs are not expected to bond as strongly as the doubly charged cations. In very acidic media the hydrogen ions will not be easily displaced from the coal. This means that there is probably a narrow pH range where the ion exchange can readily take place. Unfortunately there is no ion selective electrode for these catalytic species, which could permit a speedy optimizing of the conditions for the exchange.

The ion exchange technique is also sensitive to pH because the surface charges of the coal particles depend on the acidity. At low pH values the surface takes on a positive charge from adsorbed hydrogen ions, and this charge repels the cations. At higher pH values the cations such as Fe will precipitate as hydroxide species and are not available for exchange. Optimum catalytic loading depends on learning the best pH to achieve the cation deposition within the acidity constraints.

For the Illinois #6 coal samples the evolution of gas bubbles was observed over a long part of the acid wash, indicating that the reaction with calcite may be affecting the pH over the gas evolution period, and possibly the stability of the Ca electrode.

The initial experiments involved mixing samples (about 20 grams) of Wyodak coal that had been acid washed and rinsed with 1000 ppm solutions of either iron or nickel in 2% nitric acid (commercially available analytical standard). The solutions were stirred for 10-15 minutes, transferred to the burette with the frit, and distilled water was pumped over the coal sample with the peristaltic pump while the pH was recorded. About 200 ml of water was used. The pH increased from 1 to 3.5. The eluent water was collected and analyzed for iron or nickel. The analysis indicated that the coal took up about 125 ppm of either metal. This was much less than the desired 1000 ppm.

These initial efforts may indicate that the ion exchange process is a slow one, requiring hours for significant exchange, or that the pH needs adjustment. The method used for the latter experiments involved mixing coal samples with different solutions of catalytic metal still at a concentration of 1000 ppm of metal ion, but much less acid. The iron solution was made up of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (498.1 mg) placed in a 100 ml volumetric flask. The solution was cloudy as the water was added, and a small amount of sulfuric acid was used to clear up the solution. This will dissociate most of the iron species. The cobalt solution was made up of 403.8 mg of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$. The solution was not cloudy. The nickel solution was made up of 496.0 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ in 100 ml of water, and was not cloudy either. A 1500 ppm solution of Mo was made up of 276.1 mg of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ made up to pH 2 with .2497 gm of sodium sulfate and .2570 gm sulfuric acid.

The coal sample described above were used again. The weight of solution required to give 2000 ppm of catalyst if all of the cations were exchanged was calculated. This amount was added to the coal slurry, stirred well and allowed to exchange for about 42 hours. The solutions were then decanted into tared bottles, and the slurry rinsed three times into the tared bottles with distilled water. The weight of the solution was determined and a sample submitted for analysis. From the difference of the total amount of metal available, and the amount in the solution, and the weight of the coal, the loading of the coal was calculated.

These Wyodak samples were loaded with Fe, Ni, Co, Mo. They were sent to Anthony Cugini and Christine Curtis as part of the collaborative program to evaluate liquefaction yields. The results will be included in the monthly report after they become available.

4.12. Initial Results of Oil Yield Studies

Samples have been evaluated by Anthony Cugini at PETC. Samples of the raw coal (directly from the ampoules) were compared with water-washed and acid-washed Wyodak samples. Ash values were also obtained. The water-washed and acid washed samples were dried before the ash determination. Values for the different coal samples, moisture levels to which the samples were dried, measured ash contents, ash content on a dry basis, and the reduction in ash compared to the raw coal are summarized below.

Coal Sample	moisture	ash	dry ash	reduction
Raw	27.39	6.31	8.69	0
Water washed	6.4	7.81	8.34	4.03
Acid washed	6.96	3.46	3.72	57.19

Samples were run in microautoclave tubing bombs to establish liquefaction yields based on THF solubility (total conversion) and heptane soluble (oil yield). The liquefaction runs showed good reproducibility for 2 raw samples at 55.2 and 56.1 % conversion to THF soluble and 34% heptane soluble. The water washed was 44% THF soluble and 27% heptane soluble. The acid washed was 37% THF soluble and 24% heptane soluble. These results are summarized below.

Liquefaction results for Wyodak samples:

Raw Sample	THF soluble (total conv.)	Heptane soluble (oil yield)
Raw	55.2, 56.1	34
Water Washed	44	27
Acid washed	37	24

Conditions were: solvent 1-MeNaphthalene (non-donor) , 2:1 solvent:coal; 425 C, 30 minute reaction, cold charge at 1000 psi H₂, (1700-1800 hot).

The total conversion and oil yields of the three initial samples decreased with the extent of treatment. This effect may be due to the amount of handling, which represents an opportunity for partial oxidation. The samples were kept under a layer of water to avoid oxidation. However, the nitric acid treatment does give an oxidizing environment. Consideration is being given to alternative acidic treatments to reduce the potential oxidation during the cation removal. The use of hydrochloric or sulfurous acid is being considered, as well as equipment modifications to avoid an oxidizing environment.

5. CONCLUSIONS:

1. A number of the ion exchange properties of low rank coals can be observed and understood by titrating with the burette system described.
2. Alkali cations are removed early in the acid titration, and alkaline earth cations are removed throughout the acid treatment.
3. More acid is consumed in the titration than the equivalent amount of cations which are recovered.
4. The ion exchange behavior of the Wyodak and the Illinois #6 coals are similar in the initial reactions with the acid. The amount of acid which reacts with the Wyodak is larger than that which reacts with the Illinois #6 coal, indicating a greater capacity for the Wyodak to exchange catalysts.

5. Catalysts can be added by both the ion exchange and adsorption technique. The reaction is slow indicating that adsorption may be the dominant mode of addition in these cases.

6. A significant amount of inorganic material in the coal must be neutralized before the release of cations involved in ion exchange can be carried out.

7. Some aluminum is solubilized.

8. Clay is released following the acid treatment. This clay is possibly associated with the exchanged cations.

9. Clays present in the coal are probably involved in some of the ion exchange behavior and will provide a clay-supported catalyst in the coal sample in addition to the organically bound catalyst.

10. The initial oil yields indicate some reduction in going from raw to water washed to acid washed coal, which is thought to be due to the greater amount of handling or oxidation that may have occurred with the latter samples.

6. FUTURE WORK:

Samples of Illinois #6 coal have been acid washed and rinsed. These will be treated with Fe, or Co, or Ni, or Mo. The treated samples as well as the acid washed without catalysts will then be sent for liquefaction evaluation.

A similar set of studies will be carried out with the Beulah-Zap lignite for comparison and observation of trends with coal rank.

The Wyodak coal will be treated with a less oxidizing acid, such as sulfurous, or hydrochloric, to try to limit the potential oxidation of the sample.

The technique of catalyst addition will be refined to better understand the conditions which permit exchange of catalytic material with the coals. This work will be extended to addition of mixed catalysts, for example Fe or Co or Ni with Mo.

7. ACKNOWLEDGMENTS:

The principal investigator acknowledges support from the U. S. Department of Energy, Office of Fossil Energy for the support which made this work possible.

Thanks are expressed to Joe Gregar for the preparation of the burette, to Robert McBeth for the preparation of standard solutions for the calibration of the ion selective electrodes, to David French for the FTIR analysis, and to Gene Hodel and Brad Staats for assistance with data acquisition from some of the Illinois #6 samples.

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Figure 1.

DIAGRAM OF EQUIPMENT FOR ACID LEACHING
AND CATALYST APPLICATION FOR COAL SAMPLES

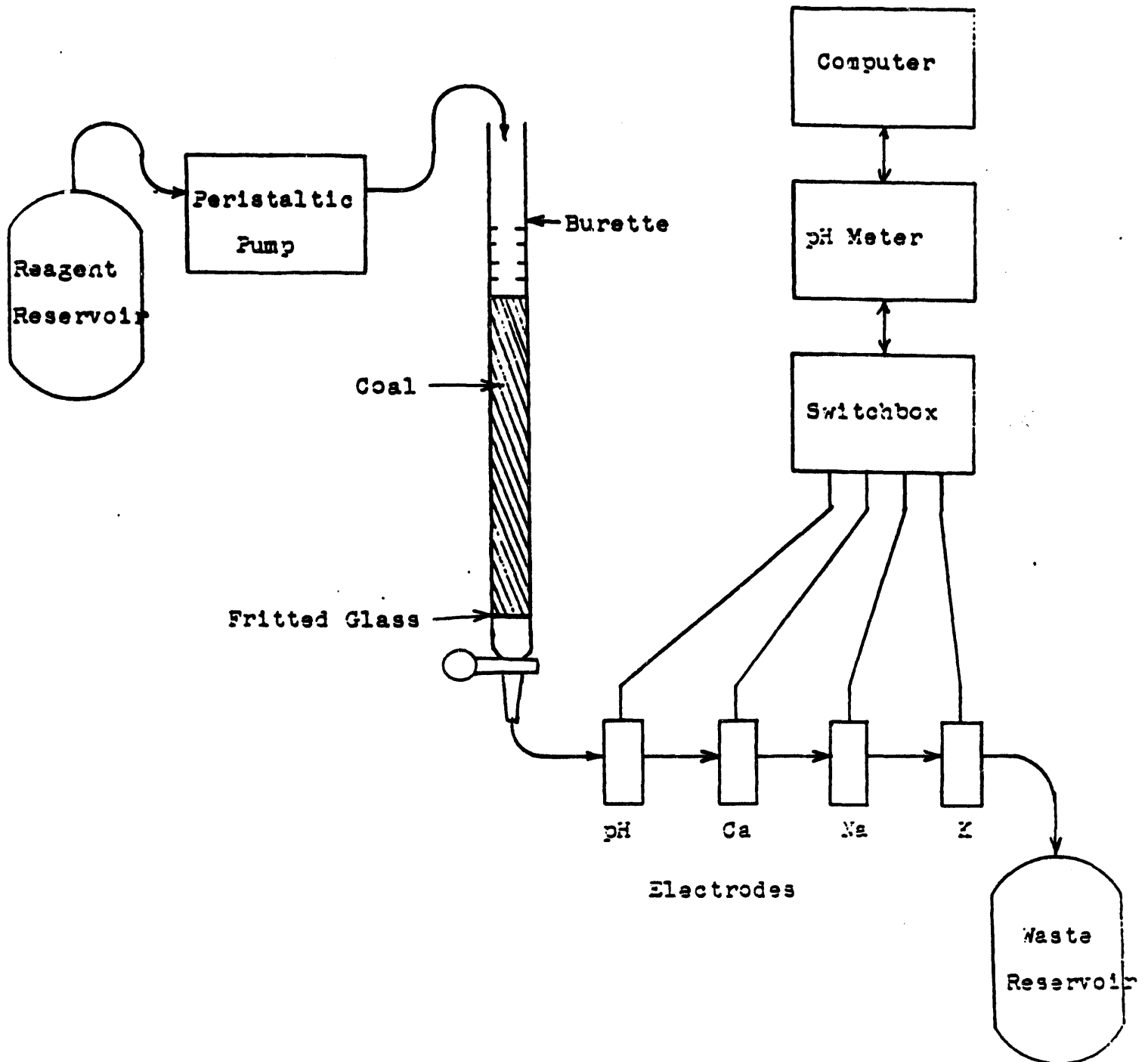
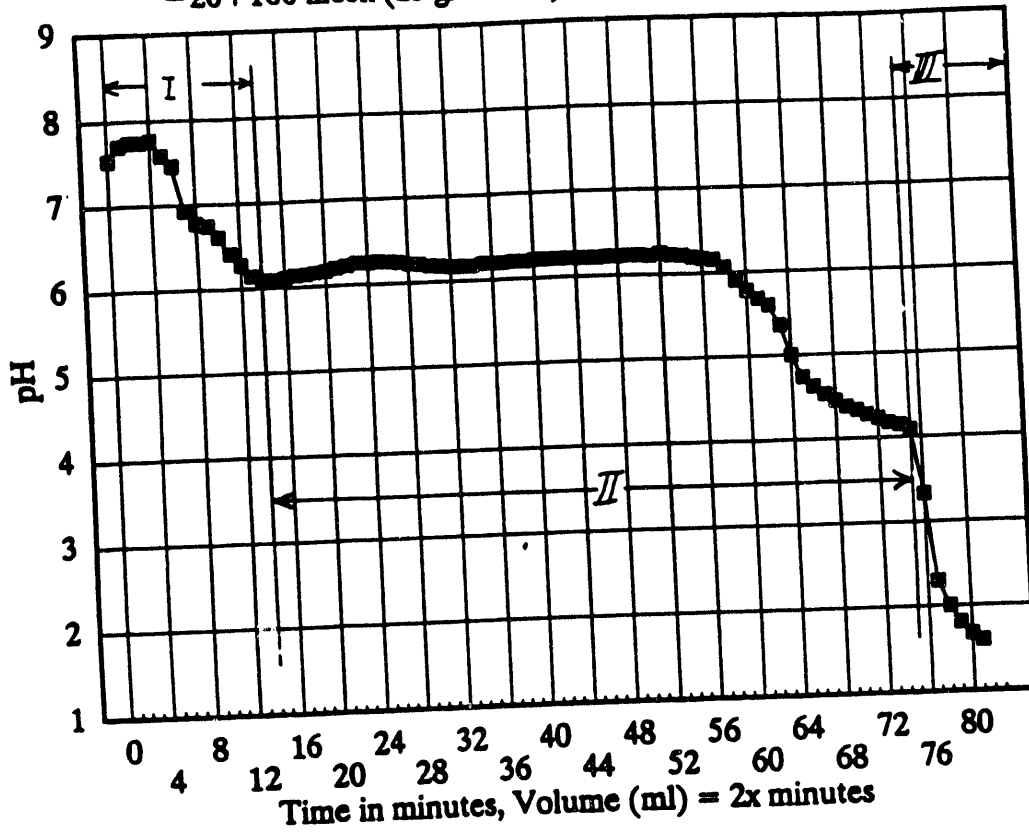


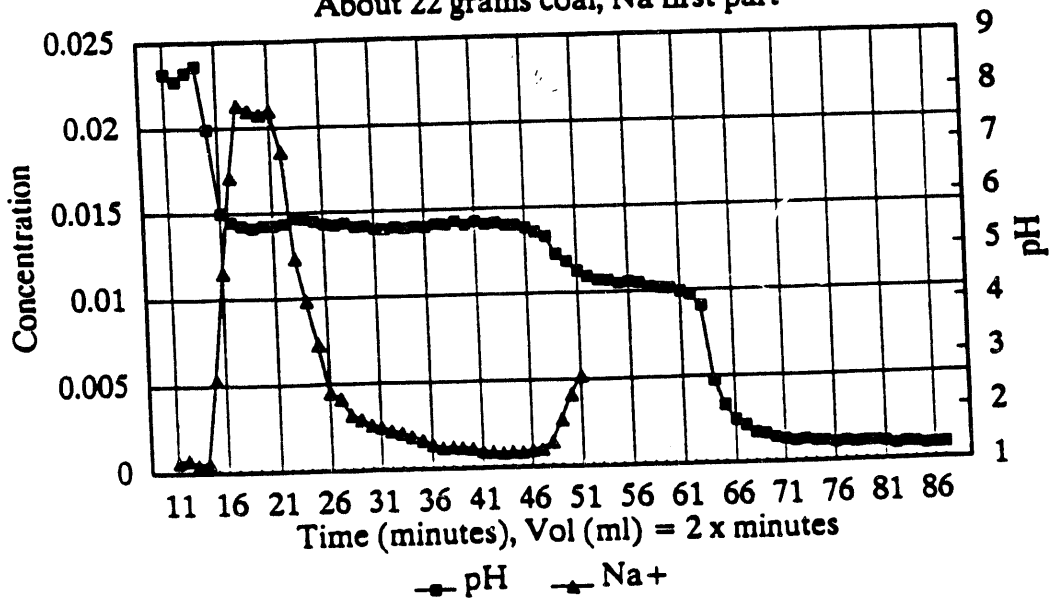
Fig. 2. pH Changes for Wyodak Coal
 -20+100 mesh (23 gms coal) titrated with 0.1 N HNO₃



IWY01

Fig. 3 Wyodak Acid Treatment

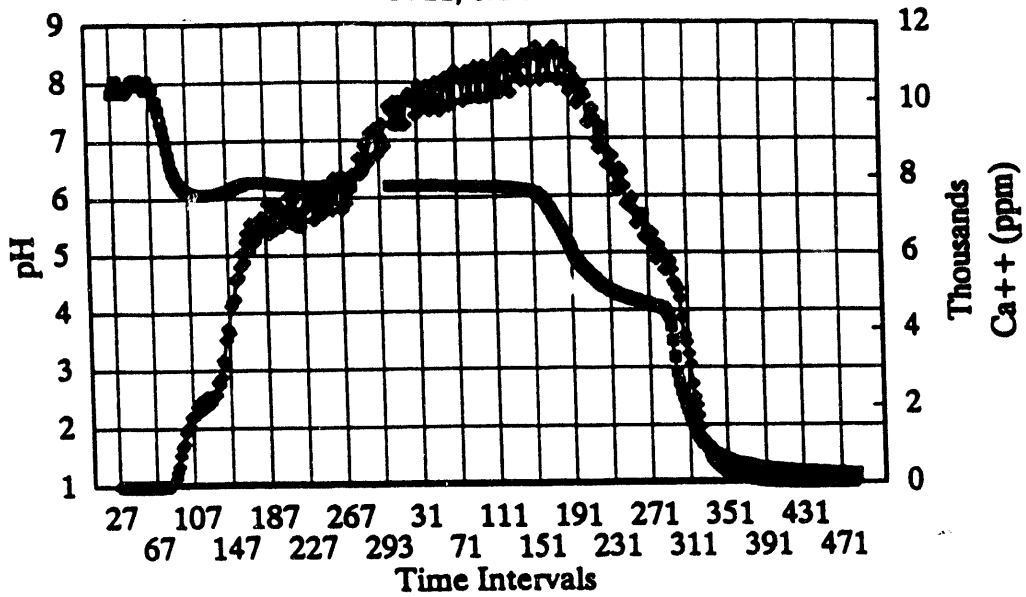
About 22 grams coal, Na first part



WY604
 conc.Na

Fig. 4, Wyodak, First Acid Wash

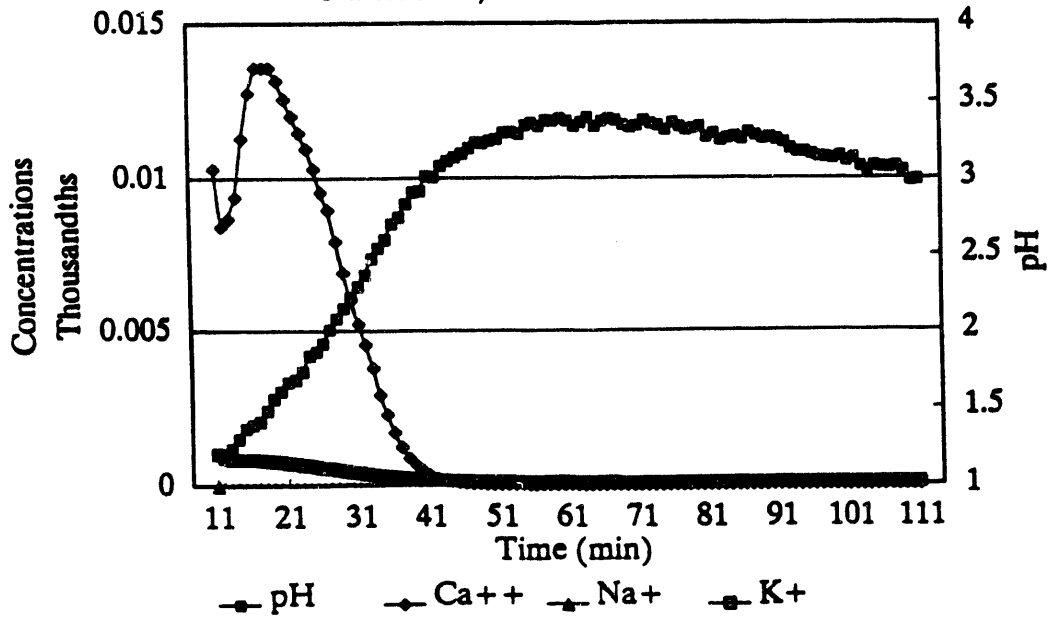
WY521, 0.1 HNO₃



WY521 composite

Fig. 5, Wyodak First Water Rinse

Na omitted, Electrode interference



WY604A

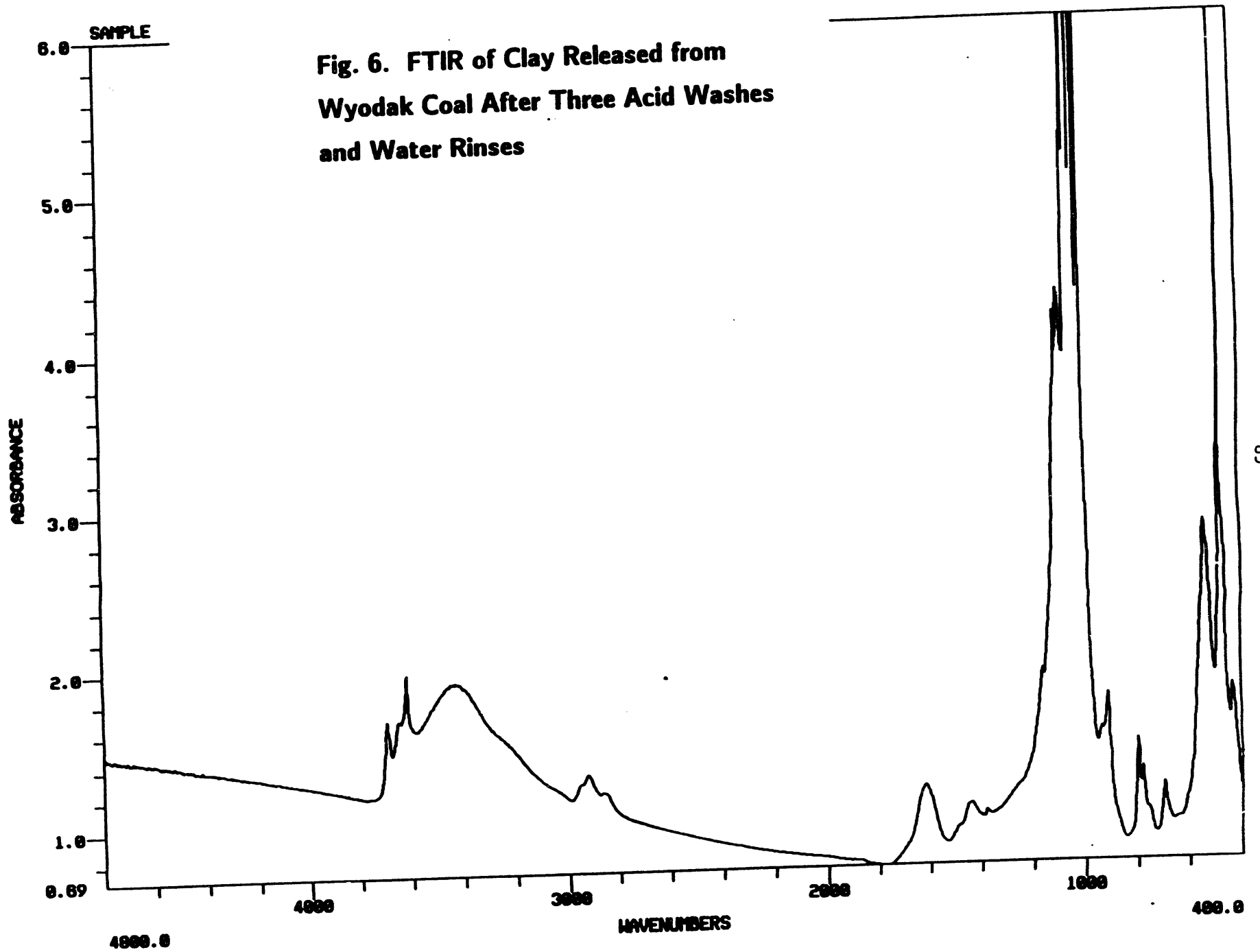
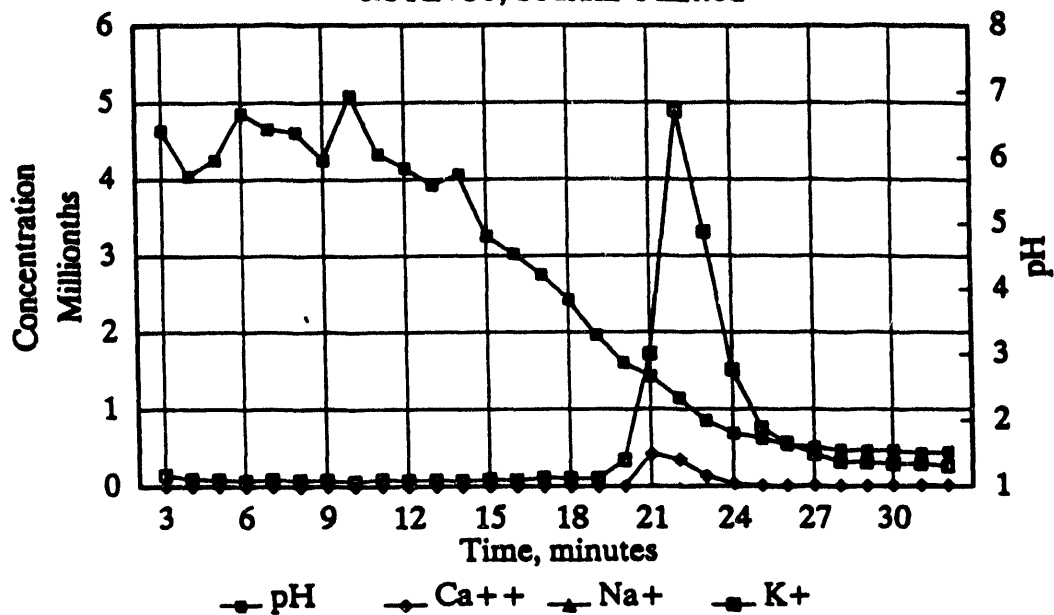


Fig. 6. FTIR of Clay Released from Wyodak Coal After Three Acid Washes and Water Rinses

Fig. 7, Wyodak Third Acid Wash

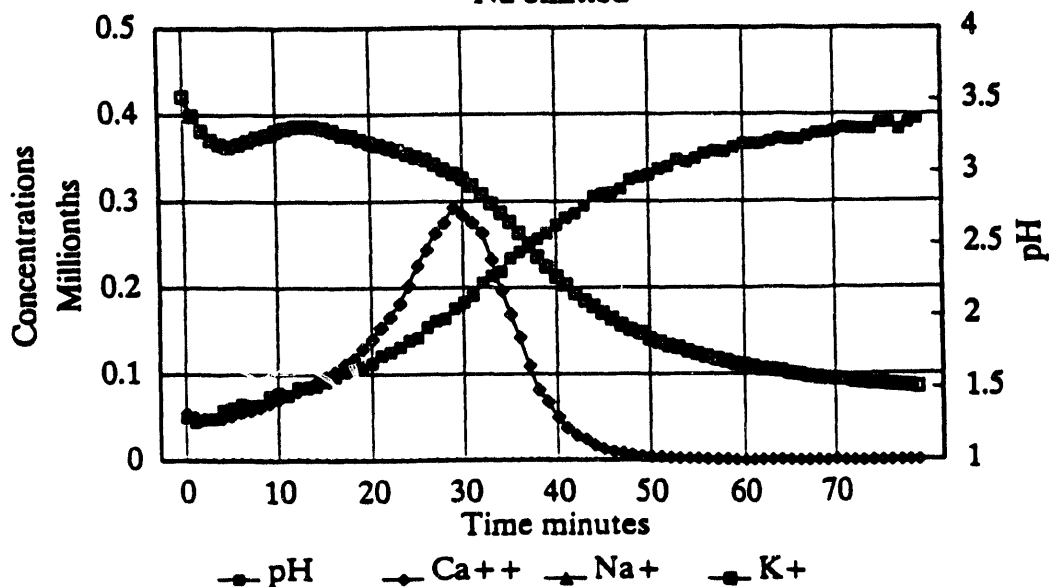
0.1 HNO₃, Sodium Omitted



WY604F

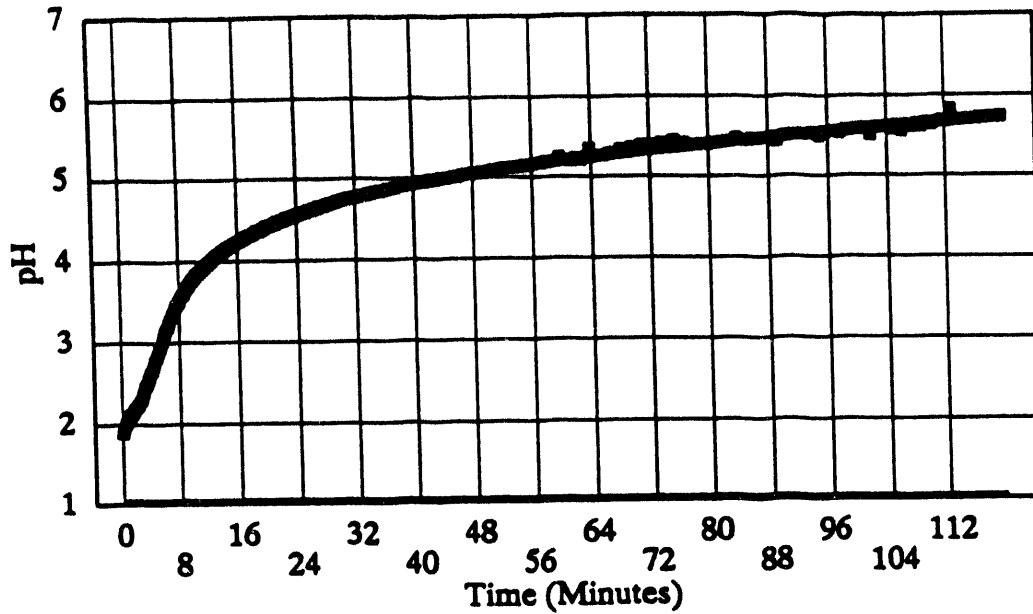
Fig. 8, Wyodak Third Water Wash

Na omitted



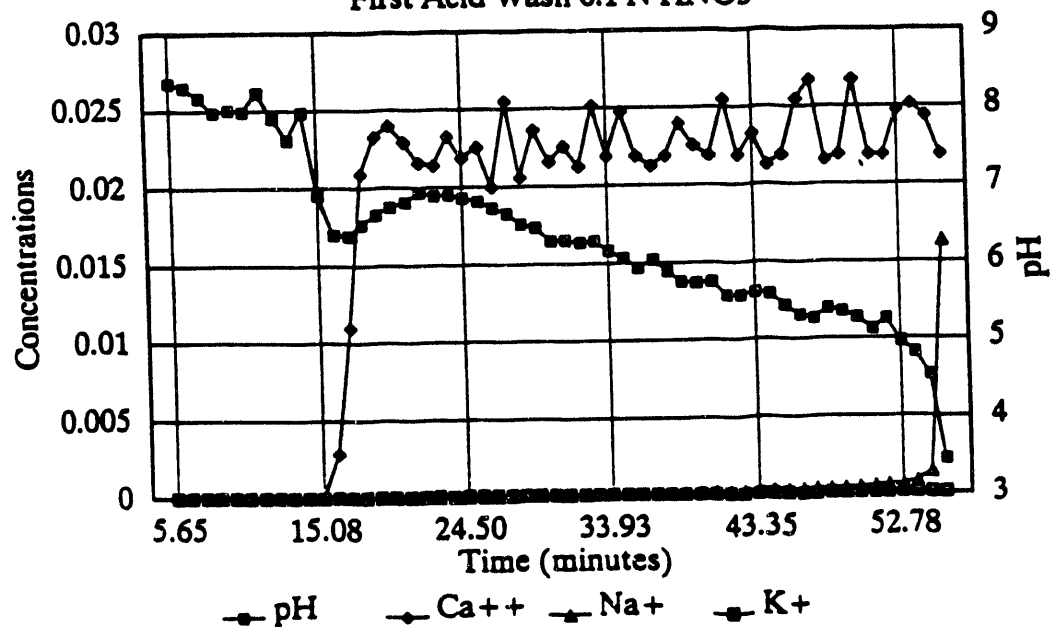
WY604G
conc-na

Fig. 9, Illinois #6 Coal
Initial Acid Slurry pH



IL629a

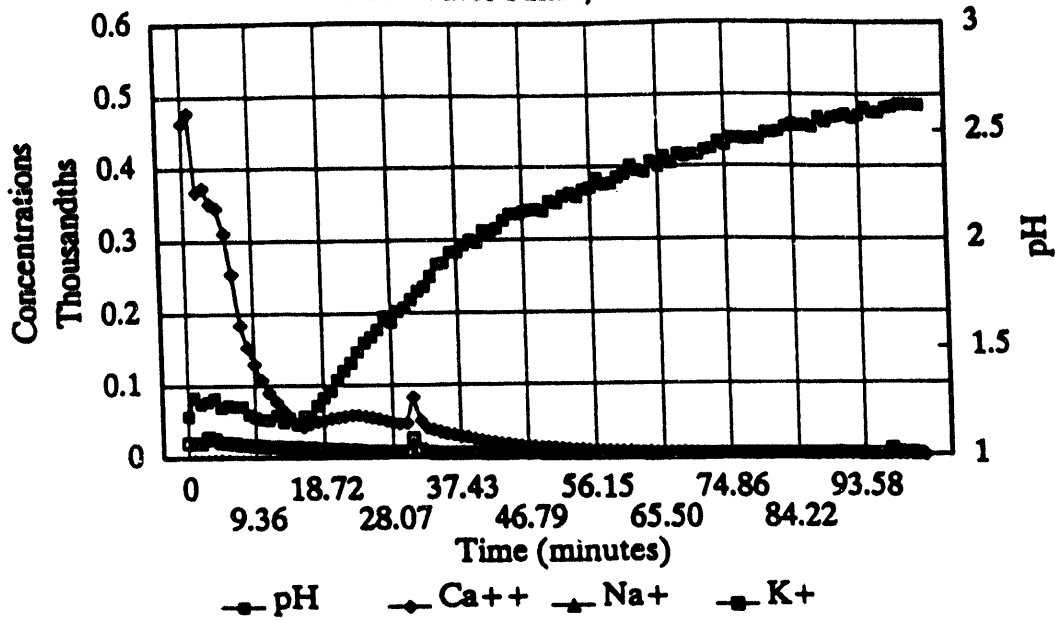
Fig. 10, Illinois #6 Coal
First Acid Wash 0.1 N HNO₃



IL630B

Fig. 11, Illinois #6 Coal

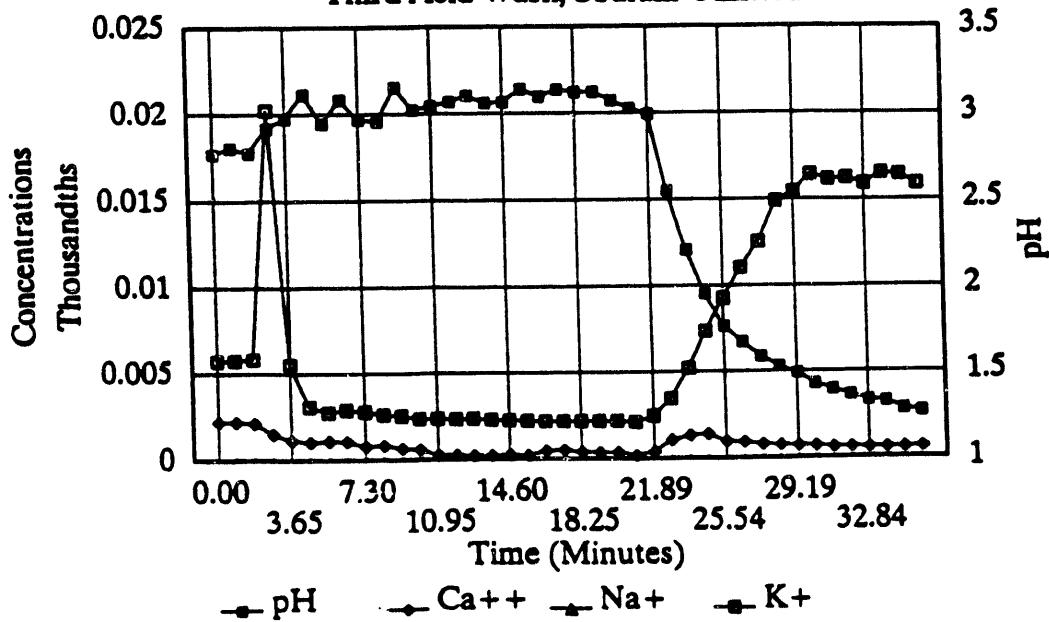
First Water Rinse, Na omitted



IL630C

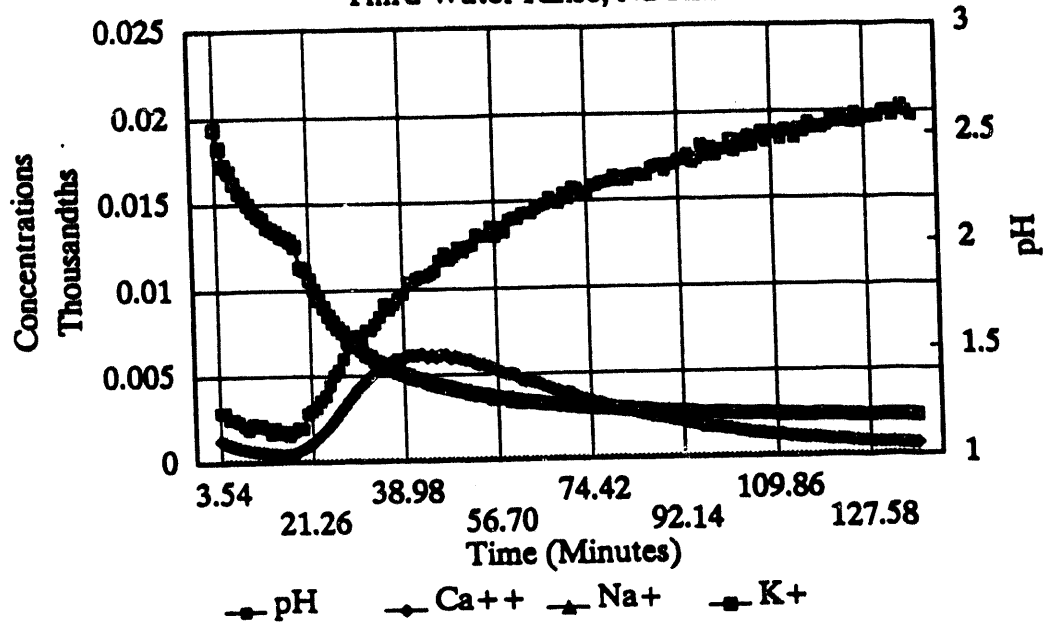
Fig. 12, Illinois #6 Coal

Third Acid Wash, Sodium Omitted



IL630F

Fig. 13, Illinois #6 Coal
 Third Water Rinse, Na omitted



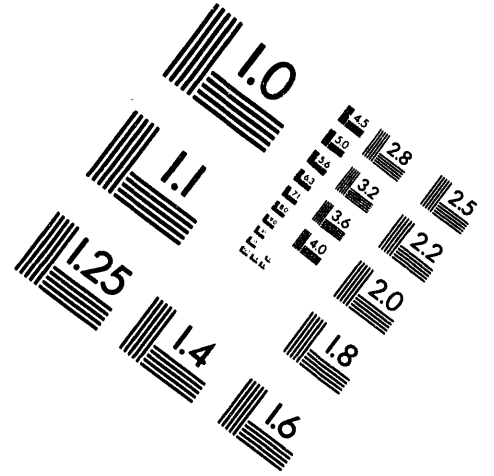
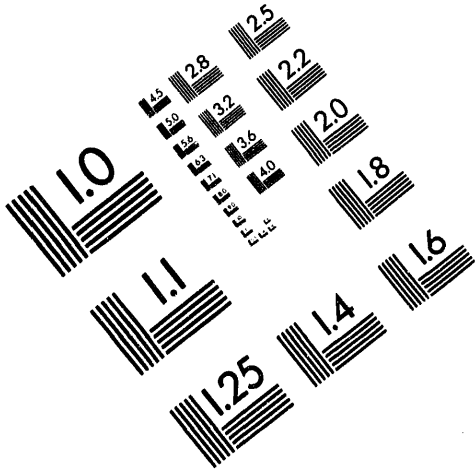
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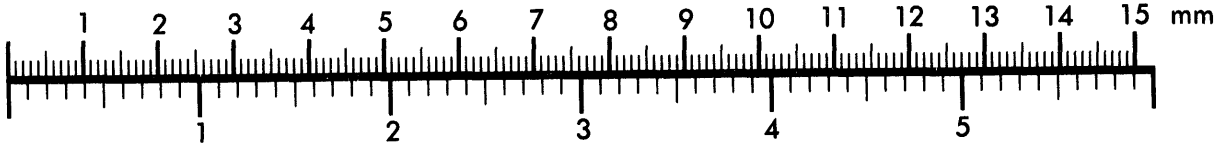
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Association for Information and Image Management

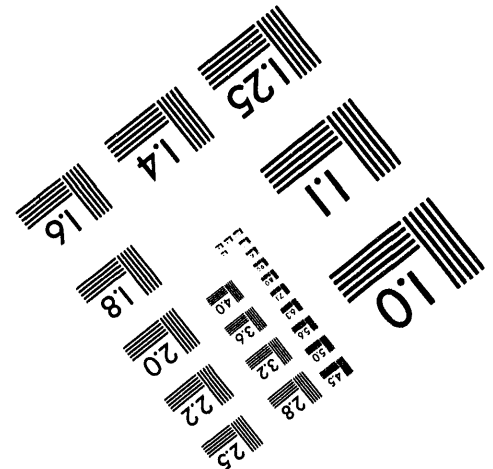
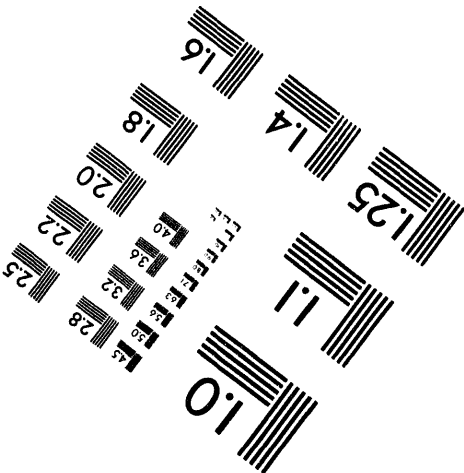
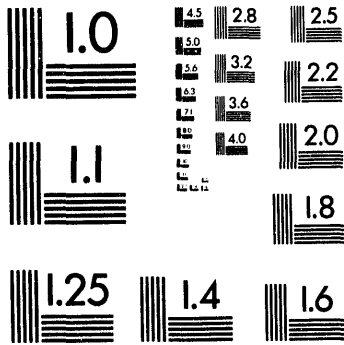
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Inches



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2 of 2

APPENDIX B

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS

TABLE B-1

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: 30/70 IPA/TOLUENE (Part 1)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo _{soln} (ppm)	ICP or XRF	EST. UP- TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{coal} (ppm)	UP- TAKE	
None	None	0	76-1	--	--	0.1ND	ICP	--	--	--	Reference soln.
8x60	MVL	100	77-2A 77-2B 77-2C 77-2D 77-2E	70	0.08 0.17 0.5 1.0 12.0	0.2 110 119 84 35	ICP	99.8 100 100 16.0 65.0	-- -- -- -- --	-- -- -- -- --	CARN 92-021871 76-1 ref. - used pressure filtration
8x60	MVL	100	78-2A 78-2B 78-2C 78-2D 78-2E 78-2F 78-2G	70	0.5 1.0 2.0 4.0 7.0 23.0 48.0	88 90 87 81 72 39 18.8	ICP	12.0 10.0 13.0 19.0 28.0 61.0 81.2	60 60 73.5 99 135 258.8 329.5	12.0 12.6 16.1 22.8 32.6 65.4 85.4	CARN 92-022728 76-1 ref.
-70	MVL	105	78-3D	70	67.5	10.4	ICP	90.1	--	--	CARN 92-022734 76-1 ref.
None	None	0	79-1	--	--	0.1ND	ICP	--	--	--	Reference soln.
8x60	MVL	275	79-2A 79-2B 79-2C 79-2D 79-2E 79-2F 79-2G	70	0.5 1.0 2.0 4.0 7.0 24.0 48.0	250 246 228 213 197 141 79	ICP	9.1 10.5 17.1 22.5 28.4 48.7 71.3	125 144 225 288.8 352.8 562.8 779.8	9.1 11.0 18.0 24.2 30.9 51.6 73.8	CARN 92-022728 (2A to 2D) CARN 92-022732 (2E to 2G) 79-1 ref.

Notes:

- [1] Estimated % Uptake = $(1 - Mo_{soln} / Mo_{soln,0}) \times 100$
 [2] Calculated % Uptake = $(Mo_{coal} / Mo_{max,i}) \times 100$ (See Appendix A)

TABLE B-1

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: 30/70 IPA/TOLUENE (Continued--Part 2)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo _{soln} (ppm)	ICP or XRF	EST. UP-TAKE [1]	CALCULATED [1]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{coal} (ppm)	UP-TAKE	
None	None	0	79-1	--	--	0.1ND	ICP	--	--	--	Reference soln.
8x60	Mo oct.	105	79-3A	70	0.5	99	ICP	5.7	--	--	CARN 92-022732 79-1 ref. -- large scatter in Mo _{soln} so only estimated uptake
			79-3B		1.0	94		10.5	--	--	
			79-3C		2.0	99		5.7	--	--	
			79-3D		4.0	81		22.9	--	--	
			79-3E		6.0	85		19.1	--	--	
			79-3F		23.0	50		52.4	--	--	
			79-3G		46.0	35		87.3	--	--	
None	None	0	139-2	--	--	5ND	XRF	--	--	--	Reference soln.
8x60	Mo oct.	105	139-2A	150	0.5	66	XRF	37.1	195	37.1	CARN 93-005940 139-2 ref. -- No precipitate observed in samples with standing (up to 6 days)
			139-2B		1.0	35		66.7	342.2	67.3	
			139-2C		2.0	19		81.9	414.2	82.9	
			139-2D		3.5	13		87.6	439.7	88.8	
			139-2E		6.17	13		87.6	439.7	89.4	
			139-2F		24.0	6		94.3	466	95.4	
			139-2G		48.17	6		94.3	466	95.7	

Notes:

- [1] Estimated % Uptake = $(1 - Mo_{soln,i} / Mo_{soln,0}) \times 100$
 [2] Calculated % Uptake = $(Mo_{coal,i} / Mo_{max,i}) \times 100$ (See Appendix A)

TABLE B-II

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: THF/TOLUENE (Part 1)
(30% THF unless specified otherwise)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo _{soln} (ppm)	ICP or XRF	EST. UP- TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{coal} (ppm)	UP- TAKE	
None	None	0	82-1	--	--	0.5ND	ICP	--	--	--	Reference soln.
8x60	MVL	109	82-2	70	137	4.9	ICP	95.5	520.5	95.5	CARN 92-023765
8x60	MVL	109	82-3A 82-3B 82-3C 82-3E 82-3F 82-3G	70	0.5 1.0 2.0 6.5 24.0 48.0	96 91 89 73 50 36	ICP	11.9 16.5 18.3 33.0 54.1 67.0	545 521 498.2 476 457.8 445.3	11.9 17.0 19.6 34.8 56.3 69.7	CARN 92-023765 82-1 ref. - no 4-hr sample withdrawn
-70	MVL	110	82-4A 82-4B 82-4C 82-4E 82-4F 82-4G	70	0.5 1.0 2.0 6.5 24.0 48.0	79 75 72 56 33 8.9	ICP	28.2 31.8 34.5 49.1 70.0 91.9	155 174 187.5 255.5 347.5 437.9	28.2 32.8 36.7 51.8 72.5 92.9	CARN 92-023765 82-1 ref. - no 4-hr sample withdrawn
-200	MVL	105	83-6A 83-6B 83-6C 83-6D 83-6E 83-6F 83-6G	70	0.5 1.0 2.0 4.0 6.0 24.0 48.0	72 70 67 60 56 30 16.2	ICP	31.4 33.3 36.2 42.9 46.7 71.4 84.6	165 174.5 188 217.8 233.8 331.3 379.6	31.4 34.4 38.4 46.1 51.1 74.6 87.0	CARN 92-023769 82-1 ref.

Notes:

- [1] Estimated % Uptake = $(1 - Mo_{soln}/Mo_{soln,0}) \times 100$
 [2] Calculated % Uptake = $(Mo_{coal}/Mo_{max,i}) \times 100$ (See Appendix A)

TABLE B-II
SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: THF/TOLUENE (Continued--Part 2)
(30% THF unless otherwise specified)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo _{soln} (ppm)	ICP or XRF	EST. UP- TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{coal} (ppm)	UP- TAKE	
None	None	0	84-1	--	--	0.3ND	ICP	--	--	--	Reference soln.
-70	MVL	110	84-2A	70	0.5	81	ICP	26.4	145	26.4	CARN 93-000215 84-1 ref.
			84-2B		2.0	73		33.6	183	34.5	
			84-2C		4.0	65		40.9	219	42.9	
			84-2D		6.0	59		46.4	244.5	49.5	
			84-2E		24.0	30.5		72.3	358.5	74.7	
			84-2F		48.0	17		84.5	409.1	86.7	
None	None	0	108-1	--	--	0.3ND	ICP	--	--	--	Reference soln.
8x60	MVL	106	108-5A	120	0.5	82	ICP	22.6	120	22.6	CARN 93-002361 108-1 ref. - rotavap water bath level low for sample 5G
			108-5B		1.0	78		26.4	139	27.3	
			108-5C		2.0	71		33.0	170.5	34.8	
			108-5D		4.0	59		44.3	221.5	46.9	
			108-5E		6.17	52		50.9	249.5	54.5	
			108-5F		24.0	21.3		79.9	364.6	82.0	
			108-5G		48.0	7.9		92.5	411.5	93.7	
None	None	0	122-1	--	--	0.3ND	ICP	--	--	--	Reference soln.
-70	MVL	102	122-1A	120	0.5	97	ICP	4.9	25	4.9	CARN 93-004764 122-1 ref.
			122-1B		1.0	85		16.7	82	16.9	
			122-1C		2.0	75		26.5	127	27.3	
			122-1D		4.0	58		43.1	199.2	44.7	
			122-1E		6.0	48		52.9	239.2	55.5	
			122-1F		24.0	13		87.2	370.4	88.3	
			122-1G		48.0	6.6		93.5	392.8	94.4	

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal}/Mo_{max,i}) \times 100$ (See Appendix A)

TABLE B-II

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: THF/TOLUENE (Continued--Part 3)
(30% THF unless otherwise specified)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo _{soln} (ppm)	ICP or XRF	EST. UP- TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{coal} (ppm)	UP- TAKE	
-70	Mo oct.	103	123-2A	120	0.5	52	ICP	49.5	260	49.5	CARN 93-004771 122-1 ref.
			123-2B		1.0	47		54.4		56.5	
			123-2C		2.33	36.9		64.2		67.1	
			123-2D		4.0	28.5		72.3		75.9	
			123-2E		6.5	20		80.6		84.2	
			123-2F		24.0	7.2		93.0		95.3	
			123-2G		48.0	9		91.3		95.7	
None	None	0	138-1	--	--	5ND	XRF	--	--	--	Reference soln.
8x60	MVL	103	136-7A	120	24.0	29	XRF	71.8	370	718	CARN 93-005931 138-1 ref. - no precipitate with standing (up to 13 days)
8x60	MVL	102	136-8A	70	24.0	58	XRF	43.1	510	43.1	CARN 93-005932 138-1 ref. - no precipitate with standing (up to 13 days)

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal}/Mo_{max}) \times 100$ (See Appendix A)

TABLE B-II

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: THF/TOLUENE (Continued-Part 4)
(30% THF unless otherwise specified)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo _{soln} (ppm)	ICP or XRF	EST. UP- TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{coal} (ppm)	UP- TAKE	
None	None	0	138-1	--	--	5ND	XRF	--	--	--	Reference soln.
8x60	Mo oct.	104	138-1A 138-1B 138-1C 138-1D 138-1E 138-1F 138-1G	120	0.5 1.0 2.0 4.0 6.0 24.0 48.0	46 39 32 26 24 9 17	XRF	55.8 62.5 69.2 75.0 76.9 91.3 83.6	290 323.2 354.7 380.2 388.2 444.4 444.4	55.8 63.6 71.1 77.5 80.2 92.9 93.4	CARN 93-005936 138-1 ref. - trace of blue immiscible film at bottom of 1A and 1B; none in others after 8 days standing
None	None	0 (20% THF)	110-1	--	--	0.3ND	ICP	--	--	--	Reference soln.
8x60	MVL	107 (20% THF)	109-6A 109-6B 109-6C 109-6D 109-6E 109-6F 109-6G	120	0.33 1.0 2.0 4.0 6.0 24.25 48.0	92 89 79 74 67 38 18.6	ICP	14.0 16.8 26.2 30.8 37.4 64.5 82.6	75 89.2 134.2 155.4 183.4 292.2 360.1	14.0 17.4 27.4 33.1 40.6 67.2 84.1	CARN 93-002362 110-1 ref.
8x60	MVL	104 (20% THF)	110-7A 110-7B 110-7C 110-7D 110-7E 110-7F 110-7G	70	0.5 1.0 2.0 4.0 6.0 24.0 48.0	101 97 93 88 84 65 53	ICP	2.9 6.7 10.6 15.4 19.2 37.5 49.0	15 34 52 73.2 89.2 160.4 202.4	2.9 6.9 11.1 16.4 21.0 39.7 52.1	CARN 93-002359 110-1 ref.

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal}/Mo_{max}) \times 100$ (See Appendix A)

TABLE B-III

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: 30/70 DMSO/TOLUENE (Part 1)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo _{soln} (ppm)	ICP or XRF	EST. UP- TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{coal} (ppm)	UP- TAKE	
None	None	0	99-1	--	--	0.2ND	ICP	--	--	--	Reference soln.
8x60	MVL	110	99-2A	70	0.5	31.5	ICP	71.4	392.5	71.4	CARN 93-001880 99-1 ref.
			99-2B		1.0	18.6		83.1	453.8	83.7	
			99-2C		2.25	14.3		87.0	473.2	88.0	
			99-2D		4.0	13.2		88.0	477.9	89.5	
			99-2E		6.33	10.7		90.3	487.9	92.0	
			99-2F		24.0	9.8		91.0	491.3	93.1	
			99-2G		48.0	8.0		92.7	497.6	94.7	
			8x60		MVL	109		100-3A	150	0.5	
100-3B	1.25	--		--			498.8*	91.9*			
100-3C	2.17	8.4		92.3			502.4	93.0			
100-3D	4.08	6.9		93.7			508.8	94.6			
100-3E	6.0	6.0		94.5			512.6	95.6			
100-3F	24.0	--		--			--	--			
100-3G	48.0	--		--			--	--			
8x60	MVL	109		101-4A			150	0.5		10.4	ICP
			101-4B	1.0	8.7	92.0		501.1	92.4		
			101-4C	2.0	7.8	92.8		505.2	93.5		
			101-4D	4.0	6.1	94.4		512.4	95.2		
			101-4E	6.0	5.3	95.1		515.6	96.1		
			101-4F	24.0	3.5	96.8		522.4	97.6		
			101-4G	48.0	3.4	96.9		522.8	97.8		

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln}/Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal}/Mo_{max,i}) \times 100$ (See Appendix A)

TABLE B-III

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: 30/70 DMSO/TOLUENE (Continued-Part 2)

COAL MESH	CATALYST		SAMPLE ID 16103-	IMPREGNATION		Mo _{soil} (ppm)	ICP or XRF	EST. UP- TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{soil} (ppm)	UP- TAKE	
None	None	0	124-3	--	--	0.5ND	XRF	--	--	--	Reference soln.
8x60	Mo oct.	103	124-3A	70	0.58	76	XRF	26.2	--	--	CARN 93-005921 124-3 ref - after 18-20 days standing, precip. observed in 3A to 3E, no sediments in 3F and 3G - large scatter in Mo _{soil} so only estimated uptake
			124-3B		1.0	87		15.5	--	--	
			124-3C		2.0	79		23.3	--	--	
			124-3D		4.0	72		30.1	--	--	
			124-3E		6.0	69		33.1	--	--	
			124-3F		24.0	42		59.2	--	--	
			124-3G		48.0	30		70.9	--	--	
8x60	Mo oct.	104	125-4A	150	0.5	51	XRF	51.0	--	--	CARN 93-005924 124-3 ref - after 18-20 days standing, immiscible film observed at bot- tom of sample vials - large scatter in Mo _{soil} so only estimated uptake
			125-4B		1.0	30		71.2	--	--	
			125-4C		2.0	33		68.3	--	--	
			125-4D		4.0	11		89.4	--	--	
			125-4E		6.0	13		87.5	--	--	
			125-4F		24.0	5ND		95.2	--	--	
			125-4G		48.0	5ND		95.2	--	--	

Notes:

- [1] Estimated % Uptake = $1 - Mo_{soil} / Mo_{soil,0} \times 100$
 [2] Calculated % Uptake = $Mo_{soil} / Mo_{soil,0} \times 100$ (See Appendix A)

TABLE B-IV

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: IMPREGNATION SOLUTION: TOLUENE

COAL MESH	CATALYST		SAMPL E ID 16103-	IMPREGNATION		Mo _{soln} (ppm)	ICP or XRF	EST. UP- TAKE [1]	CALCULATED [2]		COMMENTS
	TYPE	ppm		Temp. (°F)	Time (h)				Mo _{coal} (ppm)	UP- TAKE	
None	None	0	134-5	--	--	5ND	XRF	--	--	--	Reference soln.
-70	MVL	101	134-5A	150	0.5	84	XRF	16.8	85	16.8	CARN 93-005926 134-5 ref - after up to 15 days standing, no precipitates observed in the samples
			134-5B		1.0	78		22.8	113.5	23.4	
			134-5C		2.0	77		23.8	118	25.4	
			134-5D		4.0	74		26.7	130.8	29.4	
			134-5E		6.0	68		32.7	154.8	36.3	
			134-5F		24.0	54		46.5	207.3	50.6	
			134-5G		48.0	39		61.4	259.8	65.6	
-70	MVL	103	135-6A	70	0.5	92	XRF	10.7	55	10.7	CARN 93-005927 134-5 ref. - after up to 15 days standing, no precipitates observed in the samples
			135-6B		1.0	92		10.7	55	11.2	
			135-6C		2.0	90		12.6	64	13.6	
			135-6D		4.0	87		15.5	76.8	17.2	
			135-6E		6.0	88		14.6	76.8	18.1	
			135-6F		24.0	82		20.4	95.6	23.7	
			135-6G		48.0	73		29.1	127.1	33.2	

Notes:

[1] Estimated % Uptake = $(1 - Mo_{soln} / Mo_{soln,0}) \times 100$

[2] Calculated % Uptake = $(Mo_{coal} / Mo_{max}) \times 100$ (See Appendix A)

TABLE B-V

SUMMARY OF EXPERIMENTAL CONDITIONS AND RESULTS: FURTHER SWELLING OF COALS SWOLLEN/IMPREGNATED WITH 30/70 THF/TOLUENE

**Ambient swelling with fresh 30/70 THF/toluene
Mo in coal and swelling solution measured by ICP**

COAL MESH	SAMPLE ID 16103-			Swelling time	Mo _{soln} (ppm)	Mo _{coal} (ppm)		COMMENTS
	Starting coal	Final swollen coal	Final swelling solution			Meas.	Calc. [1]	
8X60	83-3	--	--	0	--	2ND	--	Dry coal analysis
8x60	82-3	83-1	83-4	48.0 hr	1.0	370	445	CARN 92-023766
-70	82-4	83-2	83-5	48.0 hr	1.7	500	511	CARN 92-023766
-70	84-3	---	--	0	--	420	409	CARN 92-00218 part of dried coal from 84-2 series
-70	84-2	84-4	84-5	14 days	0.9	410	409	CARN 92-00218

Notes:

[1] Calculated Mo concentration on the simultaneously swollen and impregnated coals as outlined in Appendix A (i.e., on the starting coal for the subsequent swelling performed). Comparison of the measured Mo on the subsequently swollen coal and the calculated concentration on the starting coal indicates no re-extraction of the Mo by the swelling solution.

APPENDIX C

APPENDIX C.

CALCULATION OF MOLYBDENUM UPTAKE BY COAL

For the simultaneous swelling and impregnation experiments where samples were withdrawn at given times from the same starting coal-solvent slurry, the sample withdrawal depletes the solvent in molybdenum. The corrections for Mo concentration on the coal and the remaining available Mo for uptake by the coal are discussed.

The major assumptions are: (1) there is negligible coal loss from the slurry with the sampling; and (2) the solution density is approximately unity.

At a given sampling schedule i , the concentration of Mo on the coal is given by:

$$MO_{coal,i} = MO_{coal,i-1} + (MO_{soln,i-1} - MO_{soln,i}) \times \frac{V_{soln,i}}{W_{coal}} \quad (1)$$

where the subscripts i and $i-1$ refer to any two successive sampling schedules

MO_{coal} is the concentration of Mo (on coal)

MO_{soln} is the concentration of Mo in the sampled solution

V_{soln} is the volume of the solution remaining

W_{coal} is the weight of the coal in the slurry (assumed constant at 100 g).

At any given time, the amount of available Mo for uptake by the coal is $MO_{coal} = MO_{max}$. This is calculated from

$$MO_{max,i} = MO_{max,i-1} - MO_{soln,i-1} \times \frac{V_{sample,i-1}}{W_{coal}} \quad (2)$$

where V_{sample} is the volume of the sample withdrawal (constant at 25 ml)

Note that

$$MO_{max,0} = MO_{soln,0} \times \frac{V_{soln,0}}{W_{coal}} \quad (3)$$

where $MO_{soln,0}$ is the initial Mo solution concentration (e.g., 100 ppm)

$$V_{soln,0} = 500 \text{ ml}$$

Catalyst uptake is then estimated by

$$Uptake_i = \frac{MO_{coal,i}}{MO_{max,i}} \quad (4)$$

Assuming the catalyst uptake is irreversible (see discussion in Experimental section), then the concentration of Mo on the coal can either increase or remain constant with time. This can only happen if $MO_{soln,i-1} \geq MO_{soln,i}$. For cases where $MO_{soln,i-1} < MO_{soln,i}$ (due to experimental error), it is assumed that

$MO_{\text{coal},i} = MO_{\text{coal},i-1}$ and $MO_{\text{max},i}$ is calculated from Equation (3) using the measured value of $MO_{\text{soln},i-1}$.

In cases where there is fluctuation of $MO_{\text{soln},i}$ values, no correction is applied and uptake is estimated by

$$Uptake_i = 1 - \frac{MO_{\text{soln},i}}{MO_{\text{soln},0}} \quad (5)$$

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