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CATALYSTS AND PROCESS DEVELOPMENTS FOR TWO-STAGE LIQUEFACTION

Final Technical Report

(10/01/89-09/30/92)

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By

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EXECUTIVE SUMMARY

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

The major results are summarized here and they are described in more detail under each Task. In Tasks 2 and 3.1 and 3.3 for coal pretreatment and beneficiation, it was shown for coal handling that drying of both lignite (Martin Lake, Texas) or subbituminous coals (Black Thunder, Wyoming) using warm air, vacuum oven or exposing to air for long time was detrimental to subsequent liquefaction. Coal beneficiation is done to remove mineral matter and unreactive components (inertinites) from the coals prior to liquefaction. Both laboratory and bench-scale beneficiations indicated that in order to achieve increased liquefaction yield for Illinois No. 6 bituminous coal, size separation with in sink-float technique should be used. With this method, the fines fraction is rejected to reduce mineral matter & inertinites and low density fraction (float) is separated. For Black Thunder coal, the best beneficiation was aqueous SO_2 treatment, which reduced mineral matter. The same beneficiation was also suitable for Spring Creek subbituminous coal if sodium removal is necessary. In case of Martin Lake lignite, the fines should be rejected prior to aqueous SO_2 treatment and sink-float gravity separation. Pretreatment in coal-derived solvent or tetralin, even in presence of soluble catalyst showed little decarboxylation in temperatures

up to 700°F. Up to 5 wt% of CO_x is removed when the temperature is increased up to 800°F. A slight increase in liquefaction yield was seen by pretreating the Black Thunder coal with acetic acid, however, aqueous SO_2 treatment is more effective and preferred. Caustic pretreatment was shown to be detrimental to liquefaction.

In liquefying coals with supported catalysts in both first and second stages, coal conversion was highest (93%) with Illinois No. 6 coal, which also had the highest total liquid yield of 80%, however, the product contained unacceptably high level of resid (30%). Both low rank coals (Black Thunder and Martin Lake) gave lower conversion (85-87%) and liquid yields (57-59%), but lighter products (no resid). The analysis of spent first stage catalysts indicated significant sodium deposits from Black Thunder and calcium from Martin Lake liquefactions causing severe deactivation. The second stage catalysts were in better condition showing high surface areas and low coke and metal deposits. The use of dispersed catalyst in the first stage would combat the severe deactivation that was seen, especially liquefying Black Thunder coal.

In Task 3.2.1, first stage catalyst testing, the high temperature liquefaction study with Illinois No. 6 coal showed that the use of supported AMOCAT™ 1C above 820°F is not recommended due to significant deactivation. Using dispersed Molyvan L in the first stage and supported AMOCAT™ 1C in the second stage is a good combination. Molybdenum on sulfated iron oxide (Wender's catalyst) was even better than Molyvan L, and if the preparation cost would be low enough, this would be the

preferred catalyst for Illinois No. 6 coal liquefaction. Powdered molybdenum carbide and nitride did not perform as well as oil-soluble molybdenum catalysts. For Black Thunder coal liquefaction, molybdenum on Wender's sulfated iron oxide and a sulfiding agent again showed the best performance. Supported catalysts like AMOCAT™ 1C gave high initial coal/resid conversion but deactivated quickly from coke and calcium deposition. Prehydrogenation of the solvent (hydrogen-rich) was shown to improve Black Thunder coal liquefaction.

In Task 3.2.2, second stage catalyst screening, various NiMo catalysts had similar activities for resid conversion and it is difficult to develop resid conversion catalysts due to deactivation by coke and asphaltenes. Noble metals (Pt, Rh, Ir) were poisoned by sulfur in the feed. Molybdenum carbides and nitrides had good initial activities on active site basis, however, low activities on volume basis.

In Task 3.2.3, the screening results from the mini-ager unit warranted further testing of the Sandia's hydrous titanate catalysts in the continuous two stage unit. These catalysts, especially thin film titanate on AMOCAT™ support with NiMo promoters showed significantly high distillate yields compared to the reference AMOCAT™ 1C catalyst. The Sandia catalyst should be tested with other heavy feedstocks in the future.

This project had an extension for an additional year and its total value was $1,946,990.

BACKGROUND

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

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

There are no commercial direct coal liquefaction plants in operation anywhere in the world. However, several direct coal liquefaction

technologies, such as the H-coal and the Exxon donor solvent processes, have been extensively studied. For many years, the most promising direct coal liquefaction route was a two-stage, close-coupled catalytic liquefaction process studied at the Advanced Two-Stage Coal Liquefaction Facility at Wilsonville, Alabama. This facility is now shut down. It served as a research and demonstration plant to test new process options and catalysts for converting coal on a 6 tons of coal per day scale. HRI has currently a 3 ton/day DOE-supported proof-of-concept facility. Projected costs for direct coal liquefaction have dropped from over $90 per barrel in 1981 to about $36 per barrel today primarily because of improvements tested and demonstrated at Wilsonville. While the cost is still high, direct coal liquefaction by the two-stage process continues to show improving economics and viability as a commercial technology.

The two-stage, close-coupled liquefaction process is a hydrotreating process that is conducted in two reactors in series with minimal residence time between reactors. This has been designated as "close-coupling." The first reactor is the primary coal conversion reactor where coal, a recycled coal-derived solvent, and hydrogen react to produce a hydrogenated coal product slate. The first reactor may be operated as either a catalytic or a thermal (non-catalytic) stage. The second reactor is operated with catalyst and serves to upgrade the first stage products by removing oxygen, nitrogen, and sulfur heteroatoms, increasing the hydrogen content of the products, and further reducing the boiling point of the products. The process is optimized to produce a maximum distillate product slate, optimum hydrogen utilization, high coal conversion, and

sufficient coal-derived solvent for recycle. While the class of reactions taking place in both reactors are similar, each reactor sees a different feedstock because of the ongoing conversion. It is thus probable that each reactor will need to be optimized to produce the best overall liquefaction process. Two obvious areas for improvement to the two-stage process are improved catalysts and improved process options to reduce hydrogen consumption.

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

PROGRAM OBJECTIVES

The overall objectives of this program were to develop and evaluate new catalyst formulations and process improvements for use in two-stage, close-coupled coal liquefaction. Improved catalysts are needed that can

lead to higher coal conversion at lower temperatures while maintaining high distillate yields. First stage catalysts were optimized primarily for enhanced coal conversion, and second stage catalysts for coal-resid upgrading. Process improvements included pretreatment to lower the oxygen content and unreactive components in coal prior to liquefaction. This program required close cooperation between Amoco Oil and other Department of Energy-sponsored research efforts, particularly the now shutdown Wilsonville Advanced Two-Stage Coal Liquefaction Facility, where some of the technology studied here was demonstrated.

PROJECT DESCRIPTION

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

Our overall approach to catalyst development was to prepare new formulations and modify existing refinery catalysts as candidates for

either first or second stage coal liquefaction processing. First stage catalysts need to be accessible to large coal fragment molecules and promote both further fragmentation and hydrogen transfer to radical fragments. Second stage catalysts are required to promote aromatics saturation and heteroatom removal as well as reduce molecular weight to produce usable distillable liquids.

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

Seven tasks were identified to bring about the above objectives. Task 1 called for the completion of a detailed project management plan, which was issued. Task 2 was a general laboratory support task for the coal

liquefaction tests. It provided the analytical support for characterizing most of the liquefaction samples and catalysts being tested. It included microautoclave tests to more fully understand the results of larger scale experiments and qualification of solvents used or produced during liquefaction. Task 3.1 was directed toward determining the liquefaction behaviors of standard coal samples and comparing them with the beneficiated or pretreated samples. Pretreatment procedures emphasized methods for oxygen removal and beneficiation to remove ash and inert materials.

Catalyst development and testing were done under the three parts of Task 3.2. Task 3.2.1 was used to test a series of candidate first stage catalysts and the best second stage catalysts as first stage catalysts with Illinois No. 6 bituminous and Black Thunder subbituminous coals in our continuous pilot plant unit. The objective was to identify a high-activity first stage catalyst.

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

Other process developments were evaluated under Task 3.3. Decarboxylation of low-rank coals by hydrothermal and caustic- or catalyst-aided

treatments were tested. The reporting of the results from Task 3.3 is done under Task 3.1, since decarboxylation and acid-base treatments fit in the coal pretreatment section, where beneficiation is also discussed.

RESULTS AND DISCUSSION

Task 2: Laboratory Support and Microautoclave Runs

In this task, general analytical support was provided for characterization of catalysts and liquefaction samples. In addition, micro- and batch autoclave tests were conducted to characterize the liquefaction behavior of the coals and to qualify solvents.

EXPERIMENTAL

Description of Research Units

Prior to describing the work in detail in Task 2, it is pertinent to briefly explain the various research microunits and pilot plants used during this contract. They were as follows:

1. Microreactors - 20 ml reactors that are immersed in a pre-heated sand-bath that allows rapid screening of coals and solvents and provides a test for initial activity.

2. Batch Autoclaves - 300 ml Autoclave Engineers reactors with glass liners.

3. Pilot plants

   a) AU-44L, a continuous flow single-stage CSTR unit with 300 ml reactor capable of operating with coal slurries. It's limited to short space times (20-40 minutes) and can only be operated with dispersed catalysts.

   b) AU-51L and AU-135L, two-stage continuous flow units with two one-liter reactors capable of operating with coal slurries. These reactors can be configured with catalyst baskets. They are primarily operated with long space times (1-2 hours) and can provide catalyst deactivation data.

   c) AU-126L, a catalyst mini-ager flow unit with five parallel fixed bed reactors in a single sand bath, capable of studying initial activity and aging characteristics of up to five catalysts at one time. Only coal liquid feeds can be used.

Experiments in Task 2 were carried out in a microautoclave system, SGU-1 (Figure 1), and a 300 cc autoclave. SGU-1 consisted of 50 cc tubular reactors in a sandbath, which were charged with 15 g coal/solvent blend, pressurized with 500 psig of hydrogen. The heat-up and cooling times were fast (1-3 minutes). The 300 cc autoclave was a standard Autoclave Engineer's unit with a glass liner. While the heat-up and cooling times

in the autoclave are longer, larger samples (75-90 g) can be tested and if presoak is needed, it can be done without air exposure. Reaction products were analyzed using Soxhlet extraction with toluene, THF and hexane. Coals of varied ranks were tested raw, beneficiated and dried.

RESULTS

Solvent characteristics were evaluated in microautoclave tests at varying conditions and solvent/coal ratios (Table 1) using Indiana No. 5 coal (Old Ben Mine). Conversion to THF solubles was insensitive to varying conditions, however, the level of toluene solubles was dependent on operating conditions and thus it was used for comparing solvent qualities in further studies.

Microautoclave Testing of Beneficiated Coals

The objective of beneficiation is to remove mineral matter and unreactive components from coals prior to their liquefaction. More detailed discussion on coal beneficiation is in Task 3.1. Five drums of Burning Star Illinois No. 6 coal were received; three drums were pulverized under nitrogen at Resource Engineering and two drums were beneficiated by heavy media (magnetite) separation at Hazen Research. These samples were liquefied using tetralin as a solvent (solvent to coal ratio of 2 to 1). In Table 2, the conversions at 755°F for 60 minutes to tetrahydrofuran (THF) solubles on moisture-ash-free basis (MAF) were 87.1% (Hazen sample) and 65.6% (Resource Engineering sample). The conversion for the sample

from Resource Engineering did not improve at higher temperature and it was concluded that this sample was contaminated and consequently it was discarded.

Microautoclave runs were also made with beneficiated Martin Lake lignite from Texas. Table 3 shows high levels of conversion (86-88%) to THF solubles with the fine (-60 mesh) lignite sample. Conversion levels of the coarse fractions (raw, sulfurous-acid treated, overflow and underflow) varied between 76 and 86%.

Testing of Dried or Aged Coals

Experiments with dried/aged Black Thunder subbituminous coal and Martin Lake lignite were carried out using both the microautoclave, SGU-1 and batch autoclave reactors. The samples were subjected to one or more of the following drying and/or aging procedures:

1. Drying overnight in vacuum oven with nitrogen at 210°F.
2. Partial drying for a specified time in air at ambient temperature.
3. Partial drying in flowing steam at 220°F followed by nitrogen at ambient conditions.
4. Heating in boiling tetralin (405°F) using Dean Stark apparatus to azeotrophe the water over to a condenser for removal.

RESULTS

Black Thunder Subbituminous Coal

The reference liquefaction runs with raw Black Thunder coal and tetralin (solvent/coal ratio of 2/1) are given in Table 4. As expected, higher conversions to THF solubles were obtained with increasing temperature. The liquefaction results of the dried and aged samples in Table 5 show that the coal conversion decreased from 87 to 80% when the coal was dried at 210°F overnight in a vacuum oven. However, a limited aging by air exposure (overnight) with some drying was not detrimental to conversion as seen in Table 5. Comparable results were also seen in a test, where the sample exposed to air overnight showed similar conversion to THF solubles as a non-oxidized sample, however, resid conversion was lower, which shows some loss in reactivity (Table 6). Detailed results of the latter experiment are discussed in Task 3.1 Feedstock Effects.

Martin Lake Lignite

The reference runs were done in 300 cc autoclave at 750°F and at 825°F with raw lignite (Tables 7-9). Again, as expected, higher conversions to THF solubles were seen at increased temperature or increased reaction time: 69% at 750°F and 81% at 825°F; 69% at 750°F for 10 minutes and 81% at 750°F for 60 minutes (Tables 7-9).

The drying of Martin Lake lignite overnight in a vacuum oven at 210°F was detrimental for subsequent liquefaction (Tables 7-9). Similarly, air exposure for longer periods of time, or warm air (140°F) decreased the conversion considerably (Table 8). The conversions to THF, toluene and hexane solubles decreased in both cases between 10-15%. Even if water was removed by azeotrophing it overhead with boiling tetralin using Dean Stark apparatus, conversions fell in subsequent liquefactions (Table 8). On the other hand, partially drying the lignite for a short time, only minimal loss of conversion was seen. Further testing with overnight air exposed sample showed again no loss of conversion to THF solubles but 15% more resid (Table 10). More detailed discussion of this experiment is given in Task 3.1. For a reference, two liquefaction runs were made with retained samples of lignite from Wilsonville Run 255. As shown in Table 9, the lignite samples had relatively low moisture levels (11 to 16%), but they had aged as indicated by reduced liquefaction yields. It cannot be determined if the aging was due to the Wilsonville handling procedure or to subsequent storage.

SUMMARY ON COAL DRYING AND AGING

The drying of both Black Thunder subbituminous coal and Martin Lake lignite using warm air or vacuum oven was detrimental to subsequent liquefaction, as was exposure to air for extended periods of time (7 days or more).

Shorter exposures to air showed very little or no loss in conversion, however, some loss in reactivity of the subbituminous coal or lignite occurred as indicated by increased resid make.

Task 3.1: Feedstock Effects

Feedstocks

In this task, the liquefaction behavior of various rank coals was studied and comparisons were made between beneficiated, pretreated and raw coals.

Three feedstock coals used in the program were Illinois No. 6 (bituminous), Wyoming Black Thunder (subbituminous) and Texas Martin Lake lignite. The feedstock analyses are in Table 11.

Beneficiation

The objectives of the beneficiation study were to remove mineral matter and unreactive components from the coals prior to liquefaction and evaluate the liquefaction behavior of the beneficiated samples.

Both physical and chemical beneficiations were used, where the goals and methods are different. In physical beneficiation, the goal is to reduce mineral matter and unreactive coal macerals (physical discrete constituents of coal) such as inertinites by size (redistribution of fine mineral matter) and by gravity separation (inertinite reduction in low

density fractions). In chemical beneficiation, the goal is to reduce the level of alkali and alkaline metal cations associated with carboxylic acids in low rank coals by washing with mild acidic solution (Figure 2). Both laboratory and bench-scale experiments were conducted.

Laboratory-Scale Beneficiation

Martin Lake lignite samples were beneficiated using a combination of sizing, aqueous sulfur dioxide treatment, and sink/float density gradient separation. This work was done in cooperation with Professors A. Davis and P. Luckie of Pennsylvania State University. The goal was to reduce the levels of ash and unreactive macerals. The results of this work are reported in Appendix 1. The major findings are summarized here.

Martin Lake lignite contains 13.4 wt% ash and 13.3 wt% inertinite macerals. Both of these are generally detrimental to liquefaction. Density gradient separation is often an effective technique for removing mineral matter. Because the less reactive inertinites are more dense than the reactive vitrinite and exinite macerals, they can be removed with high density fraction during density gradient separation. Low rank coals also contain alkali or alkaline earth metals tied up as carboxylic acid salts that cannot be removed by density gradient separation. However, Amoco demonstrated that aqueous SO_2-treatment was effective in removing these metals. The first sample was heavy media separated (< 1.40 specific gravity) and the ash content decreased to 6.2% but the overall recovery was only 62%. The second sample was treated with SO_2 prior to the

separation and contained only 2.5% with 82% overall recovery. Thus the combined SO_2 and density gradient separation produced less ash and had higher recovery.

Petrographic analyses of the various fractions were performed to determine the distribution of macerals after the treatment process. As expected, the reactive vitrinite fractions were concentrated in the < 1.40 specific gravity fraction and the inertinites were in the heavy (> 1.40 sp. gr.) fraction. The exinites were distributed in both fractions and seem to be associated to some extent with the mineral matter and cannot, therefore, be easily removed by density gradient separation.

Bench-Scale Beneficiation

Large-scale beneficiation of Illinois No. 6 coal, Martin Lake lignite and Spring Creek coal were done at Hazen Research, Inc. (Boulder, Colorado) in order to prepare sufficient samples for two-stage liquefaction experiments.

Illinois No. 6 Coal

Two drums of Illinois No. 6 coal were crushed to pass 8 mesh screen. The fines (-60 mesh) sample was removed and remaining 8 x 60 mesh sample was isolated. A sample was set aside for liquefaction tests and the rest was separated by using heavy media cyclone. Based on laboratory results, a bulk sample was separated using a magnetite slurry with a specific gravity

of 1.35, which resulted in a 70/30 split between overflow and underflow coal product. The ash contents were 6.5% (overflow) and 18.5% (underflow). The procedure, which includes several steps of screening, pulverizing, filtering, is in Figure 3. The analyses done by Commercial Testing and Engineering Co. are in Table 12.

Martin Lake Lignite

Two drums of Martin Lake lignite were beneficiated using a combination of sizing, density gradient separation and SO_2-treatment (Figure 4). The analyses of the beneficiated lignite samples are given in Table 13. The ash level in the fines (-60 mesh) was high and thus, these fines could not be used as a plant fuel in a commercial liquefaction facility. The treatment of the coarse lignite with aqueous SO_2 reduced the ash from 13.2 to 10 wt%. The overflow contained 5.6 and the underflow 39.3 wt% ash.

Spring Creek Coal

Spring Creek subbituminous coal was used in Wilsonville Run 258 and was chosen as a feedstock because of its low ash content of 4%. Although initial liquefaction results were good, performance rapidly declined, and the liquefaction catalyst was shown to be heavily contaminated by sodium salts and coke. The ash levels of Spring Creek coal were low but one of the major metals was sodium, which is a powerful catalyst poison. SO_2 washing of Spring Creek coal should remove most of the sodium, and size and density separation could remove additional ash. Because of potential

large benefits of production of a reactive, super-low ash feed, beneficiation studies with Spring Creek coal were substituted, with DOE's permission, as one of the tests.

Fresh samples of Spring Creek coal were obtained from Nerco Coal Corporation. Portions of the coal were pulverized under nitrogen and subsequently stored at 40°F. The samples were beneficiated by SO_2 treating and sink/float density separation.

The product distribution of a bench-scale beneficiation run made with Spring Creek at Hazen Research, Inc., is shown in Figure 5. Size separation (Table 14) gave a fines stream with lower hydrogen content (H/C of 0.83 vs. 0.89) and a higher ash content (6.01 vs. 3.99), which probably should be used as fuel rather than as a liquefaction feedstock. Because of the small size of the fines stream, composition of the coarse stream and the starting feed were similar. Metals present in coarse and fines streams were quite different, with sodium and calcium enriched in the coarse sample and iron and silicon depleted in the coarse sample.

Aqueous SO_2 treatment (Table 15) removed most of the sodium and one third of the calcium, but did not significantly reduce total ash content. Much of the calcium was not removed, indicating that calcium was present in the form of clay minerals, not exchangeable organic carboxylate salts.

Density beneficiation of the SO_2 treated coal removed some ash in the sink fraction, showing some selectivity for removal of silicon minerals and

enrichment of calcium minerals in the float fraction. Ash removal by density beneficiation was small (3.3% vs. 3.8%), and would not be economically justified.

SUMMARY ON BENEFICIATION

1. Size separation in combination with gravity (sink/float) beneficiation is effective in preparing coal for liquefaction. With Burning Star Illinois No. 6 coal and Martin Lake lignite, crushing followed by screening to remove fines resulted in coarse fractions that were lower in ash content than the feed coal.

2. Heavy media gravity beneficiation was shown to be effective for ash reduction. With bench-scale separation of Illinois No. 6 coal, the ash content of the float and sink fractions were 6.5 and 18.3% respectively, while that of the feed was 10.7%. The recovery of the float fraction was 66% of unit feed. However, recovery can be increased without a substantial increase in ash content of the float fraction.

3. With raw Martin Lake lignite in laboratory-scale equipment, the float and sink fractions contained 6.8 and 18.4% ash, respectively. In this case, recovery of the float fraction was only 62%.

4. Aqueous SO_2 treatment of lignite improved ash removal. With Martin Lake lignite, about 30% ash removal was achieved in bench-scale runs, and up to 50% in laboratory-scale runs. Subsequent density separation resulted in a float fraction containing only 5% ash, and recovery was about 65% of the overall feed and 75% of that to the gravity unit. Again, it is likely that these yields can be increased by optimizing the treatment procedure and cut points.

5. Size beneficiation of Spring Creek subbituminous coal rejected a low-hydrogen, high-ash fraction. Washing with aqueous SO_2 removed sodium and some calcium, but did not significantly decrease ash content. Density separation gave little additional benefit. Samples severely degraded in cold storage, which may indicate that Spring Creek coal is very sensitive to storage and handling.

Liquefaction of Beneficiated Samples of Illinois No. 6 Coal

The objective of experimentation was to evaluate the liquefaction behavior of the various fractions of beneficiated Illinois No. 6 coal using a two-stage, continuous flow unit.

EXPERIMENTAL

The analyses of beneficiated Illinois No. 6 coal are given in Table 12. Portions were pulverized and screened under nitrogen and subsequently stored at 40°F prior to use.

The liquefaction solvent (V-203/V-1074) was obtained from the Wilsonville facility. It was derived from the liquefaction of Illinois No. 6 coal in Run 257. The analysis of this solvent is given in Table 16.

The bench-scale liquefaction runs were made in AU-51L, which operates in a once-through, continuous mode with regard to H_2, solvent, and coal, and in a batch mode with catalyst. Each stage functions as a continuous, stirred-tank reactor (CSTR). Presulfided AMOCAT™ 1C catalyst was used in both reactors. Operating pressure was 2500 psig, temperatures in the two stages were 790°F and 740°F, and nominal residence times were 1.5 and 1 hour, respectively. Feed slurries with the samples of Illinois No. 6 coal were 33/67 coal/solvent. Catalyst was lined out for about one week. Subsequent samples were run for about three days each. A solvent only period was also included.

Coal conversion was defined as tetrahydrofuran (THF), toluene, and hexane soluble material determined by Millipore filtration. Modified ASTM distillations were carried out with subsequent conversion to atmospheric pressure. Products were analyzed for C, H (Leco), N (Auto Kjeldahl), S (X-ray fluorescence), and metals (Inductively Coupled Plasma spectroscopy/ICP).

RESULTS

Differences in conversion, resid yield, and hydrogen consumption in the liquefaction of the Illinois No. 6 coal fractions are shown in Table 17.

The sink fraction produced about 2% less conversion to THF solubles than the float fraction. This is indicative of a high inertinite content. However, liquid product from the sink fraction was of very high quality, containing virtually no resid. Conversely, product from the float fraction contained higher boiling distillate but less resid than product derived from the reference coarse coal. Therefore, sink/float beneficiation of Illinois No. 6 coal did more than just change the level of unconverted coal and ash. The removal of some of the mineral components, which probably had catalytic properties, affected the upgrading aspects of liquefaction.

The effect of beneficiation is also indicated by the level of hydrogen consumption. An internal catalyst was present in the sink fraction, as indicated by hydrogen consumptions of 6.0% for the sink fraction and 4.7% for the float fraction. Iron was the likely internal catalyst as shown from the metals analyses in the unconverted coal solids (Table 18). The sink sample was enriched in Fe, and to a lesser extent Ca. Lower nitrogen and oxygen contents of the sink fraction (Table 12) may have contributed to the resulting higher quality of the resulting liquefaction product.

The product derived from the float fraction was about the same as that from the reference coarse sample in terms of conversion to the various solubility fractions and boiling range of products. First, about two-thirds came from the coarse fraction. Secondly, there may have been an effect of minerals. The float fraction contained a lower iron content, which is known to be catalytic. However, the contents of calcium, iron,

and other metal salts in the float fraction were also lower (Table 18), and this may have resulted in an offset in conversion.

A reference solvent only period was added near the end of each run to measure the extent of solvent upgrading. Corrections for solvent upgrading reactions were subtracted from the reported results (Table 17). These corrections were assumed to be constant throughout the run, but they actually should have been larger at the beginning of the run when the catalyst was fresh. The results given in Table 17 were obtained with lined-out catalyst, so yields should provide a good basis for evaluating the beneficiated samples as feedstocks.

A period using reference coarse coal was included after the solvent only period to study catalyst deactivation. Results from this period (Samples 21-22) gave an unusually high C_4-650°F distillate yield, high apparent conversion (98.9%), and 650°F+ residue that could not be fractionated. The high yield of light distillate was probably a result of solvent cleaning of the catalyst prior to this period; such cleaning gives a temporary increase in activity. Apparent high coal conversion probably resulted from holdup of solids in the catalyst bed. Because results from the end-of-run reference sample were not representative, they were not used.

Elemental analyses of fractions that boiled in the same range were similar (Table 19) with the exception that the heteroatom content slowly increased with sample number, reflecting slow catalyst deactivation. All fractions

boiling below 975°F were low in sulfur (less than 0.1%), and even the residue (975°F+ and unconverted coal) from the coarse and float samples contained only about 1% sulfur. Residue from the sink sample contained over 2% sulfur, which was probably due to mineral matter (pyrites, etc.) Distilled fractions derived from the sink sample were low in nitrogen, reflecting either the low nitrogen content of this fraction or the catalytic activity of the mineral matter.

In summary, differences in elemental analyses of distilled fractions from beneficiated samples were small. However, there were significant differences in mineral content and the yields of distillable product from the beneficiated samples. The float sample was the preferred feedstock due to its low ash content (6.5%) and high distillate yield. The coal sink fraction should be rejected in the design of a commercial unit due to its high ash content (18.3%), even though the product here was especially light.

SPENT CATALYST ANALYSES

Analyses of spent catalyst recovered from the Illinois No. 6 run are given in Table 20. The first stage catalyst contained larger deposits of coke and metals than the second stage catalyst. This first stage catalyst had lower surface area and pore volume. This difference in catalyst characteristics is normal for two stage catalytic liquefaction. Deactivation of the first stage catalyst was severe, but sufficient pore

volume was available to provide reasonable hydrogenation activity in the first reactor even at the end of the run.

Liquefaction of Beneficiated Samples of Martin Lake Lignite

The objective was to evaluate the liquefaction behavior of the fractions of sulfurous acid washed and density beneficiated Martin Lake lignite using the two-stage continuous flow unit.

EXPERIMENTAL

The analyses of the beneficiated samples are given in Table 13. Feedstocks differed primarily in ash and sulfur content. Size beneficiation gave a coarse fraction with 13.1% ash compared to 14.6% ash in the combined feed. The fines fraction contained 23.6% ash which was enriched in silicon but had a lower amount of iron (Table 21). The SO_2 washed coarse fraction contained 10.0% ash, reflecting removal of calcium, magnesium, sodium, and some iron, but the SO_2 was retained in the sample, increasing sulfur by 0.9%. Adsorbed SO_2 could probably be removed by additional washing. Subsequent density beneficiation gave a float fraction with a normal sulfur level. The SO_2-treated float fraction contained 5.6% ash; roughly equal portions of all metals were removed. The SO_2-treated sink fraction was heavily contaminated with magnetite.

All lignite samples were dried under ambient nitrogen and sieved through a 100 mesh screen for liquefaction tests. The liquefaction solvent

consisted of 650 to 1000°F product that was derived from the liquefaction of Black Thunder subbituminous coal in Wilsonville Run 258. The analysis of this solvent, designated V-203/V-1074, is given in Table 16.

Bench-scale liquefaction runs were made in AU-51L in the same manner as described above for the Illinois No. 6 samples, except that feed slurries were 25/75 lignite/solvent. Two runs were made; both runs included periods with sulfurous acid-washed coarse lignite and solvent only periods at the end to serve as tie points.

RESULTS

Conversion of sulfurous acid-treated lignite to THF solubles was higher than that of the untreated lignite (Table 22). The second lignite liquefaction run was made only with samples of sulfurous acid treated lignite. Surprisingly, conversions of both the sink and float samples were lower than that of the coarse treated material that was used as their feedstock (Table 23). The treated sink fraction gave only 82% conversion, which is consistent with a high inertinite level.

The yield of resid from sulfurous acid-treated lignite was significantly higher than from untreated lignite, 12% vs. -6%, respectively. The difference between resid yields in a plant with solvent recycle would not be as large. In this test, conversion of resid in the solvent was higher at the beginning of the run, which decreased resid yields from lignite.

However, there was at least 10% more resid produced from the treated lignite, regardless of contributions from solvent reactions.

High yields of distillable product, defined as 975°F- liquids, were obtained from the treated float and sink fractions. In fact, no resid was recovered from processing the treated float or sink fractions. There was a large negative resid yield in the case of the sink fraction, indicating that much of the resid present in the feed solvent was converted in addition to that generated from the lignite. The sink fraction was heavily contaminated with magnetite (Table 21), which apparently acted as an upgrading catalyst. Hydrogen consumption was 2% higher for the contaminated sink fraction, which suggests that magnetite acts as a hydrogenation catalyst when present at high levels.

Elemental analyses of the distilled fractions are reported in Tables 24 and 25. In general, fractions that boiled in the same range had similar elemental analyses, with the exception that heteroatom content slowly increased with sample number, reflecting slow catalyst deactivation. All fractions boiling below 975°F+ were low in sulfur (less than .03%), and even the residue (975°F+ and unconverted coal) samples contained less than 1% sulfur. (The high sulfur level in the SO_2-treated feed sample in the second lignite run is probably an error). Hydrogen to carbon atomic ratios for products from tie point periods were lower in the second lignite run (Table 26). Together with lower hydrogen consumption in this run, the lower H/C ratios are evidence of increased catalyst deactivation which was confirmed by spent catalyst analyses.

In summary, the SO_2-treated float fraction was the preferred feedstock due to its low ash content (5.6%) and high distillate yield. The sink fraction should be rejected as a liquefaction feedstock due to its high ash content and low conversion. The fines fraction should also be rejected due to its high ash content (23.6%). Elemental analyses of distilled fractions from all beneficiated lignite samples were similar.

SPENT CATALYST ANALYSES

Analyses of spent catalysts recovered from the beneficiated Martin Lake lignite runs are given in Tables 27-28. As in the Illinois No. 6 run, the first stage catalysts contained larger deposits of metals and coke than the second stage catalysts. The first stage catalysts also had lower pore volumes and surface areas, which is normal for two stage catalytic liquefaction. There was a sizeable difference in catalysts from the two lignite runs with higher deposits, lower pore volumes, and lower surface areas in the second run that used all SO_2-treated lignite feed. Severe deactivation in the second run was most likely from initial operation with the SO_2-treated sink fraction, which gave low conversion and may have caused heavy deposits on the catalyst. In spite of this deactivation, catalyst from the second run was still able to provide enough hydrogenation activity to produce a resid-free product from the SO_2-treated float fraction, the last lignite sample in the run. Bimodal catalysts like AMOCAT™ 1C catalyst have the advantage of good performance under conditions of severe deactivation, as was demonstrated in the second lignite run.

Liquefaction of Beneficiated Spring Creek Coal

EXPERIMENTAL

Feed slurries consisted of 33/67 mixtures of -100 mesh coal in Black Thunder solvent. The catalyst, molybdenum on sulfated iron oxide powder, was added directly to the feed (0.7% Fe and 100 ppm Mo/coal). The reactor temperature was 820°F, with a nominal residence time of 1.5 hours. Analyses of the beneficiated coal samples are given in Table 15.

RESULTS

Liquefaction of the coarse fraction before SO_2 treatment and the SO_2-treated coarse fraction were carried out 1.5 years after the samples were prepared. Although the samples were stored at 40°F under nitrogen (in plastic buckets), no conversion of the coal was seen in the continuous pilot plant run. These were the least-reactive samples that ever were encountered.

CONCLUSIONS ON BENEFICIATION

Illinois No. 6 Bituminous Coal:

1. Reject the fines fraction to reduce levels of mineral matter and inertinites.
2. Separate a low density (float) fraction to achieve increased liquefaction yield.

Black Thunder Subbituminous Coal:

1. Beneficiate with aqueous SO_2 treatment to reduce mineral matter.
2. No advantage for gravity separation.

Spring Creek Subbituminous Coal:

1. Beneficiate with aqueous SO_2 treatment only if sodium removal is necessary.

Martin Lake Lignite:

1. Reject the fines fraction to reduce levels of mineral matter.
2. Beneficiate with aqueous SO_2 treatment to remove alkali and alkaline metals, improve density separation and liquefaction.
3. Separate a low density (float) fraction to achieve increased liquefaction yield.

Pretreatment of Low Rank Coal to Decompose Oxygenates

Although pretreatment and decarboxylation studies were carried out under Task 3.3 (Additional Process Developments), the reporting of the results is done here after beneficiation, where it complements the section for coal treatments prior to liquefaction.

INTRODUCTION

There are numerous reasons to pretreat low-rank coals to reduce the content of organically bound oxygen prior to liquefaction. Low-rank coals are richer in oxygen than bituminous coals, and much of the additional oxygen is present as carboxylic acid groups and their salts. These groups bind water strongly, making low-rank coals expensive to dry. Also, water and metal ions liberated from the salts accelerate catalyst deactivation, and the metal ions retard liquefaction. Under liquefaction conditions, decarboxylation liberates CO_2 that lowers reactor H_2 partial pressure. This necessitates scrubbing CO_2 from recycle gas stream.

Some literature sheds light on the underlying chemistry of decarboxylation of coal. Steam pretreatment to activate coals for subsequent liquefaction has been studied by Ross,[1] Chao et al.,[2] and Graff and Brandes.[3] In each case, conversion of the pretreated coal was significantly enhanced, although the conditions of the subsequent conversion step differed widely. Recently, Brandes and co-workers[4] elucidated the chemistry responsible for this activation. Upon treatment with subcritical steam at 320°-360°C, the oxygen content of Illinois No. 6 coal decreased from 12.84% to 9.20%. However, a comparison of IR spectra showed that hydroxyl content was increased by the steam treatment. This was confirmed by O-alkylation, which indicated that the steam-treated coal contained 7.4 OH's/100 C's, while a sample heated under helium contained only 2.6 OH's/100 C's. The added OH-groups are largely phenols. Brandes, et al.[4] dried their steam-treated coals at room temperature under a flow of helium. In

contrast, decarboxylated coals were dried overnight at 110°C in the present work. Also, Ross has observed that hydrothermal activation is partially transient and can be lost on air exposure.[1]

Because decarboxylation occurs during the initial stages of liquefaction, it is likely that partial decarboxylation can be achieved during a presoak period before liquefaction. Therefore, a limited number of such experiments was included in the research plan of this project.

Testing in Batch Autoclave

EXPERIMENTAL

Samples of Martin Lake lignite and Black Thunder subbituminous coal were treated with solvent or water at elevated temperatures using one of the following conditions:

1) Contacting with water, as above, but with the addition of non-donor solvent, Panasol (methyl naphthalenes), to prevent air exposure during solids recovery using a modified agglomeration technique.

2) Contacting with hydrogen donor solvent, tetralin, to observe the combined effect of decarboxylation and pre-soaking.

The pretreatment and liquefaction experiments were carried out in the 300 cc batch autoclave (a standard Autoclave Engineer's unit with a glass liner). While heat-up and cooling times were 45 and 60 minutes, respectively, the vessel was at reaction temperatures of 750°F or more for only 5 to 10 minutes longer than that of the set reaction time. A total charge of 75 to 90 g was normally used. When water and panasol were used for pretreatment, the water was removed as a separate phase, and coal was retained in the organic phase. Tetralin was added to the organic phase for the subsequent liquefaction run. Liquefaction reaction products were analyzed using Soxhlet extraction with toluene, tetrahydrofuran (THF), and hexane, unless otherwise specified. Selected samples of gases from both the pretreatment and liquefaction runs were collected over water and analyzed using gas chromatography.

Caustic pretreatment experiments were made by charging Black Thunder coal with NaOH solution (1 or 5 wt%) to a batch autoclave, heating at the set temperature and time, and recovering the product slurry. A portion of the coal dissolved with the generation of a gel product. This gel was diluted with water and filtered using a 100 mesh screen. The filter cake was washed with additional water. The filtrate and wash water were then re-filtered. The filter cake was partially dried under a vacuum at 100°F. A sample of the solids was then liquefied in tetralin.

The organic and carbonate carbon contents of the aqueous phase were determined to observe the level of coal dissolution and to calculate an overall carbon balance.

Pretreatment runs using acetic acid were made in a similar manner, but direct filtration was used to recover the treated coal for sampling and liquefaction.

RESULTS

Presoaking in Donor Solvent

Laboratory-scale experiments were made in the 300 cc batch autoclave to observe the effect of presoaking upon decarboxylation and subsequent coal liquefaction of both Martin Lake lignite and Black Thunder subbituminous coal. Slurries of coal in tetralin (1/2 ratio) were heated under nitrogen (50 psig, cold) at temperatures between 400° and 600°F for 30 minutes. The products were cooled, gases vented and analyzed, and the slurries reheated for liquefaction using a hydrogen atmosphere (500 psig, cold) at conditions of about 825°F and 10 minutes. It is noted that the reaction intermediates were not exposed to air between the presoaking and liquefaction periods.

The results of the series using Martin Lake lignite are summarized in Table 29. The conversion of raw lignite to THF solubles was 82.3%, while those of the presoaked samples were in the range of 81.7 to 84.7%, so statistically hardly any effect of presoaking at reduced temperatures followed by liquefaction at 825°F was observed. An effect was seen in the conversion of coal to toluene solubles. The conversion of raw lignite to toluene solubles was about 71%, while those of the presoaked samples

(temperatures of 500° to 600°F) were in the range of 72 to 78%. With low conversion, there is a quite a bit of variation in measured yields to oils plus gases (hexane solubles) and to asphaltenes, thus these results will not be discussed here in any detail. These data are, however, available in each of the tables for the two coals.

The results of liquefying the pretreated Black Thunder coals are given in Tables 30 through 32. As shown in Table 30, the conversion of presoaked (607°F and 30 min.) coal to THF, and toluene solubles was the same as that of two runs with untreated coal when subsequent liquefaction was carried out at 750°F and 10 minutes. At liquefaction conditions of 810°F and 10 minutes, a slight increase was observed in the conversion of coal to toluene, and THF solubles as a result of presoaking at 605°F for 10 minutes (Table 31). When the treated coals were liquefied at the more severe conditions of 825°F and 10 minutes, conversions of raw and treated coals to THF and toluene solubles were essentially the same with averages of 87% and 77%, respectively (Table 32).

The above conversion data indicate that there is little advantage to presoaking Black Thunder coal or Martin Lake lignite in a hydrogen-donor solvent, such as tetralin, at temperatures up to 600°F. There was a nominal increase in coal conversion to toluene solubles of about 2% when the liquefaction runs were made at 810 to 825°F and a short reaction time of 10 minutes. However, our previous experience from runs made with different heat-up cycles shows that conversion equilibrates at long reaction times, such as that used at Wilsonville. Only the gases released

during the presoaking stage of the treatment of Martin Lake lignite were analyzed, as given in Table 33. The release of CO_2 was about 2.0 wt% CO_2 based MAF feed lignite at pretreatment temperatures of 500 and 550°F. The results of the two runs made using tetralin at 600°F were widely different with yields of 3.0 wt% (Run 164) and 7.2 wt% (Run 167). There may have been some un-recorded variation in reactor temperature that accounted for this difference. A pretreatment run (175) made with Panasol (methyl naphthalenes) resulted in an intermediate yield of 5.5 wt% CO_2.

The gases generated during the Black Thunder presoaking and liquefaction runs were analyzed. The results are summarized in Table 34. The CO_2 released during presoaking increased at higher temperatures as shown in the following summary. The CO_2 released during the liquefaction stage is also shown for reference.

CO_2 Released During Pretreatment and Liquefaction (Wt% MAF)

Coal Pretreatment, °F	Raw	400	500	600	
Presoaking	---	0.8	0.9	1.3	
Liquefaction	5.5	3.3	5.1	3.1	
Total	5.5	4.1	6.0	4.4	(Avg. 5.0%)

The amount of decarboxylation that occurred during the presoaking of Black Thunder coal in tetralin in the temperature range of 400 to 600°F was relatively small. The presoaking stage accounted for less than 25% of the

total CO_2 that was generated during the combined presoaking and liquefaction stages.

Presoaking in Water

Literature indicates that decarboxylation is only advantageous when the resulting treated coal is handled in the absence of air. To partially achieve this, experimentation was undertaken using feed mixtures of coal (or lignite) with water and Panasol. The goal was to have solvent coat the coal particles and provide a means to separate the coal from the aqueous phase in a manner similar to spherical agglomeration.

The reactor was charged with about 20g coal, 5g Panasol, and 40g of water. The slurry was heated to 600°F for 30 minutes. Typical maximum reactor pressures were about 1600 psig. After cooling, removal of most of the aqueous phase was carried out, tetralin was added, and the liquefaction run was made at about 825°F.

The procedure of adding Panasol to wet coal for subsequent removal of an aqueous phase is difficult in laboratory-scale equipment. It was found that a number of runs had to be aborted, because excess water remained and the pressure increased to the maximum rupture disk pressure during the subsequent liquefaction run.

The results of the successful Martin Lake lignite pretreatment and liquefaction run are summarized in Table 35. The levels of conversion of

treated lignite to THF and toluene solubles were about equal to those of the reference run made with untreated lignite.

The results of the runs made with Black Thunder coal are given in Table 36. Run 1 was planned to be made at liquefaction conditions of 825°F and 10 minutes; however, excess water remained and the run was terminated early due to excess reactor pressure. The liquefaction results are included for reference. Run 8 was made successfully. However, there was a significant decrease in coal conversion levels as a result of the pretreatment with water and Panasol. A sizeable amount of time was used in separating the phases, and the treated coal may have had excess contact with air.

The gas generated during the aqueous pretreatment of Martin Lake lignite was analyzed to determine the level of CO_2 formation. The results are summarized in Table 37. The yield of CO_2 at a pretreatment temperature of 500°F was 2.3 wt%, based on MAF coal. The average yield of the 600°F runs was 5.6 wt%. Within the range of reproducibility (0.6 wt%), the yield was not affected by the choice of liquid system (water, Panasol, or water plus Panasol).

The yield of CO_2 generated during the aqueous pretreatment of Black Thunder coal at 600°F was 2.8 wt% (Table 38, Run 1). When a sample of similarly treated coal was liquefied at 825°F, an additional 2.1 wt% CO_2 was generated. The total 4.9 wt% was nominally less than the yield of 5.5 wt% generated by the direct liquefaction of untreated Black Thunder

coal in tetralin. It is noted that the above 2.8 wt% is greater than the 1.3 wt% yield observed when pretreatment took place in tetralin.

The levels of decarboxylation of both Martin Lake lignite and Black Thunder subbituminous coal were relatively low at pretreatment temperatures up to 600°F. Yields of CO_2 were equal to or less than 6 wt%. This is equivalent to about 4.4 wt% oxygen, or about one-fourth of the organic oxygen content of the raw low rank coals. For reference, the yield of CO_2 approaches 7 wt% during thermal (non-catalytic) liquefaction of Black Thunder coal in the Wilsonville facility. Therefore, more severe pretreatment conditions were necessary, and experimentation was conducted using higher temperatures in the AU-44L continuous flow unit.

Presoaking with Additives

Pretreatment runs were made with Black Thunder coal with added molybdenum octoate or ferrous sulfate to explore alternate approaches for decarboxylation and liquefaction. The results of the molybdenum octoate series are given in Table 39. Runs 71 through 80 were made with the addition of a solution of molybdenum octoate (The Shepherd Chemical Company, Cincinnati, OH) at a level of about 2000 ppm Mo on feed slurry. Conversion of coal to THF and toluene solubles were about equal both with and without presoaking and with and without additive (Runs 71, 80 and 199). The level of THF solubles of Run 80 appears to be too low considering the level of toluene solubles. In Runs 74 and 77, coal with added molybdenum octoate was pretreated with water at 600°F, filtered in a

micropore unit, and then partially dried with a stream of nitrogen at ambient temperature. The liquefaction results indicate that the coal samples had lost some of their reactivity by the treatment. Perhaps excessive drying and/or exposure to air had occurred. These latter results are consistent with the concept that a process must be developed in which air exposure is avoided.

The results of experiments made with ferrous sulfate are given in Table 40. The ferrous sulfate was added as crystalline powder; therefore, two runs were made using a mild pretreatment (200°F, 30 min) for increased coal/catalyst contact before liquefaction. These mild pretreatment conditions were thought to be adequate for activation. Based on the liquefaction data, there was no benefit gained from adding ferrous sulfate by this method.

Pretreatment with Acids and Bases

The contacting of low rank coals with acids and bases can significantly affect subsequent liquefaction; therefore, exploratory laboratory-scale experiments were undertaken with emphasis toward the pretreatment aspects. The base used in the preliminary experiments was sodium hydroxide due to its reactivity in solubilizing low rank coals.[5] With respect to mild acid treatment, previously tests were done with low rank coal which was treated with aqueous SO_2 for cation reduction, so supplemental experimentation was limited to making runs with acetic acid at 200° and 400°F. For reference, extensive experimentation has been reported[5]

using the addition of hydrochloric acid. While this addition is beneficial, it has been studied widely and the presence of chlorides is detrimental for most liquefaction units, which are constructed of stainless steel. Therefore, no work was done with hydrochloric acid.

The results of the pretreating experiments in which Black Thunder coal was contacted with aqueous sodium hydroxide solution are summarized in Table 41. When the runs were made with 1 wt% caustic at 210°F at reaction times of 5 or 30 minutes, 2 to 4 wt% of the organic portion of the coal dissolved in the aqueous phase. About 25% of the dissolved material was CO_2 as carbonates. Therefore, little decarboxylation occurred. When the caustic concentration was increased to 5 wt%, about 30% of the organic portion of the coal dissolved at temperatures of 200° and 400°F. On the average, 12% of the dissolved organics were carbonates. This is equivalent to 4.2 wt% of the MAF coal being released as CO_2. Again, this is a fairly low level of decarboxylation considering that Black Thunder coal contains about 17 wt% organic oxygen.

It was very difficult to recover the solids from the caustic-treated coal slurries. The dissolved coal formed gel particles that blinded filter paper. After losing several runs, it was found that the slurry could be filtered through a 100 mesh screen. The cake was washed with water, and the total liquids were then filtered through coarse paper. If a process was to be developed using this caustic pretreatment step, more research in the area of solids separation would be necessary.

Three pretreatment experiments were carried out at a 30 minute reaction time using 5 wt% acetic acid solution; one at 200°F and two at 400°F. No appreciable dissolution of organics occurred as indicated by coal/solids balances of 100.6% through 103.3% (some retention of acetic acid) and a lack of color in the aqueous phase. The levels of demineralization were 28.2%, 35.2%, and 21.4% with an average of 28.3%. This level is about equal to 32% observed for aqueous SO_2 treatment. At ambient temperature, demineralization with acetic acid is much less effective than that with SO_2.

The analyses of selected samples of the pretreated Black Thunder coals are given in Table 42. The results fall within a normal distribution with the exception of that of the sodium hydroxide treated sample in which the H/C ratio was low and the ash level high. Results given in Table 43 confirm that sodium retention occurred as a result of caustic treatment, thereby accounting for the increased ash level. Table 43 also confirms that pretreatment with acetic acid results in a reduction of alkali and alkaline earth metals in the product coal.

Samples of the acid and base treated coals were liquefied using tetralin at 825°F and 10 minutes. The results are given in Table 44.

In comparing the results of Run Nos. 122 with 25, there is an increase of coal reactivity measured as THF solubles as result of acid treatment. However, at the higher reaction temperature (825°F), both the THF and toluene solubles are similar (Run Nos. 46 and 199). Considering

the above indicated reduction in cation content, there is some justification for further study of acetic acid treatment. However, since aqueous SO_2 treatment was more effective at lower temperatures, no further work was done with acetic acid.

Treatment with caustic solution does not appear to be beneficial as shown in Table 44. After Black Thunder coal was treated with 1 wt% sodium hydroxide solution, conversion to THF and toluene solubles decreased significantly. This decrease was greater than the 2 to 4% dissolution of coal into the aqueous phase that occurred during the pretreatment step. In the case of pretreatment with 5 wt% sodium hydroxide, a sizable fraction of the coal was dissolved into the aqueous phase (35% at 200°F and 28% at 400°F; Table 41). If these yields are assumed to be THF solubles and are normalized into those of the liquefaction runs, the overall conversions to THF solubles are 80 to 83%. These values are less than the 88% achieved with liquefaction alone. Considering reduced overall coal conversion, the difficulty of solid separation in the caustic treatment step, and the sodium addition to the treated coal solids (sodium is a liquefaction catalyst poison), no further research in caustic pretreatment was undertaken in conjunction with donor-solvent coal liquefaction.

In summary, laboratory-scale pretreating experiments showed little advantage for presoaking Black Thunder coal or Martin Lake lignite in a hydrogen-donor solvent, such as tetralin, at temperatures up to 600°F prior to liquefaction at higher temperatures. Only a nominal increase in

coal conversion to toluene solubles was observed. The amount of decarboxylation that occurred during the presoaking of Black Thunder coal in tetralin in the temperature range of 400 to 600°F was also relatively small. Experimentation using a bench-scale flow unit at higher reactor temperatures was undertaken. There was a limited positive effect as a result of acetic acid pretreatment of Black Thunder coal. A reduction in cation content of the coal occurred, and there was a nominal improvement in coal liquefaction. However, aqueous SO_2 treatment is more effective, and is preferred. No further research in caustic pretreatment was done in conjunction with donor-solvent coal liquefaction, because overall coal conversion was reduced, solid separation was difficult in the caustic treatment step, and sodium (catalyst poison in liquefaction) addition to the treated coal solids was seen.

Testing in a Continuous Unit

a) AU-44L

Further experimentation was carried out using coal-derived solvent and Black Thunder coal as feed to the AU-44L continuous-flow unit over a range of operating temperatures. The primary goal was to determine the extent of decarboxylation and changes of the structure of the unconverted coal samples.

EXPERIMENTAL

Flow experiments were carried out in the AU-44L continuous flow, bench-scale, liquefaction unit. The unit consists of a heated feed tank, Moyno slurry recirculation system, Milton Roy high-pressure piston pump, preheater, 300 cc CSTR reactor, pressure letdown valves, product receivers, and gas metering systems (Figure 6).

After a line-out operating period, product slurry samples were collected and analyzed using Soxhlet extraction with toluene, tetrahydrofuran (THF), and hexane. Elemental analyses of selected fractions were carried out. Samples of product gases were also collected and analyzed using gas chromatography. In addition, product slurry samples were extracted with THF alone. The THF insolubles, representing unconverted coal, were dried in a vacuum oven with nitrogen gas flow at 60°C to minimize thermal effects. These solids were characterized using FTIR.

RESULTS

The initial series of runs were made at a reaction temperature of 600°F with Black Thunder coal and coal-derived solvent (V-1072, 650-1000°F) at a ratio of 1:2. The first period had a nominal space time of about 20 minutes. Molybdenum octoate was added to the feed in the second and third periods, which operated with space times of 15 and 27 minutes, respectively. This space time is calculated as the reactor volume divided by the volumetric feed rate measured at ambient conditions. Considering

reaction temperature and entrained gases in the reactor, the actual slurry residence time is probably about one-half of the reported space time.

As shown in Table 45, little conversion of the feed coal to THF solubles occurred at 600°F. The extraction results of the feed and product slurries are reported on a basis of 100 units of either total slurry or coal. The "negative" values of the feed slurry resulted because some of the heavy portion of the solvent was retained in the coal during extraction. This solvent retention also probably occurred in the extraction of the product slurries; therefore, higher levels of conversion of coal to liquids and gases actually occurred than were reported.

As shown in Table 46, conversion of coal to THF solubles increased with increasing reactor temperature (except from 625 to 650°F). These results are summarized below, after averaging duplicate extractions:

Temperature, °F	600	625	650	675	700
THF Solubles, Wt%	4.8	9.2	6.3	16.5	24.2

In summary, the liquefaction of Black Thunder subbituminous coal just starts to get under way at reaction temperatures above 650°F when reactor residence time is relatively low.

The level of decarboxylation was also relatively low at the above reaction conditions, as shown in Table 46 and summarized below:

Temperature, °F	600	625	650	675	700
CO_2 Yield, Wt% MAF	1.1	1.4	1.5	2.1	2.7

It appears that presoaking in coal-derived solvent, or even in tetralin as discussed above, is not an effective means to achieve decarboxylation.

The study was extended with the use of higher temperatures and the addition of Molyvan-L (an organometallic compound containing molybdenum, sulfur, and phosphorus). This additive previously had been shown by Amoco to be effective for promoting coal liquefaction. Reactions have been completed in the AU-44L unit at temperatures between 650 and 800°F. The results are summarized in Table 47.

Coal conversion to THF solubles was in the range of 17 to 70 wt% on an MAF feed coal basis when Molyvan-L was added to the feed and the nominal space time was about 30 minutes. A graph of coal conversion to hexane and THF solubles as a function of reactor temperature is given in Figure 7. Again, more significant coal conversion starts to occur at reaction temperatures above 650°F.

Even in the presence of Molyvan-L catalyst, little decarboxylation occurred at reaction temperatures up to 700°F. The combined yields of CO and CO_2 gas were less than 0.5 wt%. As shown in Figure 8 and Table 47, there appeared to be a step increase in CO_2 yield as temperature was increased further. A correlation of CO_x generation and coal conversion is in Figure 9.

To test the above observations and to further describe changes of coal functionality during liquefaction, selected samples of unconverted coal (THF insolubles) were analyzed using FTIR. The samples were prepared in an inert atmosphere as quantitative KBr pellets. Transmission FTIR spectra were then obtained at 4 cm^{-1} resolution using 1000 scans on a Mattson Cygnus 100 FTIR spectrometer. The following manipulations were performed on the spectra:

1. A mild smoothing was done to eliminate spectral fringing. This smoothing did not distort the broad spectral absorbances in the carbonyl region.

2. Spectral subtraction of the H-bonded water spectrum was used to eliminate the absorbance feature near 1630 cm^{-1} due to the bending vibration of water absorbed or chemically bound to the sample or KBr.

3. Baseline correction was done near 1770 and 1515 cm^{-1} endpoints.

4. A curve fitting program ("Curvefit" in Spectra Calc software from Galactic Industries) was used to fit the spectra to individual lineshapes (Gaussian/Lorenzian profile).

The intensities of significant wavenumbers are given in Table 48, and the assignments of these wavenumbers are given in Table 49. The intensity of the carboxyl band at 1700 cm^{-1} of the undissolved coal remained essentially constant up through a liquefaction temperature of 700°F, after which the intensity dropped by one-half. This is consistent with the CO_2 yield data. However, it is noted that the band at 1655 cm^{-1}, assigned to carboxylate salts, did not undergo such a reduction. It's intensity that varied somewhat as the coal dissolved.

The ester band at 1735 cm^{-1} essentially disappeared at a liquefaction temperature of 750°F. The ether and alcohol bands at 1040 and 1100 cm^{-1} remained flat or increased; this is consistent with the occurrence of cross-linking. The on-set of cross-linking is confirmed by examining the intensities of the 1010 cm^{-1} band which is attributed to dibenzofuran-type linkages. The intensity of this band increased by about an order of magnitude at a point when most (70%) of the coal was dissolved. The increase is at least twice that which could be attributed to concentrating all of the dibenzofurans in the unconverted coal if the converted coal fraction contained none.

The level of aliphatic CH (2900 cm^{-1}) varied significantly as the coal was converted. The biggest change occurred between 700° and 750°F, when the step in conversion occurred. In confirmation, a similar step of intensity of the 1450 cm^{-1} band (also attributed to aliphatic CH) occurred between these two temperatures. As anticipated, the aromaticity (1600 cm^{-1}) of

the unconverted coal fraction increased with increasing levels of dissolution.

b) AU-135L

Decarboxylation of coal is enhanced by the presence of water and inhibited by the presence of hydrogen. In AU-44L pilot plant, hydrogen is introduced before the reactor, which also sweeps water from the coal out of the system. Hydrogen feed to the pretreatment reactor is not needed in AU-135L pilot plant, which has independent hydrogen supply to the second liquefaction reactor. Conditions would be more favorable for decarboxylation, and liquefaction would be close-coupled, eliminating problems from storage of unstable decarboxylated product.

EXPERIMENTAL

Analyses of the Black Thunder subbituminous coal feed, obtained from the mine and ground at the University of North Dakota, are given in Table 50. Coal sample FCL-135 was used for this test. Liquefaction solvent was a blend of V-1074 and V-203 liquids from Wilsonville Run 258. The analyses of the Black Thunder solvent used in these studies, FSN-136, are given in Table 51. The bench-scale liquefaction runs were made in AU-135L continuous, two-stage pilot plant with 1-liter stirred autoclave reactors. Feed slurries consisted of 33/67 mixtures of coal/liquefaction solvent. A molybdenum on sulfated iron oxide dispersed catalyst was used which was developed by Wender and Pradhan[6]. Sulfated iron oxide was precipitated

from a solution of ferrous sulfate with ammonia[6], dried at 125°F, ground to -100 mesh, impregnated to incipient wetness with a solution of ammonium molybdate in water, dried at 125°F, and used without calcining. Physical and chemical properties of the catalyst are described in Table 52. Catalyst was added directly to the feed slurry to give 100 ppm Mo/coal and 0.7% Fe/coal. TPS-20, an oil-soluble sulfiding agent containing 20% sulfur, was added directly to the feed.

Both stages were operated at 2500 psig pressure. Nominal residence times were 1-1.5 hours in each reactor. The first stage temperature was varied from 650-750°F, and the second stage was kept constant at 800°F. The first stage hydrogen rate was varied from 0-1000 SCFB, and hydrogen was added to the second stage to maintain a total rate of 5000 SCFB.

Product solubility was determined by millipore filtration, distillate yields were determined by modified D-86 and D-1160 distillation, and distilled fractions were analyzed for C, H, S, N, O, and aromatic carbon by ^{13}C NMR. Unconverted solids were analyzed for metals by ICP (inductively coupled plasma spectroscopy).

RESULTS

Net yields from coal and hydrogen consumptions are given in Table 53. Carbon oxide gas yields were about 5%, the same as from liquefaction without the pretreatment stage, even for pretreatment at 750°F and essentially zero hydrogen rate in the pretreatment stage. Product resid yields increased from 12% with no pretreatment to 34% with 750°F

pretreatment, becoming higher as the temperature of the pretreatment stage increased. High resid yields indicate that retrogressive reactions during pretreatment had damaged the reactivity of the coal. Coal conversion to THF solubles increased from 85.6% (no pretreatment) to 89.7% (700°F pretreatment). Distillate yields dropped sharply from 48% (no pretreatment) to 30% (700°F pretreatment).

Analyses of product with and without the pretreatment stage are given in Table 54. Oxygen analyses are higher for all fractions with pretreatment, and the H/C atomic ratio of the resid plus unconverted coal is substantially lower (.80) with pretreatment than without (.84).

CONCLUSIONS ON DECARBOXYLATION AND PRETREATMENT

Presoaking in coal-derived solvent or tetralin, even in presence of Molyvan L catalyst little decarboxylation occurred at reaction temperatures up to 700°F. There seems to be a step change at higher temperature and up to 5 wt% (MAF basis) of CO_x is removed at 800°F. Pretreating Black Thunder subbituminous coal in a low-temperature, low-hydrogen pressure stage did not reject additional oxygen as carbon oxide gases. The pretreatment had a strong detrimental effect on resid reactivity, resulting in high resid yields and lower hydrogen content. Moist thermal pretreatment is not recommended prior to catalytic liquefaction.

Feedstock Liquefaction Studies

The objective was to evaluate the liquefaction behavior of three coals of varied rank: Illinois No. 6 bituminous and Black Thunder subbituminous coals, and Martin Lake lignite in a two-stage, continuous-flow unit. The Illinois No. 6 coal run was used as a reference for both feedstock and first stage catalyst testing.

EXPERIMENTAL

The experimental procedures for Black Thunder coal and Martin Lake lignite were identical, but differed slightly for Illinois No. 6 coal.

Two drums of Black Thunder subbituminous coal or Martin Lake lignite were pulverized under nitrogen at the University of North Dakota, Energy and Environmental Research Center, using a 200 lb/hr Micro pulverizer (hammer mill with a 325-mesh screen). The coal or lignite was ground twice to obtain a reasonably fine grind. Sieve fractions of the pulverized sample are given in Table 55 for Black Thunder and 56 for Martin Lake. The pulverized coal or lignite was sieved through a 100-mesh screen at Amoco to remove large particles (1.65% larger than 100 mesh) that would interfere with smooth operation of the pumps. The analyses are for both coal and lignite are given in Table 57. A small sample (20 lb) of the pulverized coal was exposed to ambient air for three days. This coal sample was not analyzed, but was used in the liquefaction runs.

The liquefaction solvent (a blend of V-1074 and V-203 liquids) was obtained from the Wilsonville facility. It was derived from the liquefaction of Black Thunder subbituminous coal in Run 258. The same solvent was also used for the Martin Lake run, since lignite derived solvent was not available. The analysis is given in Table 51.

In the case of Illinois No. 6 coal, a pulverized sample from Wilsonville Run 257 was received and tested for reactivity before its use in the continuous pilot plant.

Samples were liquefied in tetralin (6:1 coal:tetralin) under 2000 psig flowing hydrogen for 1 hour at 750°F with equilibrium AMOCAT™ 1C catalyst. Several samples of Illinois No. 6 coal were tested, including an Argonne Premium sample and a poor-performing sample (DOE-1) originally tried in the Illinois No. 6 feedstock reference test. Sample DOE-2 was used in the Illinois No. 6 beneficiation studies reported earlier, and Sample DOE-3 was used in all liquefaction studies on Illinois No. 6 coal in this contract. Results are summarized in Table 58.

The batch liquefaction test showed that DOE-3 sample gave good liquefaction yields and should be a good feedstock for the continuous tests. Sample DOE-1, which gave low conversions in continuous tests, also gave a low conversion in the batch test. Originally, it was thought that the DOE-1 sample was contaminated during grinding, but analyses before grinding were very similar to those after grinding (Table 59). The

unreactive DOE-1 had low H/C ratio, low sulfur and oxygen and high nitrogen content.

Complete analyses of the Illinois No. 6 coal feed for the continuous tests (DOE-3) are given in Table 57. The pulverized coal was sieved through a US 100-mesh screen and stored in plastic bags under nitrogen in a sealed barrel. Liquefaction solvent (a blend of V-1074 and V-203 liquids) was obtained from the Wilsonville facility. It was derived from the liquefaction of Illinois No. 6 coal in Run 257. The analysis is given in Table 16.

The bench-scale liquefaction runs for Black Thunder and Martin Lake were made in a two-stage unit, AU-51L (Figure 10), which operates in a once-through, continuous mode with regard to H_2, solvent, and coal and in a batch mode with regard to catalyst. Each stage functions as a continuous, stirred-tank reactor (CSTR). Presulfided AMOCAT™ 1C catalyst was used in both reactors. Operating pressure was 2500 psig, and temperatures in the two stages were 790°F and 740°F, and nominal residence times were 1.5 and 1 hour (0.1-0.15 kg coal/sec/m^3 catalyst), respectively. Feed slurries with the samples of Black Thunder coal or Martin Lake lignite were 33/67 coal/solvent. For the Black Thunder coal run, the catalyst was lined out for 17 days with normal feed, then the air-oxidized sample was tested for three days. The run was ended with a solvent-only period. For Martin Lake lignite, the catalyst was lined out for 13 days with normal feed , then air-oxidized sample was tested for three days, followed by a three-

day solvent only period and the run was ended with a three-day normal feed period.

AU-135L used for the Illinois No. coal run is virtually identical to AU-51L. Again presulfided AMOCAT™ 1C was used in both reactors. Operating pressure was the same as previously (2500 psig) but the temperatures were 790°F and 760°F, instead of 740°F in the second stage. Higher second-stage temperature was used in order to increase the yields of distillable liquids. Again feed slurries were 33/67 coal/solvent. The run was operated with slurry feed for 18 days and then ended with a three-day solvent-only period.

Coal conversion was defined in terms of tetrahydrofuran (THF), toluene, and hexane-soluble material as determined by Millipore filtration. Modified ASTM distillations were carried out with subsequent conversion to atmospheric pressure. Products were analyzed for C, H [Leco], N [Auto Kjeldahl], S [X-ray fluorescence], and metals [inductively coupled plasma spectroscopy (ICP)].

The distillation end point was decreased from 975 to 935°F for Illinois No. 6 run and all subsequent continuous runs to improve the precision of the resid/heavy distillate cut. Residence time in the reboiler of the two stills was different, leading to different amounts of cracking at high temperature. Limiting the maximum temperature of the reboilers should reduce the amount of cracking and give better agreement in results from the two stills. In addition, one of the vacuum pressure sensors was

replaced because the zero drifted rapidly. Both sensors were calibrated more frequently to ensure reproducibility of distillation results. Even with the improved apparatus and procedures, distillate yields from coal are subject to about 5% error because coal is only 30% of the feed and product distillations are accurate to about ± 1%. Several distillations for this run were repeated, and the new distilled samples were analyzed.

RESULTS

a) Black Thunder Subbituminous Coal

Conversions, yields of distilled fractions, gas yields, and hydrogen consumptions are shown in Table 60 and B-1 in Appendix. Product from the fresh samples of Black Thunder coal contained no resid and over half of the liquid distilled below a 650°F end point. The amount of 650°F distillate remained constant throughout the run, in spite of catalyst deactivation (Figure 11). Calculated resid yields for the fresh samples were negative because more resid from the solvent was converted early in the run when the catalyst was fresh (corrections for solvent reactions were determined with aged catalyst at the end of the run). Hydrogen consumption remained constant for the fresh coal samples.

Coal conversion to THF solubles was 86%, which is on the low side of the 86-95% conversion range observed at Wilsonville in Runs 258 and 260, presumably because reactor temperatures were fairly low (Stage 1 was 790°F, and Stage 2 was 740°F). These conversions are similar to

Wilsonville periods 260-E and 260-F (C/T at 790/797°F and 775/804°F, respectively), but no resid was produced in this C/C run (Wilsonville 260-E and 260-F gave 6% and 9% resid). Resid conversion is clearly improved by the presence of catalyst in both reactors.

Compared with the Wilsonville results, however, C_1-C_3 gas yields are higher in this C/C run, 8-9% vs. 5-6%, leading to higher hydrogen consumption (6.2% for this test vs. 5.6% for Wilsonville 260-E and 5.4% for Wilsonville 260-F). The cost of higher hydrogen consumption may be acceptable, however, because distillate yields are very high (63% 975°F- material, assuming zero resid make) for C/C liquefaction. It may be possible to operate at higher temperatures in the C/C mode with a dispersed molybdenum catalyst to further increase coal conversion. A C/C liquefaction test with a molybdenum catalyst was done as part of the first-stage catalyst program.

There was a lot of scatter in yields of 650-975°F distillate and 975°F+ resid, as shown in Figure 11. This has been shown to depend on the time that the distillation flask is kept above 600°F. One of the two distillation stands was slower and invariably produced less resid (more thermal cracking). This source of error was corrected in the next runs.

The air-oxidized sample gave about the same conversion but more resid than the fresh sample (10.6% 975°F+). Hydrogen consumption was lower for the oxidized sample, which is consistent with the lower reactivity of the liquid. Also, the oxygen content was very high, 4.9%, for the resid and

unconverted coal from the oxidized sample compared with 2.3-3.1% for the fresh coal (Table 61). Oxygen in the resid and unconverted coal is determined by difference and is subject to higher-than-average error, but triplicate analyses were obtained for the oxidized sample and all showed high oxygen in the residue. The high oxygen and low resid conversion may indicate retrogressive reactions that lowered the reactivity of the oxidized Black Thunder sample. Elemental analyses of other distilled fractions were similar for the fresh and oxidized coal.

Spent Catalyst Analysis

Analyses of spent catalysts from the Black Thunder reference run are given in Table 62. As in most C/C liquefaction runs, deposits were higher on the first-stage catalyst. Surface areas were reasonably high for both catalysts.

b) Martin Lake Lignite

Conversions, yields of distilled fractions, gas yields, and hydrogen consumptions are shown in Table 63 and B-2 in Appendix. Product from Martin Lake lignite was very light, giving no resid, except in the last period where the catalyst may have been deactivated by operation with the oxidized lignite sample. Half of the product boiled below 650°F, and 10-15% C_4-360°F distillate was recovered. Yields of C_4-360°F and 650-975°F distillates were fairly constant throughout the run for fresh lignite samples, in spite of catalyst deactivation (Figure 12). The 350-650°F

distillate yield was low at the end of the run, which could also be from catalyst deactivation. Additional evidence for catalyst deactivation was seen in the hydrogen consumption, which was 1% lower for the fresh lignite sample at the end of the run compared with the same sample in the middle of the run.

Conversion was not particularly high at 82-87%; however, it is still better than the 80% conversion achieved with Martin Lake lignite, the C/C portion of Wilsonville Run 255. The Wilsonville C/C test used Shell 324 catalyst and our test used AMOCAT™ 1C catalyst. Conversion might be increased with AMOCAT™ 1C catalyst by raising temperatures in one or both of the reactors, which operated at 790 and 740°F. The AMOCAT™ 1C catalyst can be used at as high a temperature as 810°F with acceptable deactivation rates.

It is difficult to compare distilled product yields with those from the T/C portion of Wilsonville Run 255 (the C/C portion of this run was too unstable to get accurate yields), because organic losses in the CSD were quite high (20-22%) for most of the run. Even so, resid yields were significant, 7.5% for period 255-A, at Wilsonville. This C/C test with AMOCAT™ 1C catalyst gave less than 20% resid plus unconverted coal, which is a distinct improvement over the results at Wilsonville, 20% losses plus 7.5% resid, but a different solids separation process would have to be used in view of unstable CSD operation with C/C liquefaction of lignite.

Sulfur levels in the distilled fractions were less than 0.02 wt% and were less than 0.8 wt% in the residue (Table 64). The resid plus unconverted coal fraction could be used as a low-sulfur boiler fuel. Nitrogen in the distillate was relatively high at 0.4-0.5 wt% for all the fractions, which would require significant hydrotreating. The resid plus unconverted coal contained about 0.8 wt% nitrogen.

The air-oxidized sample produced 15% more resid than the previous fresh sample at the expense of 650-975°F distillate (Table 63) and also gave 6% CO_2 compared with 3% CO_2 from the fresh feed. The resid contained 2.9% oxygen from the oxidized lignite compared with 1.6% for fresh lignite. (Note that sample 4 also has high oxygen in the resid, but the first-stage reactor heater was off and conversion was low). Air oxidation of lignite is clearly detrimental, giving higher resid yields without affecting conversion. Substantial oxidation of the lignite occurred, giving enough additional oxygen to measure in the resid fraction and increase production of carbon dioxide gas.

Spent Catalyst Analysis

Analyses of spent catalyst from Martin Lake lignite reference run are given Table 65. Deposits were higher in the first-stage than in the second-stage catalyst, which is normally observed for C/C runs. The low pore volume, low surface area, and high carbon deposits indicate severe deactivation of the first-stage catalyst. Calcium deposits are also high on the first-stage catalyst. Generally, catalyst from both

stages was in worse shape after liquefaction of Martin Lake lignite than after liquefaction of Black Thunder coal (Table 62).

c) Illinois No. 6 Bituminous Coal

Results here reflect the new analyses (different distillation) which gave higher resid yields, different heteroatom analyses, and lower hydrogen consumption than described previously with beneficiated coals.

Conversions, yields of distilled fractions, gas yields, and hydrogen consumptions are shown in Table 66 and B-3 in Appendix. The operation of the pilot plant was very smooth until about 300 hours on-stream, when a valve handle came loose and led to complete opening of the product receiver, which was not apparent until the end of the run. Solids were retained in the unit after the valve malfunctioned, giving low apparent coal conversions at the end of the run. Thus, the data points taken before 300 hours of operation are the most reliable.

A significant amount of resid was produced from Illinois No. 6 coal, and the yield of resid is fairly steady except for initial periods. The production of C_4-360°F, 360-650°F, and 650-935°F distillate decreased slightly as the catalyst aged (Figure 13). Distillate yields were steady, indicating that the revised distillation procedure gave good results. Yields for light hydrocarbon and carbon oxide gases were low, similarly hydrogen consumptions were also low.

The analyses of the products (Table 67) showed a steady increase in oxygen and nitrogen levels in distilled fractions as the catalyst aged. The hydrogen and sulfur content of the distilled fractions was relatively steady after initial catalyst deactivation. Carbon and hydrogen elemental analyses were repeated on a new Perkin Elmer instrument, and total elemental analyses are consistently near 100%, which is an improvement over earlier results from a Leco instrument.

Overall, results from Illinois No. 6 coal showed good conversion to liquids, but a high-boiling product was produced. Once-through yields from coal are reported in Table 66, and about 10% of the resid would be converted during solvent recycle. Allowing for recycle, resid yields are still about 30%, which is too high by Wilsonville standards. Reaction severity must be increased. Higher reaction temperatures are the cheapest way to increase severity, but a supported catalyst like AMOCAT™ 1C deactivates rapidly at high temperatures. Upper temperature limits for use of this catalyst were not previously known and a study of the use of this catalyst at high temperature was completed as part of the first stage catalyst program.

Spent Catalyst Analysis

Spent catalyst analyses are reported in Table 68. Two thirds of the surface area were lost in the first stage catalyst, in spite of the moderate operating temperature of 790°F. Loss of the surface area is normal for first stage catalysts and was also seen for the Martin Lake

lignite and Black Thunder feedstocks. This could be a consequence of the presence of large, low-solubility coal liquids in the first stage. Second stage catalyst retained most of its original surface area. A significant amount of coke was measured on the first stage catalyst. Metal deposits from coal ash were low except for 1.5% titanium on first stage catalyst. Most of the ash components were removed with unconverted coal. Although the molybdenum content of the spent catalyst samples is low, the ratio of molybdenum to aluminum is fairly constant for fresh and spent samples, indicating that loss of molybdenum has not occurred.

Comparison of Feedstocks

This section compares yields and product quality from Black Thunder subbituminous coal, Martin Lake lignite and Illinois No. 6 bituminous coal for C/C liquefaction with AMOCAT™ 1C catalyst. First stage temperatures were 790°F, and second stage temperatures were 740°F for the low rank coals and 760°F for Illinois No. 6 coal. Process conditions were similar for all three feedstocks, which allowed comparison of coal reactivities, but did not give optimum yields for any of the feedstocks. Results of these tests and other work show that for liquefaction of the lignite and subbituminous coal, an iron catalyst is required to give high conversion of THF insolubles, and supported catalyst may not be needed in both reactors. When resid conversion is limiting the performance, supported catalysts in both stages may be beneficial. However, deactivation of supported catalysts is extremely rapid. For Illinois No. 6 coal, higher severity is needed to increase resid conversion.

Product yields were calculated two ways. Yields in Table 69 include contributions from coal and solvent reactions, and are the best that could be achieved with solvent recycle. Resid yields that appear negative resulted when there was less resid in the product than in the original solvent (Black Thunder and Martin Lake): net resid would be zero in actual recycle operation. Once-through yields from coal, with corrections for solvent reactions, are given in Table 70. Actual yields will be between corrected (once-through) and uncorrected values. Recycle results will be closer to corrected values (Table 70) for low rank coals and closer to uncorrected values (Table 69) for Illinois No. 6 coal. General conclusions about feedstock reactivities and yield structures are the same, regardless of which set of numbers is used.

Illinois No. 6 coal gave the highest total liquid yield, about 80%, and the highest conversion, 93%, but the product contained a significant amount of resid. Both low rank coals gave low conversion (85-87%) and lower liquid yields (57-59% C_4-975°F+), but products contained no resid. The high oxygen content of the low rank coals and low conversion contributed to the low liquid yields. Hydrogen consumption was high for the low rank coals, which is consequence of the high C_1-C_3 gas make, light product formation, and hydrodeoxygenation. Hydrogen consumption could be decreased by use of catalyst in only one reactor or by rejecting oxygen as carbon dioxide.

Martin Lake lignite produced the lightest product: most of it distilled below 650°F. Black Thunder subbituminous coal gave product with the lowest sulfur: less than 0.2% sulfur in the resid plus unconverted solid

fraction. Illinois No. 6 coal gave the highest conversion to liquids, and the heaviest product.

Spent AMOCAT™ 1C catalysts from the first stage from the three feedstocks are compared in Table 71. Spent catalyst from Martin Lake lignite showed the greatest deactivation, retaining very little surface area (17 m^2/g) or pore volume, and containing the highest coke levels (33%). Spent first stage catalyst from Martin Lake lignite should have very low activity. Spent catalysts from Black Thunder subbituminous coal and Illinois No. 6 coal have coke levels, surface areas, and pore volumes that are typical of spent first stage catalysts. The spent catalysts from Black Thunder run contained 0.4% sodium, which suggested that sodium poisoning of active sites could be significant during extended use with this feed. The catalyst from Martin Lake lignite test contained 2% calcium. Spent first stage catalyst from Illinois No. 6 coal contained 1.6% titanium. Spent first stage catalysts from both low rank coals had significant iron deposits, which may indicate the presence of ion-exchanged iron in the parent coals.

Spent catalysts from the second stage all had high surface areas, high pore volumes, low coke levels, and low levels of metal deposits. All spent second stage catalysts should have good activity. Complete analyses of spent first and second stage catalyst samples are given in Table 62 (Black Thunder), Table 65 (Martin Lake lignite), and Table 68 (Illinois No. 6).

CONCLUSIONS ON FEEDSTOCK

Feedstock tests showed that Black Thunder subbituminous coal and Martin Lake lignite gave lighter products than Illinois No. 6 coal at similar process conditions (C/C liquefaction with AMOCAT™ 1C catalyst at 790/740-760°F). The C/C liquefaction process was probably too severe for Black Thunder and Martin Lake especially due to long residence times in this study, however, and use of supported catalyst in only one stage is recommended. In addition, supported catalyst should not be used in the first stage for liquefaction of Martin Lake lignite because deactivation is severe. The conversion of Black Thunder subbituminous coal and Martin Lake lignite could possibly be increased by using a dispersed iron catalyst. Use of supported catalyst in the first stage only and use of dispersed iron with Black Thunder feed was tested as part of Task 3.2.1 First-Stage Catalysts.

Conditions were not severe enough for high resid conversion with Illinois No. 6 coal. Severity can be increased by raising the temperature, but catalyst deactivation will increase as the temperature is raised. Dispersed catalysts can be used successfully at high temperature, and may be preferred in the first stage where catalyst deactivation is most severe. A high-temperature C/C liquefaction of Illinois No. 6 coal with AMOCAT™ 1C catalyst and a test with dispersed catalyst in the first stage with Illinois No. 6 coal feed were completed as part of Task 3.2.1 First Stage Catalysts.

Task 3.2.1: First Stage Catalysts

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

First Stage Catalyst Tests with Illinois No. 6 Coal

Several different catalysts and their combinations were tested with Illinois No. 6 coal:

- AMOCAT™ 1C at high temperature
- Molyvan L/AMOCAT™ 1C
- Molyvan L or molybdenum octoate
- Novel dispersed catalysts
  - Molybdenum carbide, molybdenum nitride
  - Wender's sulfated iron oxide/molybdenum
  - Sandia powdered hydrous titanate (discussed in Task 3.2.3)
- Sandia thin film titanate on AMOCAT™ alumina (discussed in Task 3.2.3)

INTRODUCTION

Illinois No. 6 coal served as the reference liquefaction feedstock at the Advanced Coal Liquefaction facility in Wilsonville, Alabama, for several years. The process evolved over time from single-stage, high-severity to two-stage, moderate severity. Significant improvements were made in coal conversion, energy rejection during solids separation, distillate yield,

and coal throughput. The best results were obtained using a new catalyst, EXP-AO-60 (with a pore structure similar to AMOCAT™ catalysts), in the two-stage catalytic process.

High-temperature use of AMOCAT™ 1C catalyst at Wilsonville was frequently proposed as a way of increasing both resid and coal conversion. Amoco has consistently recommended a 810-820°F maximum operating temperature for AMOCAT™ 1C catalyst. This temperature limit was determined in earlier work with other versions of AMOCAT™ catalysts that differed in pore structure (less macroporosity), extrudate, diameter, and other properties. An evaluation of the high-temperature performance of the new generation of AMOCAT™ 1C catalyst was undertaken to test the validity of the old temperature limits. The Illinois No. 6 reference test had shown considerable coke deposition on the first stage catalyst at 790°F, but modest coke deposition on the second stage catalyst at 760°F. The high-temperature run pushed the capacity of the second stage AMOCAT™ 1C catalyst with the first stage at 800°F and the second stage at 860°F.

Because it is becoming increasingly difficult to develop a new supported catalyst that gives a large beneficial effect on process economics, oil-soluble molybdenum catalysts were tested for liquefaction of Illinois No. 6 coal in place of the supported catalyst in one or both stages. The use of oil-soluble catalysts would simplify the reactor design and decrease its cost. Molyvan L (8% Mo, $3.20/lb.) and molybdenum octoate (8% Mo, $2.00/lb.) are commercially available oil-soluble lubricant additives. Molyvan L was used as a first stage catalyst for liquefaction of Black Thunder coal in Wilsonville Run 262 and 263 (Shell 324 in stage 2). In this work, the use of Molyvan L and molybdenum octoate for

liquefaction of Illinois No. 6 coal was examined. Results were very promising, suggesting that oil-soluble molybdenum compounds are good alternative catalysts for a Wilsonville-type process with Illinois No. 6 coal feed.

EXPERIMENTAL: FEEDSTOCK DESCRIPTIONS AND TEST METHODS

Analyses of the Illinois No. 6 coal feed, from Wilsonville Run 257, are given in Table 57. Liquefaction solvent was a blend of V-1074 and V-203 liquids from Wilsonville Run No. 257. Its analysis is given in Table 16. The bench-scale liquefaction runs were made in AU-135L continuous, two-stage pilot plant with 1-liter stirred autoclave reactors. Feed slurries consisted of 33/67 mixtures of coal/liquefaction solvent. Molyvan L or molybdenum octoate was added to the feed tank without additional sulfiding agent. Two runs with dispersed catalyst were completed, one with Molyvan L added to the feed as the first stage catalyst and AMOCAT™ 1C catalyst in the second reactor, and one with Molyvan L or molybdenum octoate and no supported second stage catalyst. AMOCAT™ 1C catalyst was presulfided with 8% hydrogen sulfide in hydrogen before use. Product solubility was determined by millipore filtration, distillate yields were determined by modified D-86 and D-1160 distillation, and distilled fractions were analyzed for C, H, S, N, O, and aromatic carbon by ^{13}C NMR. Unconverted solids were analyzed for metals by ICP (inductively coupled plasma spectroscopy).

Illinois No. 6 Coal: High-Temperature Test with AMOCAT™ 1C Catalyst

Operating pressure was 2500 psig and temperatures in the two stages were 800°F and 860°F, and nominal residence times were 1.5 hour in each stage or 3.0 hour overall. The run was 11 days long. A solvent-only period was not included.

RESULTS

Yields for the high-temperature run are compared with yields from the Illinois No. 6 reference run in Table 72 and Figure 14. Resid yields were low when the catalyst was relatively fresh, but increased at the end of the run because of severe catalyst deactivation. It should be noted that catalyst deactivation for the reference run was modest. Gas yields (C_1-C_3) were high. Except for the initial period where catalyst activity was high, liquefaction with AMOCAT™ 1C catalyst at 800/860°F did not improve results compared with liquefaction at 790/760°F.

Distilled product analyses for the high-temperature and reference runs are compared in Table 73. The product from the high-temperature run had less nitrogen, sulfur, and oxygen when the catalyst was fresh, but performance declined sharply as the catalyst aged. At the end of the run, the heteroatom content of distilled fractions was the same as or higher than from the reference run. The product from the aged catalyst actually contained less hydrogen than the product contained when the catalyst was fresh. At high temperature, the equilibrium is shifted toward dehydrogenation, and an active catalyst will increase rates of dehydrogenation as well as hydrogenation. At the end of the run when the

catalyst was severely deactivated, the product was more hydrogen rich because dehydrogenation rates were slow.

Spent catalyst analyses are given in Table 74. Because stirred autoclave reactors have a large liquid volume compared with the catalyst volume, thermal reactions are more important in AU-135L pilot plant than at Wilsonville. Catalyst in AU-135L accumulates more coke at a given operating temperature than the catalyst in Wilsonville reactors. Relative catalyst coking rates in the two units are not known, but it is probably safe to say that a catalyst can be used at 10-20°F higher temperature at Wilsonville than in AU-135L. Even the small increase in first stage catalyst temperature from 790 to 800°F caused an increase in carbon deposits from 25% to 40%, a decrease in surface area from 65 to 29 m^2/g, and a decrease in pore volume from 0.16 to 0.08 cc/g. The higher first stage temperature increased Fe and Ca deposits but decreased Ti deposits. Based on these results, AMOCAT™ 1C catalyst should not be used above 820°F in the first stage at Wilsonville type of operation, typically with short residence times.

Spent second stage catalyst was in worse shape. Compared with the reference second stage catalyst at 760°F, carbon deposits at 860°F increased from 9% to 45%, the surface area decreased from 151 to 10 m^2/g, and the pore volume decreased from 0.38 to 0.03 cc/g. Second stage catalyst deactivation was much too severe at 860°F. Metal deposits were not much different at the high temperature. Coke deposits on the catalyst were the limiting factor for high-temperature operation of the second stage, which should be kept well below 860°F.

SUMMARY

Use of AMOCAT™ 1C catalyst above 820°F for the first stage reactor of a close-coupled two stage direct liquefaction is not recommended. In the first stage, catalyst deactivation increased significantly with a 10°F increase in reactor temperature near the high-temperature limit. Operation of the second stage at extremely high temperature (860°F) is not recommended because catalyst coking was severe. Overall, deactivation was rapid in the high-temperature run and net results were worse than from the reference run because more light hydrocarbon gases were produced.

Illinois No. 6 Coal: Molyvan L Stage 1/AMOCAT™ 1C Stage 2

Liquefaction of Illinois No. 6 coal may place greater demands on the catalyst for hydrogenation of aromatics than liquefaction of Black Thunder coal. This test used Molyvan L in the first stage and AMOCAT™ 1C catalyst in the second stage to keep hydrogenation activity high. Feed slurries contained 800 ppm of Molyvan L (192 ppm molybdenum as a fraction of coal). Operating pressure was 2500 psig, temperatures were 800-820°F for the first stage and 760 °F for the second stage. Nominal residence times were 1.5 hour in each stage or 3 hours overall. The run was operated with slurry feed for 15 days and then with solvent-only feed for 6 days.

RESULTS

Product yields are compared with those from the reference run with AMOCAT™ 1C in Table 75 and Figure 15. The run with Molyvan L in the first stage is labelled T/C, and the reference run with AMOCAT™ 1C catalyst in the first stage is labelled C/C. The resid yield was lower with Molyvan L (800°F) than with AMOCAT™ 1C (790°F) catalyst in the first stage (15% vs. 28%). Resid yield decreased to 7% with Molyvan L when the first stage temperature was raised from 800 to 820°F. Heavy distillate (650-935°F) increased from 5% to 13% with Molyvan L, and yields of 360-650°F distillate increased at the higher first stage temperature from 35% to 43%. Hydrocarbon gas yields and hydrogen consumption increased slightly at 820°F.

Analyses of distilled products are given in Table 76. AMOCAT™ 1C catalyst in the first stage gave better hydrogenation and heteroatom removal in the lightest (360-650°F) fraction than Molyvan L. This result is not surprising because smaller pore catalysts are more effective for hydrotreating light distillate fractions. The Molyvan L acts like a very large-pore catalyst and does not very effectively hydrotreat light fractions.

Product yields from solvent-only periods showed similar trends (Table 77). Resid conversion and distillate yields were higher from Molyvan L (first stage 800°F) than from AMOCAT™ 1C (first stage 790°F). Resid conversion and distillate yield increased with Molyvan L in the first stage at 820°F. Product analyses from solvent-only periods, Table 78, showed better

hydrogenation of 650-935°F distillate, which was also seen with AMOCAT™ 1C catalyst in the first stage.

Spent second stage catalyst analyses are given in Table 79. With Molyvan L in the first stage, the second stage catalyst was in worse shape than when it was protected by AMOCAT™ 1C first stage catalyst. Carbon levels were higher (25% vs. 8%), the surface area was lower (84 vs. 151 m^2/g), as was the pore volume (0.21 vs. 0.38 cc/g), and metal deposits were higher. Solids appear to deposit on the first supported catalyst that is available. In fact, spent second stage catalyst from the run with Molyvan L is similar to spent first stage AMOCAT™ 1C catalyst. The second stage catalyst replacement rate would have to increase if Molyvan L was used in the first stage.

SUMMARY

Overall, a process with Molyvan L catalyst in the first stage and AMOCAT™ 1C catalyst in the second stage gave a higher distillate yields than a process with AMOCAT™ 1C catalyst in both stages. Because Molyvan L catalyst can be used in a less expensive slurry reactor, it would be the preferred first stage catalyst for liquefaction of Illinois No. 6 coal. With Molyvan L in the first stage, deactivation is more rapid for supported second stage catalyst, and the catalyst addition rate would have to be increased. Also, hydrogenation of light distillate was not as good, which would require additional hydrotreating.

Illinois No. 6 Coal: Dispersed Molybdenum Catalysts in Stages 1-2

Molyvan L or molybdenum octoate were tested without supported catalyst for liquefaction of Illinois No. 6 coal at 192 ppm and 84 ppm Mo:coal (64 and 26 ppm Mo:slurry) for Molyvan L, and 96 ppm Mo:coal (32 ppm Mo:slurry) for molybdenum octoate. Operating pressure was 2500 psig and temperatures were 800-820°F for both reactors. The nominal residence times were 0.75-1.5 hour in each stage or 1.5-3.0 hours overall. Each set of conditions was maintained for 3 days to obtain representative samples. At the end of the run, a solvent-only feed was processed with Molyvan L catalyst (48 ppm Mo:solvent).

RESULTS

Product yields from all conditions were good (Table 75, columns labelled "slurry"). Resid yields were 3-8%, C_4-935°F distillate yields were 66-72%, and coal conversions were 94-96%, which was as least as good as from the first stage test with Molyvan L. Hydrogen consumption was somewhat lower (4.8-5.7%) than from AMOCAT™ 1C (5.6%) or for first stage Molyvan L (5.4-6.1%).

Product yields did not change when the molybdenum level was decreased from 192 ppm to 84 ppm. Product yields were also unchanged when the residence time was decreased from 3 to 1.5 hours and the temperature was raised from 800 to 820°F. In this study, molybdenum octoate gave less resid than Molyvan L at the same conditions and would be the preferred oil-soluble molybdenum catalyst because it is less expensive.

Distillate product quality, Table 76, was not as good as when AMOCAT™ 1C catalyst was present. Nitrogen and oxygen levels were higher, but sulfur and hydrogen levels were about the same. It is interesting to note that the resid plus solid fraction has a higher H/C ratio (0.98) with Molyvan L catalyst at 800°F than with AMOCAT™ 1C catalyst (0.95-0.96). It seems that there is better hydrogenation of the heaviest components with Molyvan L. At reactor temperatures of 820°F, the H/C ratio of the resid plus solids fraction dropped to 0.92, reflecting a shift in equilibrium toward dehydrogenation. Molybdenum octoate was not as active for hydrogenation of resid plus solids, giving a H/C ratio of 0.91 at 800°F.

Unlike results from coal, solvent-only periods with Molyvan L did not show higher resid conversion than for runs with AMOCAT™ 1C catalyst (Table 77). This implies that dispersed molybdenum catalysts are most active for conversion of the heavy primary products from coal. Analyses of the product from the solvent-only period was about the same as when AMOCAT™ 1C catalyst was present in the second stage, indicating that good solvent quality would be maintained with Molyvan L catalyst (Table 78).

SUMMARY

A process with dispersed molybdenum compounds as the only catalyst offers several advantages over liquefaction with AMOCAT™ 1C catalyst, including a less expensive reactor design and simpler operation of the reactors. Product was better than when AMOCAT™ 1C catalyst was used in both reactors and as good as when AMOCAT™ 1C was used in stage 2 with Molyvan L in stage 1. Low levels of molybdenum, 84 ppm Mo:coal, were effective. Production of a low-resid product at 1.5 hours residence time

and 820°F was demonstrated. Molybdenum octoate, a less expensive dispersed molybdenum catalyst, performed well, perhaps because of the high sulfur content of Illinois No. 6 coal. Use of dispersed molybdenum catalysts for liquefaction of Illinois No. 6 coal is recommended.

Illinois No. 6 Coal: First Stage Catalyst Tests vs. Wilsonville Results

Yields from Wilsonville Run 261-B with Illinois No. 6 coal were compared with the best first stage catalyst results from this study (Table 80). The best yields with Illinois No. 6 coal feed were obtained with Molyvan L catalyst in the first stage and either Molyvan L or AMOCAT™ 1C catalyst in the second stage. Resid yields were the same as those from Wilsonville, within experimental uncertainty (± 2%). Distillate yields were 3-4% higher than those from Wilsonville. Hydrogen consumptions were fairly close to those from Wilsonville (4.9-6.1% vs. 5.7%). Light hydrocarbon gas yields were 10-11% vs. 5% from Wilsonville, which might be explained by the high temperature (820°F) of the dispersed catalyst run and the relatively low space velocity (coal wt./reactor vol.) of the Molyvan L/AMOCAT™ 1C run. In spite of the high gas yields, distillate yields were good for both runs with Molyvan L, suggesting that Molyvan L is a good alternative catalyst in stage 1 or stages 1-2 of a Wilsonville-type liquefaction process.

Other Dispersed Catalysts

Other dispersed catalysts were tested for liquefaction of Illinois No. 6 coal. The first was molybdenum on sulfated iron oxide, developed by Professor I. Wender[6], which was also tested for liquefaction of Black

Thunder subbituminous coal. In addition, high-surface-area molybdenum carbide and nitride powders prepared by Professor T. Oyama[7] were evaluated. These were part of the second stage catalyst testing also.

These bench-scale liquefaction runs were made in AU-51L continuous, two-stage pilot plant with the same feedstock (coal and solvent mixture) as for the earlier runs. Dispersed catalyst powders were added directly to the feed without a sulfiding agent. All powders were 100 mesh or smaller. Nominal residence times of 1-1.5 hours were achieved by operation of the first stage at reaction temperature (800-820°F) and operation of the second stage at 500°F. Product handling was identical to previous runs.

Illinois No. 6: Mo/Sulfated Iron Oxide

Preparation of the molybdenum/sulfated iron oxide catalyst was described in Task 3.1. Standard amounts of 100 ppm Mo/coal and 0.7% Fe/coal were used, and results were compared with those from Molyvan L at the same molybdenum level (no added iron). The reactor temperature was 820°F.

RESULTS

Molybdenum on sulfated iron oxide was an extremely active catalyst for Illinois No. 6 coal liquefaction. Net yields from coal are summarized in Table 81. Resid yields for this run were much higher than in previous tests, indicating that this batch of coal was relatively unreactive, but comparisons of catalyst activities within the run should be valid. Mo/sulfated iron oxide gave much less resid (22% vs. 51%), and more 650-935°F distillate (37% vs. 7%) than Molyvan L. Product elemental analyses,

Table 82, show lower aromaticity and higher H/C atomic ratios for 360-650°F distillate from Mo/sulfated iron oxide, which confirms that is a more active catalyst. Other elemental analyses of product fractions from the two catalysts were comparable.

SUMMARY

Molybdenum on sulfated iron oxide was better than Molyvan L for liquefaction of Illinois No. 6 coal at 100 ppm Mo/coal. Superior performance of the iron catalyst may be attributed to significant hydrogenation activity of highly-dispersed iron sulfide, which is produced in situ from the sulfated iron oxide. If the cost of preparation of sulfated iron oxide is low enough, it would be a preferred catalyst for liquefaction of Illinois No. 6 coal.

Illinois No. 6 Coal: MoC and MoN_2 vs. MoS_2

Molybdenum carbide, nitride, or sulfide powders were added to coal slurry feed to give 300-600 ppm Mo/coal. The molybdenum carbide and nitride catalysts were prepared by Professor T. Oyama[7] and were used without calcining or pre-reduction. The molybdenum carbide had a surface area of 42 m^2/g (N_2 BET) and a CO uptake of 98 μmoles/g. The molybdenum nitride had a surface area of 80 m^2/g and a CO uptake of 59 μmoles/g. Operability of the pilot plant was very poor with all three catalysts because of the poor product quality. Pilot plant operability and product quality improved immediately when a proven catalyst, Molyvan L, was added, which confirmed that catalyst performance was linked to pilot plant operability.

RESULTS

Powdered molybdenum carbide, nitride, and sulfide gave low-solubility, high-boiling product in spite of the relatively high molybdenum loadings of 300-500 ppm Mo/coal. Yields are summarized in Table 83. Molyvan L gave much higher oil and distillate yields at 100 ppm Mo/coal, which is probably linked to the high dispersion of molybdenum in oil-soluble Molyvan L. Products were not analyzed because of the poor quality.

SUMMARY

Powdered molybdenum carbide and nitride, even high-surface-area forms prepared by Oyama, do not perform as well as oil-soluble molybdenum catalyst precursors. Good dispersion may be especially important in coal liquefaction because large, insoluble molecules tend to foul catalyst surfaces. Molybdenum carbide, nitride, and bulk sulfide powders are not recommended as liquefaction catalysts for Illinois No. 6 coal.

First Stage Catalyst Tests with Black Thunder Coal

Both supported and dispersed catalysts were tested for liquefaction of Black Thunder subbituminous coal.

- C/C run with AMOCAT™ 1C

- C/T run with AMOCAT™ 1C or AMOCAT™ 1B (Mo only)

- Dispersed catalysts tested with short residence time:

  Molyvan L, alone or with red mud

  Molybdenum octoate with red mud

- Dispersed catalysts tested with long residence time:

  Molyvan L + ferric sulfate

  Molyvan L + Wender's sulfated iron oxide

  Ammonium molybdate on Wender's sulfated iron oxide

  Effect of sulfiding agent on sulfated iron oxide

- Dispersed catalyst with a hydrogen-rich liquefaction solvent

EXPERIMENTAL: FEEDSTOCK DESCRIPTIONS AND TEST CONDITIONS

Analyses of the Black Thunder subbituminous coal feed, obtained from the mine and ground at the University of North Dakota, are given in Table 50. Different batches of coal were used in the Black Thunder reference test (FCL-126) and first stage catalyst tests (FCL-135). Liquefaction solvent was a blend of V-1074 and V-203 liquids from Wilsonville Run 258. The analyses of the two batches (FSN-113 and FSN-136) are given in Table 16 and 51. The bench-scale liquefaction runs were made in AU-135L continuous, two-stage pilot plant with 1-liter stirred autoclave reactors. Feed slurries consisted of 33/67 mixtures of coal/liquefaction solvent. AMOCAT™ catalysts were presulfided with 8% hydrogen sulfide in hydrogen or with TPS-20 in liquefaction solvent before use. Product solubility was determined by millipore filtration, distillate yields were determined by modified D-86 and D-1160 distillation, and distilled fractions were analyzed for C, H, S, N, O, and aromatic carbon by ^{13}C NMR. Unconverted

solids were analyzed for metals by ICP (inductively coupled plasma spectroscopy).

Improvements made in laboratory procedures reduced the time and cost of analyses of pilot plant products. Three distillations and three large-scale preparations of insolubles were completed at the same time, which allowed workup of three pilot plant samples in one day. One sample a day was analyzed at the beginning of this contract. Additional laboratory time was available for batch studies of liquefaction fundamentals. Use of tetrahydrofuran (THF), which is very expensive, was cut in half by using toluene for preparation of large-scale insolubles for analysis of ash constituents. The modified procedure gave identical ash yields and acceptable speed and ease of analysis.

Supported Catalysts

The tests that were performed used a C/T configuration with AMOCAT™ 1C catalyst or AMOCAT™ 1B catalyst in the first stage without dispersed molybdenum catalyst. C/T liquefaction of Black Thunder coal was studied in Wilsonville Run 260, but the second stage temperature was too low because of furnace limits. Iron oxide and a sulfiding agent, TPS-20, or iron sulfate were added to the feed for most of these tests.

Black Thunder Coal: C/T with AMOCAT™ 1C Catalyst in Stage 1

Operating pressure 2500 psig and temperatures 780°F and 800°F. The first week of the run was very smooth; then a few small upsets occurred that may have affected the end of the run. The decline in performance was not

immediate and did not seem reasonable in view of the minor nature of the process upsets. After the next run, which was very short, a disintegrated bearing in the first stage stirrer was discovered. It is likely that inadequate stirring could have partly been responsible for poor performance at the end of this run.

RESULTS

Catalyst activity was good for the initial part of the run and probably reflects true performance of this system. A period late in the run with low catalyst activity is also included for completeness. Yields are compared with those from the Black Thunder reference run (C/C) and a dispersed catalyst period ("slurry," Molyvan L/iron oxide/TPS-20) in Table 84.

Initial results from the C/T run with AMOCAT™ 1C catalyst showed conversion of all of the resid from the coal and some of the resid in the slurry solvent (-32% resid yield). Excess conversion could be corrected by operation at shorter residence times or lower temperatures. Light hydrocarbon gas yields were quite high, 16%, but could be decreased with lower severity. Coal conversion was excellent at 94%.

Late in the run, after the catalyst had deactivated, the resid yield had increased, coal conversion had dropped to 87%, but hydrocarbon gas yields were still high (18%). Gas yields must be strongly influenced by the thermal second stage. The product analyses for both early and late periods in the run are in Table 85.

Product analyses are also compared with those from the Black Thunder reference run and the earlier dispersed Mo catalyst run in Table 86. The hydrogen and heteroatom content of the product was about the same as with the dispersed Mo catalyst, even for C/T periods where catalyst deactivation was severe. However, deoxygenation was better initially in the C/T run, and about the same as from the dispersed Mo at the end of the C/T run when the catalyst was deactivated. Supported catalyst in stage 1 (AMOCAT™ 1C in the C/C and C/T runs) appeared to increase deoxygenation but did not have much effect on hydrogen addition, desulfurization, or denitrogenation. The supported catalyst in stage 2 (AMOCAT™ 1C in the C/C run) provided additional deoxygenation, hydrogen addition, desulfurization, and denitrogenation.

Overall, the results from the early part of the C/T run with AMOCAT™ 1C catalyst were outstanding and showed excess capacity for resid conversion. It may be possible to operate this type of process at much higher coal throughput. The severe catalyst deactivation after one week was disturbing (Figure 16). Deactivation may have been caused by poor stirring in the first stage, but could be a reproducible feature of this type of process.

Black Thunder Coal: C/T with AMOCAT™ 1B Catalyst in Stage 1

Molybdenum catalysts are more resistant to deactivation than nickel/molybdenum catalysts for certain heavy feedstocks. Molybdenum catalysts are initially less active for hydrogenation and heteroatom removal, but aged molybdenum catalysts often retain higher activity than the corresponding nickel/molybdenum catalysts. Results from the previous

C/T run were very promising initially, but the catalyst deactivated severely after about a week. This run with AMOCAT™ 1B molybdenum catalyst was an attempt to maintain higher, more stable activity for a longer period of time. Instead, product from this run deteriorated sharply after three days. When the first stage reactor was opened, it was obvious that the stirrer bearing had disintegrated and the reactor contents were not stirred at all during this run. Process conditions were the same as in previous run.

A second C/T run with AMOCAT™ 1B catalyst was completed. It had been hoped that AMOCAT™ 1B (Mo) catalyst would show more stable activity, although initial activity was expected to be low. Initial results from two runs with AMOCAT™ 1B catalyst are given in Table 87, and both show poorer conversion to THF solubles and poorer resid conversion than with the NiMo catalyst. The performance of AMOCAT™ 1B improved somewhat when ferrous sulfate was used as the iron additive instead of iron oxide/sulfiding agent. Product elemental analyses from all three tests were comparable early in the run (Table 88).

The AMOCAT™ 1B catalyst did not show more stable activity as the catalyst aged, which is shown in Table 89 and Figure 17. The first period was operated with a second stage temperature of 800°F. No supported catalyst was present in the second stage. The second stage temperature was decreased to 780°F in a successful attempt to reduce gas yields, and distillate yields also dropped, which was expected. As the run continued, resid yields increased from 12% to 27%. Product hydrogenation and heteroatom contents remained relatively constant throughout the run (Table 90). Analyses of spent catalyst from this run showed severe coke

deposition as well as formation of a calcium-rich shell on the catalyst surface. AMOCAT™ 1B catalyst is not resistant to this important mode of fouling from liquefaction of Black Thunder coal.

Effect of Solvent Hydrogenation on Conversion

Coal conversion to THF soluble material was highest in C/T runs when the catalyst was fresh. Improved conversion could be from good hydrogenation of the slurry solvent by active catalyst. The role of solvent hydrogen content on conversion of Black Thunder Coal was tested in two batch experiments. Distillate fractions (650-935°) from Black Thunder coal with H/C ratios of 1.11 and 1.22 were used to liquefy Black Thunder coal at a 1:2 coal:solvent ratio. The hydrogen-rich solvent gave 78% conversion and 0.7% preasphaltenes (1 hr, 790°F, 2000 psig). The hydrogen-poor solvent gave only 67% conversion and 7.3% preasphaltenes, a ten-fold increase in preasphaltenes, at the same conditions. Good conversion of preasphaltenes appears to be the key to good conversion of Black Thunder coal to liquid, and good hydrogen donor strength is essential. Prehydrogenation of the slurry solvent may give higher conversion at high space velocity, which has been difficult to achieve with this feedstock.

Analyses of Spent Catalyst Samples

Initial performance of all the C/T runs with Black Thunder coal was excellent. No resid was produced, and the coal conversion was over 90%. To prolong the period of high activity, spent catalyst samples were studied to determine the cause of deactivation. Samples from Professor Haynes (University of Wyoming) showed a layer of calcium on the surface of

the catalyst. Haynes noted that coke could be burnt off only after the catalyst pellets were broken, suggesting that the calcium layer hindered diffusion. Our spent AMOCAT™ 1B catalyst was easily decoked at 860°F without breaking the pellets, but they also showed a thinner, discontinuous Ca shell. Because Ca contributes to catalyst deactivation, SO_2-demineralization should improve the catalyst life.

Our AMOCAT™ 1B-1C catalysts contained more coke than the sample from Haynes (29% vs 11%, Table 91). Haynes' catalyst was used at 800°F compared with 780°F for our test. Our spent catalyst contained more coke at 780°F than at 790°F (Black Thunder reference run), possibly from poorer preasphaltene conversion at the lower temperature. Preasphaltene conversion can be improved by hydrogenation of the slurry solvent, as shown in the previous section of this report. Use of a prehydrogenated solvent may also extend catalyst life.

Black Thunder Coal: Dispersed Mo Catalysts in Stages 1-2

Two dispersed catalysts were used in the first run: Molyvan L and molybdenum octoate. Molyvan L was added to the feed tank without additional sulfiding agent and at lower concentration than in Wilsonville Run No. 263 (96 vs. 200 ppm Mo:coal). Molybdenum octoate, a less expensive oil-soluble Mo compound, was never used at Wilsonville. It required addition of a sulfiding agent, TPS-20 (20% S), to the feed. Iron oxide (red mud) was added to feed at 1 wt% (iron oxide:coal) along with 2 wt% TPS-20.

RESULTS

Most periods from the dispersed catalyst run gave good coal conversion and very little resid in the product. The one exception was the high-temperature, short-residence-time period which gave 17% resid (Figure 18). Molyvan L was an effective catalyst at 96 ppm Mo:coal, giving only 5% resid and a distillate product boiling below 650°F. When iron oxide/TPS-20 was added, no resid was produced--actually resid in the solvent was overconverted--giving a negative net resid yield. Raising reactor temperatures with Molyvan L from 800 to 820°F with iron oxide/TPS-20 overconverted the solvent 650-935°F fraction, giving a -26% yield, and produced 25% light hydrocarbon gas. Operation at 820°F and 3 hour residence time with a dispersed catalyst is too severe for liquefaction of Black Thunder coal. It should be noted that coal conversion dropped from 90% at 800°F to 88% at 820°F, possibly from increased retrogressive reactions at the higher temperature. Molybdenum octoate/iron oxide/TPS-20 gave about the same distillate yield as Molyvan L/iron oxide/TPS-20, but coal conversion was higher (92% in Figure 19).

Product analyses are given in Table 92. The difference between the reference run with AMOCAT™ 1C catalyst in both reactors and the dispersed catalyst run was much larger than with Illinois No. 6 coal. With the dispersed molybdenum catalysts, the hydrogen content was lower for distilled product and resid. All product fractions contained more oxygen, sulfur, and nitrogen (Table 93). One of the more serious consequences is that solvent quality will probably be lower with the dispersed molybdenum catalysts, which could affect coal and resid conversion.

SUMMARY

Overall, dispersed molybdenum catalysts with sulfided iron oxide were effective for liquefaction of Black Thunder subbituminous coal. High-temperature use is not recommended because of high gas yields at long residence time (3.0 hours) and high resid yields at short residence time (1.5 hours). Molybdenum octoate gave good results in the presence of iron oxide and a sulfiding agent, and may be preferred because of its lower cost. In spite of poorer product hydrogen and heteroatom contents, use of dispersed molybdenum catalysts is recommended for liquefaction of Black Thunder coal because of the simpler reactor design.

Black Thunder Coal: Other Dispersed Catalysts

This series of tests used dispersed iron plus molybdenum catalysts for liquefaction of Black Thunder subbituminous coal. Initial tests with Molyvan L dispersed molybdenum catalyst plus iron oxide gave good results at long residence times, but high resid yields at short residence times similar to those used at Wilsonville. To combat the severe deactivation that was seen with supported AMOCAT™ 1C or AMOCAT™ 1B catalysts, different forms of dispersed iron plus molybdenum catalysts were evaluated. These dispersed catalysts might be more active for hydrogenation but not be susceptible to deactivation by pore plugging like supported catalysts. This series of runs tested Molyvan L together with ferrous sulfate or Professor I. Wender's sulfate iron oxide catalyst, which are both more active catalysts than iron oxide. Wender's sulfated iron oxide was also tested as a support for molybdenum and also without

addition of a sulfiding agent to retain higher catalyst acidity, which could be beneficial.

Dispersed iron or molybdenum plus iron catalysts were added directly to the feed. Ferrous sulfate was dissolved in a minimum amount of distilled water before addition to the feed tank. Standard amounts of 100 ppm Mo/coal and 0.7% Fe/coal were used (Molyvan L contains 0.8% Mo). Sulfated iron oxide was precipitated from a solution of ferrous sulfate with ammonia[6], dried at 125°F, ground to -100 mesh, and used without calcining. TPS-20, an oil-soluble sulfiding agent containing 20% sulfur, was added directly to the feed for all except two of the test periods. Illinois No. 6 solvent was used in the last period to study effects of solvent composition (FSN-109, Table 16).

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

Black Thunder Coal: Dispersed Iron and Molybdenum Catalysts

In previous tests, Black Thunder coal was liquefied with Molyvan L dispersed molybdenum catalyst, Molyvan L/red mud (iron oxide) or molybdenum octoate/red mud at 3.0 hours nominal residence time. At this relatively long residence time, performance was good, giving over 88% coal conversions to THF solubles at 800-820°F, and less than 5% resid. Periods with iron oxide gave no resid in the net product from coal. At the end of

the run, one period was included at 1.5 hours residence time and 820°F with Molyvan L (no iron oxide). Coal conversion was good (88%), but the resid yield was very high (17%). This was much different from results of Illinois No. 6 coal, where the results were similar at 800°F/3.0 hours and at 820°F/1.5 hours. Catalyst requirements for liquefaction of Black Thunder subbituminous coal and Illinois No. 6 coal are clearly different.

Batch autoclave liquefaction of Black Thunder coal in tetralin showed that impregnation of the coal with ferrous sulfate in methanol or water gave better results than red mud. Autoclave liquefaction studies also showed good performance from an iron oxide catalyst precipitated in the presence of sulfate, developed by Wender and Pradhan[6]. Ferrous sulfate or sulfated iron oxide catalysts, used in combination with molybdenum, might give sufficient hydrogenation activity for good conversion of Black Thunder resid at reasonably short residence times.

Black Thunder Coal: Ferrous Sulfate and Molyvan L

Operating pressure was 2500 psig and temperatures 820, 800°F/500°F. The effects of temperature on the liquefaction yields from ferrous sulfate plus Molyvan L catalysts at 1.5 hours residence time are summarized in Table 94. Liquefaction at 820°F gave 87% conversion, compared with 84.5% conversion at 800°F, and the resid yield dropped to 9% from 21%, but distillate yields actually decreased to 40% from 45% because hydrocarbon gas yields nearly doubled at the higher temperature. The high gas yield also contributed to 1% higher hydrogen consumption. Analyses of the heavy distillate and resid, Table 95, showed that 650°F- product from the higher temperature was hydrogen-poor, which would make it difficult to upgrade.

Ferrous sulfate/Molyvan L catalysts gave better performance at 1.5 hours residence time than Molyvan L, but coal conversions were still too low and gas yields were too high.

Black Thunder Coal: Sulfated Iron Oxide and Molyvan L

Physical and chemical analyses of the sulfated iron oxide catalyst are given in Table 96, and the pore size distribution is shown in Figure 20. The surface area was 189 m^2/g, more than twice as high as reported by Wender and Pradhan, and surface areas of 400 m^2/g should be possible because of the small average pore radius (16Å).

Without a sulfiding agent, product yields from sulfated iron oxide catalyst and Molyvan L were about the same as from ferrous sulfate and Molyvan L, Table 97 and Figure 21. With added sulfiding agent TPS-20, resid yields dropped from 18% to 12-13%, giving more 650-935°F distillate. Reaction temperatures were kept low (800°F) to avoid high hydrocarbon gas yields, which were slightly lower in the presence of the sulfiding agent. Hydrogen consumptions were 1.2% higher with sulfiding agent, indicating that improved performance was from increased hydrogenation.

Instead of Molyvan L, molybdenum was directly supported on the sulfated iron oxide catalyst, which was used for liquefaction in the presence of a sulfiding agent. Yields were identical to those from sulfated iron oxide plus Molyvan L (Table 97, right-hand columns). The sulfated iron oxide is a good surface for dispersion of molybdenum, and the dispersed molybdenum does not appear to benefit from any unusual interaction between molybdenum and iron.

Product analyses, Table 98, showed all product fractions were more hydrogen-rich if the catalyst contained sulfated iron oxide, molybdenum, and a sulfiding agent. Good hydrogenation activity is the key to good performance of this catalyst combination. The small pore size of the sulfated iron oxide does not contribute any special cracking activity, because essentially all porosity is lost in the liquefaction reaction. The sulfated iron oxide particles probably disintegrate during sulfiding, giving well-dispersed, reactive iron sulfides.

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

Liquefaction of Black Thunder Coal in Illinois No. 6 Solvent

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

pilot plant, Black Thunder coal was liquefied in Illinois No. 6 solvent using ferrous sulfate plus Molyvan L catalysts.

Product yields are given in Table 99 and Figure 22. Illinois No. 6 solvent gave 23% more distillate, 18% less resid, and 5% higher conversion than Black Thunder solvent at the same conditions (800°F and 1.5 hour residence time). Pre-hydrogenation of Black Thunder solvent could give comparable improvements, which would have a large beneficial effect on process economics.

SUMMARY

Sulfated iron oxide plus molybdenum and a sulfiding agent is the most effective catalyst for liquefaction of Black Thunder coal. Ammonium molybdate impregnated onto sulfated iron oxide is the most economical form of the catalyst. Results are better than from supported catalysts like AMOCAT™ 1C, because the supported catalysts deactivate rapidly with this coal. Good performance of the sulfated iron oxide catalysts is linked to high hydrogenation activity, which may upgrade the primary product from coal and the liquefaction solvent. Liquefaction of Black Thunder coal improved in Illinois No. 6 solvent, which is relatively hydrogen-rich, indicating that prehydrogenation of Black Thunder solvent may improve liquefaction performance.

CONCLUSIONS FROM TASK 3.2.1

In Illinois No. 6 coal liquefaction, comparing the dispersed catalysts to C/C liquefaction with AMOCAT™ 1C catalyst, dispersed Mo is effective at

only 100 ppm level and in Stage 1 gave higher distillate yields. In both Stages 1 and 2 dispersed Mo showed good performance at short residence times, but the product had poorer quality (decrease in hydrogenation and heteroatom removal). Both Molyvan L and molybdenum octoate are effective. Mo on Wender's sulfated iron oxide catalyst may be superior to Molyvan L, because it has better resid conversion and higher distillate yields than Molyvan L. Mo carbide and nitride showed poorer coal and resid conversion than MoS_2, the catalyst dispersion was too low and the low catalytic activity caused poor pilot plant operability.

In Black Thunder coal liquefaction, AMOCAT™ 1C gave high initial coal/resid conversion but deactivated rapidly from coke and calcium deposition. Mo on Wender's sulfated iron oxide was the most effective catalyst at 1.5 hr residence time. Using a more hydrogen-rich solvent (Ill. No 6) increased the distillate yields at 1.5 hr residence time.

All dispersed catalysts will allow the use of a less expensive slurry reactor, which should have a large beneficial effect on coal liquefaction economics.

Task 3.2.2: Second Stage Catalysts

The objective was to screen commercial, modified commercial and novel experimental catalysts in a five-parallel fixed-bed sandbath reactor system. The best catalyst formulations were then further tested in the two-stage continuous unit reported in Task 3.2.1.

EXPERIMENTAL

Testing Equipment

Catalyst screening was done using five-parallel fixed-bed reactor pilot plant, called the Miniager (Figure 23). This reactor system allows the simultaneous testing of five catalysts in independent upflow fixed-bed reactors. Each reactor has its own feed supply and product receiver system and can be run at independent feed flow rates and pressures. Because all the reactors share a common heated sand bath, they must be operated at the same temperature.

The standard catalyst loading consists of 10 cc of 14 by 20 mesh catalyst particles diluted with 10 cc alundum chips in a 9/16 inch diameter reactors (Figure 24). With some of the more unconventional catalysts, same amount of active sites measured by static chemisorption of O_2 or CO) were loaded into the reactor.

Feedstocks and Process Conditions

Total of 10 runs were made in this part of the program. One of the reactors in each run was loaded with AMOCAT™ 1C, which was used as a reference catalyst. All catalysts, except those with noble metal components, were sulfided in a flowing mixture of 8 vol% H_2S in H_2. The procedure consisted of first flushing the catalysts with flowing nitrogen (140 cc/min) overnight at 300°F. The H_2S/H_2 mixture was then flowed through the reactor at a temperature of 450°F for 1 hour and at 760°F for

additional 4 hours. After sulfiding the reactors were pressurized to 2000 psig and the oil flow started.

The feedstock for all runs except 1A, 3B and 6A was FSN-106, approximately 45/55 blend of Panasol and coal resid. The properties of this feedstock are in Table 100. Panasol was a 650°F- material that is a byproduct of naphtha reforming and consists primarily of methyl-substituted naphthalenes. The coal resid was a deashed resid from the Critical Solvent Deashing (CSD) unit from Wilsonville Run No. 257 (catalytic/catalytic mode using Illinois No 6. coal). The feedstock for Run Nos. 1A and 6A was 1000°F- feed (gas oil cut) from Wilsonville Run No. 257. Its properties are in Table 101. Run 3B was used to study the effects of feedstocks and resids from Ohio No. 6 coal, Martin Lake lignite and Illinois No. 6 coal (thermal/catalytic mode). The properties of these feedstocks are in Tables 102-103.

Generally, the operating conditions were 2000 psig, 10,000 SCFB hydrogen and 760°F for the FSN-106 runs and 2000 psig, 10,000 SCFB hydrogen, 680-700°F temperature for the coal gas oil with varying space velocity of feed depending on what basis (volume vs. same amount of active sites) the reactors were loaded. The feedstocks and operating conditions for Run Nos. 1-10 are discussed in the results section.

Mass Balances

Detailed mass balances were calculated for each run. Generally, total and elemental mass balances could be closed to within 5-10%.

Catalysts

Three categories of catalysts were tested: commercial, modified commercial and novel experimental catalyst formulations, which are summarized in Table 104. The various commercial catalysts included resid hydrotreating catalysts from Amoco: AMOCAT™ 1B (Mo/Alumina), and AMOCAT™ 1C (NiMo/Alumina) used as a reference catalyst here; other resid hydrotreating catalysts: Resid HDS (a small pore, 10 wt% Mo/Alumina), RCM-4 from UOP (NiMo/alumina), zeolite containing catalyst from Idemitsu (CoMo/Alumina USY-zeolite), TK-771 from Topsoe (NiMo/Alumina); gas oil hydrotreating catalysts: NiMo/Alumina HDN-60 from American Cyanamid (now Criterion), Shell-324 and -411 (both NiMoP/Alumina and made now by Criterion).

The modified commercial catalyst had active promoters added to catalysts: Ru/AMOCAT™ 1A (CoMo/Alumina); Ti, Cr or Ca added to AMOCAT™ 1C.

Several novel catalyst formulations were also tested. AMOCAT™ support was promoted by Ru, or Ir; NiMo promoted Cabot aluminas, which have a specific "popcorn"-like pore structure; Professor Oyama's (Clarkson University) nitrides promoted by Mo, carbides promoted by Mo or W, and AMOCAT™ supported Mo-nitride or Mo-carbide. The testing of Sandia's novel hydrous titanate catalysts is discussed in Task 3.2.3.

RESULTS AND DISCUSSION

1. Testing of Commercial Catalysts

The reproducibility of the testing was compared on AMOCAT 1C™ in Runs 1-4, the ratio of standard deviation to the mean, expressed as a percent, was 5, 6, and 4% for product nitrogen, ramsbottom carbon and 970F+, respectively, indicating good reproducibility (Table 105). Additionally, Run 4 tested a thermal blanc reactor and with a reactor operated at a low LHSV of 0.2. The purpose of the latter test was to determine whether equilibrium or changes in the refractory nature of the feed with conversion were limiting. The results in Table 119 (Tests (1) and (2) show that the thermal contribution to the conversion was small and other limitations were not significant under these test conditions.

The properties of commercial catalysts tested in Runs 1, 3 and 4 are in Tables 106-108. The process conditions for the same runs are in 109-112. The first set of results are compared under standard conditions with Panasol/resid feed after 9 and 14 or 17 days on stream. The product qualities are reported in Tables 113 and 114 (Run 1B) and 115, 116 (Run 3A) and the first order rate constants for Run 3A are in Tables 117 and 118. The product qualities for Run 4 are in Table 119 and rate constants in Table 120.

Comparing the AMOCAT™ series, AMOCAT™ 1C (NiMo promoted) outperformed AMOCAT™ 1B (Mo promoted), which indicates the beneficial effect of the Ni-promoter (Run 3A). AMOCAT™ 1C, Shell 411, HDN-60 and Shell 324 gave comparable performances for hydrogenation, desulfurization, deoxygenation,

Ramscarbon and resid conversion (Runs 1B and 3A). The Resid HDS (small pore Mo/Alumina) and Idemitsu (CoMo/Alumina/Zeolite) catalyst performed poorly. The poor performance of the Idemitsu catalyst was disappointing. The addition of acidic zeolite component to this catalyst support potentially induced more coke formation. In Run 4, AMOCAT™ 1C and UOP's RCM-4 are almost identical. Topsoe's TK-771 is perhaps slightly better than AMOCAT™ 1C and RCM-4 for Ramsbottom carbon conversion (Table 119).

The ranking of the catalysts for both resid and Ramscarbon conversion was:

TK-771 => AMOCAT™ 1C = Shell 324, 411 = HDN-60 = RCM-4 > Resid HDS > AMOCAT™ 1B > Idemitsu

Shell 324 and 411 showed superior denitrogenation activity compared to the other commercial catalysts. Both of these are promoted with phosphorus, which could have an additional promotion effect. TK-771 was slightly better than AMOCAT™ 1C. The ranking of these catalysts for nitrogen removal was as follows:

Shell 324 = Shell 411 > TK-771 > HDN-60, AMOCAT™ 1C > AMOCAT™ 1B = Resid HDS > Idemitsu

Using the coal gas oil feed (1000°F- from Illinois No. 6 coal, Wilsonville Run no. 257), the results (Run 1A) after 10 days-on-oil indicate comparable performance for AMOCAT™ 1C, HDN-60 and Shell 411 for hydrogenation, sulfur and oxygen removal (Table 121). Again nitrogen removal was better with Shell 411.

The different feedstocks were studied in Run No. 3B. Product qualities are in Tables 122-124. The blends of coal resids from Ohio No. 6, Martin Lake lignite, and Illinois No. 6 from T/C operation at Wilsonville with Panasol all led to different nitrogen, Ramscarbon and resid concentrations in the feedstock. Consequently, feedstock effects had to be judged on a basis that is independent of concentration. This was done by comparing first-order rate constants calculated from:

$$k_v = [\ln C_o/C]\ [LHSV]$$

where C_o is the initial concentration of nitrogen, Ramsbottom carbon, or resid, C is the product concentration, and LHSV the liquid hourly space velocity.

Figure 25 shows the data graphed on this basis. The data indicate that the Ohio No. 6 coal-derived resid is more difficult to denitrogenate, remove Ramsbottom carbon from, or convert than the reference feedstock (Illinois No. 6 resid from Wilsonville operated in C/C mode). The resid from Martin Lake lignite, with the exception of denitrogenation, behaved remarkably similar to the reference feedstock as shown in Figure 26. Denitrogenation appears to be easier with the resid from Martin Lake lignite. The expectation was that the Martin Lake lignite coal resid would be much more reactive than the reference feedstock, because lignites are structurally quite different from bituminous coals. Figure 26 indicates that this was not the case. This is not necessarily contradictory, because the coal resid produced in Wilsonville operation was recycled repeatedly, so that the differences between liquid products could be reduced.

Figure 27 compares the rate constants for Ramsbottom carbon, nitrogen removal and resid conversion for AMOCAT™ 1C and Shell 324 for Illinois No. 6 resid from both C/C and T/C operations at Wilsonville. Again, except for denitrogenation, the reactivity of the resids are comparable, even though originally they were produced at much different conditions. Shell 324 is again superior compared to AMOCAT™ 1C for nitrogen removal.

The overall results from the commercial catalyst testing (Runs 1, 3, and 4) suggested that significant improvements could not be made in the economics of coal liquefaction by changing from AMOCAT™ 1C to other commercial catalysts. Consequently, the efforts were shifted to modified supports (to reduce coking propensity) and other novel catalyst formulations, such as nitrides, carbides (Clarkson University) and hydrous titanates (Sandia National Laboratory).

2. Testing of Modified Commercial Catalysts

Ruthenium-containing catalysts have been shown to be extremely active for desulfurization[8] and denitrogenation[9-11] of model compound feedstocks. This motivated the test of Ru-promoted AMOCAT™ 1A (prepared by Dr. Hirshon at SRI). Ru promotion does not give any additional activity and it appears that Ru is deactivated by high molecular weight components in the resid feedstock. (Table 119).

The promotion effects of chromium and titanium on AMOCAT™ 1C were examined in Run No.5. The levels of Cr and Ti were chosen to give nominal coverage of one-fourth and one-half of a monolayer of the alumina (Table 125). The process conditions are in Table 126. The differences in the

performances for HDN, Ramsbottom carbon and resid conversions were all within estimated experimental error (Table 127 and 128). The similar performance of these and other commercial catalysts was postulated to be due to the nature of the reaction network for resid conversion as modeled by Chen and Schindler[12] for the conversion of 850°F+ coal liquids. This model could explain why this reaction network makes the overall resid conversion relatively insensitive to only changes in catalyst hydrogenation activity. The hydrogen consumption is in Table 129. Other than slightly higher coke level with the reference catalyst, little difference was seen with spent catalyst properties in Table 130.

Calcium was added to AMOCAT™ 1C in order to reduce the surface acidity. It appears that this modification caused an improvement for resid conversion compared to AMOCAT™ 1C without Ca (Tables 131 and 132).

3. Testing of Novel Catalysts

a. Ru and Ir Promotion

The motivation for testing Ru and Ir promoted AMOCAT™ supports as catalysts was a large number of literature references which suggest that these two metals are among the most active for hydrodenitrogenation[13-15] and hydrodesulfurization[16-18] in model compound studies. These catalysts were not sulfided prior to use, but reduced in flowing hydrogen. The properties of these catalysts are in Table 106, and process conditions in Tables 109 and 110. As can be seen from Tables 113 and 114, these catalysts were inactive for heteroatom (N, S, O) removal and hydrogenation for various coal resids. The coal gas oil product analysis in Table 121

showed high nitrogen level after only 10 days on stream, which suggested that severe deactivation had occurred. Deactivation was probably caused by high molecular weight and heteroatom contents in the coal liquids.

b. NiMo on Cabot Alumina Support

Three different large pore volume alumina supports were obtained from Cabot Corporation. Cabot calls these fumed aluminas, which have a "popcorn" type pore structures. The nominal pore volumes were 1.2, 1.4, 1.7 cm^3/g and these catalysts were tested at both the same LHSV as the reference catalyst and in case of 1.7 cm^3/g alumina, at the same WHSV. Although the pore volumes of Cabot aluminas are probably too large, and consequently the attrition rates too high, there was still interest to test these supports to see what incentives (if any) exist for reducing intraparticle diffusion limitations by radically changing the support pore structure. The properties of these catalysts are compared to those of the reference in Table 133. The process conditions are in Table 134. These catalysts were tested in Run 2. As the results in Tables 135 and 136 show, the reference catalyst, AMOCAT™ 1C, outperformed all three Cabot catalysts for hydrogenation, denitrogenation, resid and ramscarbon conversion. It appears that the open pore structure of the Cabot aluminas does not further increase the intraparticle diffusion rates more than is already achieved by AMOCAT™ 1C. Consequently, increasing the pore volume from Cabot's nominal values of 1.2 up to 1.7 cm^3/g brings no further improvement in catalyst activity, but adversely affects the pseudo-first order rate constant (on per volume of catalyst basis) k_v (Table 137) due to accompanying decreases in bulk densities and surface area. The spent catalyst properties are in Table 138.

c. Nitrides and Carbides

MODERATE SURFACE AREA NITRIDES AND CARBIDES

The motivation for testing Professor Oyama's (Clarkson University) molybdenum carbide and nitride catalysts was the previous report[19,20] that these materials were three times as active as a sulfided commercial hydrotreating catalyst for the denitrogenation of quinoline at 1,000 psig and in a batch reactor. Tests of catalysts with model compounds, however, can be deceiving. Therefore, this testing was conducted with commercial feeds. A further motivating factor for testing these catalysts was their availability in rather high-surface-area forms (about 20 m^2/g).

Molybdenum carbide and nitride differ from molybdenum sulfide in that the former two are interstitial compounds in which the nitrogen and carbon reside in the interstices of the close-packed molybdenum atoms as shown in Figure 28A and 28B. In contrast, the molybdenum atoms in molybdenum sulfide lie within the interstices of the sulfur atoms (Figure 28C).

In the testing, a bulk molybdenum nitride and an alumina supported molybdenum carbide were compared against AMOCAT™ 1B (Mo/Al_2O_3) and Shell 324 ($NiMo/Al_2O_3$). AMOCAT™ 1B was chosen because it does not contain a nickel promoter. Shell 324 was chosen because it was used in the earlier published study of quinoline denitrogenation.[20] In addition, a blank reactor packed with inert alundum chips served as a thermal control. The comparison was made in the miniager (AU-126) which allows simultaneous comparison of all the catalysts and the thermal control.

Two coal-derived feeds were used as part of a continuous run. A coal gas oil from Wilsonville was used first, followed by the standard feed. Process conditions are listed in Tables 139 and 140.

Catalyst Characterization

The molybdenum carbide and nitride catalyst were characterized prior to use in the reactors by N_2 physisorption to determine their BET surface areas and by CO chemisorption.

Sulfided Shell 324 was characterized by static O_2 chemisorption. Shell 324 and AMOCAT^{TM} 1B were further characterized by the chemisorption of CO and O_2 in the pulse mode. This was done by pretreating the molybdenum carbide and nitride at 350°F in flowing He for 2 hours, switching the flow of helium to an 8% H_2S/balance H_2 (sulfiding gas) stream and ramping 2°C/min to 800°F, holding at this temperature for two hours, cooling to 300°F in the flowing sulfiding gas, purging with flowing N_2 for 10 minutes, and finally cooling to room temperature in flowing N_2. The catalysts were then dosed with 100 O_2 (or CO) pulses until saturation uptake was reached. Table 141 summarizes BET surface area results and the chemisorption characterization of the catalysts. The reactor packings were compared using various techniques (Table 142).

X-ray photoelectron spectroscopy (XPS) was performed on the molybdenum carbide and nitride catalysts prior to and after use in the reactors. Before XPS analyses, the catalysts were reduced at 790°F in flowing H_2 at atmospheric pressure in an ex-situ XPS reduction cell. The catalysts after reaction are referred to as "used" catalysts below.

Catalysts removed from the reactors were extracted with THF overnight and then dried at 230°F in a rough vacuum overnight before analysis by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

XRD was performed with a Scintag PAD V powder diffractometer using samples mounted on double-sided adhesive tape using curve deconvolution to remove the tape signal. XPS was done with a Surface Science Instruments SSX-100 microprobe equipped with a UHV transfer system for in situ reductions in flowing hydrogen. Surface concentrations were calculated after correcting the peak areas for differences in photoionization cross-section using the Scofield tables and differences in the electron mean free path. The software used was Version 8.2 from Surface Science Instruments. The quantitation is accurate to within 10%.

The nitrogen content of the product vs. time on oil during Run 6A is described in Figure 29. It is also apparent that the molybdenum carbide and nitride catalyst were, indeed, active by comparing the nitrogen content of their products with that of the blank reactor. Furthermore, the molybdenum carbide and nitride catalysts also yield products with lower nitrogen contents than those from Shell 324 and AMOCAT™ 1B.

Table 143 gives a more comprehensive summary of the product qualities after 256 hours on oil. The molybdenum carbide and nitride catalysts yield products that are significantly better than that from the blank reactor. Furthermore, all the measurements indicate that product qualities are better than those from Shell 324 and AMOCAT™ 1B.

Table 144 compares product qualities after one week on oil with coal resid feedstock during Run 6B. As found for Run 6A, the molybdenum nitride and carbide catalysts yield products that are substantially better than those from the thermal treatment and even those from the AMOCAT™ 1B and Shell 324 catalysts.

Activity Determination by Rate Constants

The pseudo-first-order rate constants for desulfurization, denitrogenation, and aromatic saturation are compared to Shell 324 in Table 145. The first-order rate constants are normalized by the amount of active sites in each of the reactors. As previously stated, the active sites were counted by the static chemisorption of O_2 in the case of Shell 324 and AMOCAT™ 1B and CO chemisorption in the case of molybdenum nitride.

Table 146 is a more comprehensive comparison of the rate constants for denitrogenation referred to a number of different bases--including a volume and weight basis where the rate constants were normalized relative to Shell 324. It is notable that despite the low surface area of molybdenum nitride, its value of k_v is only about one-half of that of Shell 324.

A concern with using molybdenum carbide and nitride for hydrotreating applications is that the formation of molybdenum sulfide is thermodynamically favored in the presence of sulfur.[19] Consequently, the catalysts were characterized after reaction by XRD and XPS analyses. XRD did not show the presence of crystalline MoS_2 at the detection limit

concentration of 1 wt% on the molybdenum nitride (molybdenum carbide was not examined). The results from XPS are shown in Tables 147 and 148.

The used molybdenum nitride in Table 147 had a sulfur-to-molybdenum ratio of 3.2/12.5=0.26, far below the expected ratio of 2 should MoS_2 have been formed within the sampling depth for XPS (roughly 10-20 Angstroms). Consequently, it does not appear that extensive sulfiding of the molybdenum nitride occurred during its use. The same argument and conclusion applies to Mo_2C/Al_2O_3. It cannot, however, be ruled out that some MoS_2 was formed at topmost atomic layers of the nitride (carbide) crystallite surface.

An analysis of the oxidation states of molybdenum in the used molybdenum carbide and nitride catalysts indicates that not all the molybdenum was reduced to the Mo^{+4} state (only 63% in the case of Mo_2N) during the pretreatment. To determine if the unreduced molybdenum was caused by exposure of the materials to air during their removal from the reactor, the fresh catalysts were also reduced in a separate experiment in the XPS in situ chamber at conditions resembling those used to originally pretreat the catalysts. The results from these experiments are shown in rows labelled "reduced" in Table 147 and 148. They indicate that the molybdenum in the nitride and carbide was more extensively reduced after removal from the reactors than after the in situ treatment prior to XPS. This result may be due to exposure to higher hydrogen partial pressures over a greater length of time during the pilot plant run as contrasted with the shorter reduction at atmospheric pressure during the in situ reduction prior to XPS. Because the amount of reduction and reoxidation remains unknown, the amount of the molybdenum in the Mo^{+4} state shown for

the used catalysts in Table 148 represents a lower bound for that present at reaction conditions. Unfortunately, one cannot distinguish between Mo^{+4} associated with carbon (nitrogen) and sulfur from XPS. Consequently, it is not possible to determine the degree of sulfiding from the oxidation state of molybdenum.

It is clear from the results that molybdenum carbide and nitride are active for hydrotreating under practical industrial conditions. While the feedstocks were coal-derived liquids, it is very likely that molybdenum nitride and carbide will exhibit similar catalytic properties for hydrotreating petroleum-derived liquids.

There was, however, one unique property of the coal feedstocks that may make them more amenable to conversion over carbide and nitride catalysts--it is their low sulfur content. As noted earlier, carbides and nitrides are thermodynamically unstable under practical hydrotreating conditions and should form molybdenum sulfide. If such a transformation were to occur, it is likely the materials would exhibit catalytic properties similar to that of conventional hydrotreating catalysts and, consequently, the effort of making carbides and nitrides would be wasted.

The XPS and XRD characterization of the catalysts did not indicate that the catalysts were extensively sulfided, even after hydrotreating coal residuum (0.08% sulfur). Unfortunately, the formation of molybdenum sulfide at the topmost atomic layers of the carbide and nitride cannot be ruled out at this time. However, the issue of the sensitivity to sulfur remains crucial for the carbides and nitrides to become viable substitutes for conventional supported molybdenum sulfide. An additional critical

issue for the practical application of carbides and nitrides is their activity. Because the preparations of molybdenum nitride and carbide catalysts did not have optimal surface areas, it was important to attempt to compare the activities of these materials on a basis that is independent of surface area. Motivated by the successful use of the concept of turnover numbers (number of reaction events per unit time and per active site) in other areas of heterogeneous catalysis,[21] the catalysts were chosen to be compared on an active site basis. Unfortunately, there is much controversy over what are reliable techniques for counting active sites on sulfide catalysts.[22]

Here, the active sites on the carbides and nitrides were counted by the chemisorption of carbon monoxide because CO is known to chemisorb on metals. There is also a reason to believe the surface molybdenum atoms have similar chemisorption characteristics. For the conventional hydrotreating catalysts, the chemisorption of O_2 in a static adsorption apparatus[19,20] was used. This method may have problems because there is work to support the contention that the static chemisorption of oxygen on molybdenum sulfide at room temperature is corrosive;[23,24] that is, the oxygen atoms are not only adsorbed at the surface of the sulfide crystallites, but they also penetrate into crystallite. Consequently, attempting to measure active sites with such a method may lead to high values. Bartholomew,[23,24] for example, noted that as much as 3-5 times as much oxygen is adsorbed during static chemisorption as contrasted with chemisorption in the pulse mode.

For this reason, the sites were counted by the chemisorption of O_2 in the pulse mode (Table 142). Pseudo-first-order rate constants were then

renormalized to these values and are shown in Table 146. Comparing these rate constants (1.75×10^{-3} for Shell 324 and 2.57×10^{-4} for AMOCAT™ 1C) with those for molybdenum carbide and nitride suggests that the carbide and nitride catalysts possess slightly lower activities than do the conventional catalysts for denitrogenation during Run 6A. On the other hand, if it's assumed that the total surface area as measured by BET is the appropriate method, then Mo_2N has a higher rate constant than Shell 324 (2.36×10^{-4} vs. 1.85×10^{-4}).

Overall, the gas oil and resid product qualities from the moderate-surface-area carbide and nitride catalysts were significantly better than the thermally treated liquids, indicating the materials were indeed active under practical hydrotreating conditions. When the catalyst activities were compared on an active site basis, the nitrides and carbides were estimated to have activities two to five times those of Shell 324 and AMOCAT™ 1B. However, in determining the activity, conclusions of this work are very sensitive to the method used to count active sites. Rather than attempt to determine the optimal site counting method, the practicality of these materials was assessed by preparing them in higher-surface-area forms and then comparing them at constant volume against Shell 324 and AMOCAT™ 1B.

HIGH SURFACE AREA CARBIDES AND NITRIDES

The previous study, with moderate-surface-area, unsupported Mo_2N and Mo_2C/alumina, was the first test of these materials in pilot plant operation at commercial hydroprocessing conditions and with practical feedstocks--coal-derived gas oil and resid.

Mo_2N and Mo_2C/Al_2O_3 performed remarkably well considering that based on thermodynamics favoring the conversion of these materials to sulfides, they would be poisoned by sulfur present in the feed.[25] Indeed, when the catalytic activities were compared on site basis, turnover rates for Mo_2N and Mo_2C/Al_2O_3 exceeded those for a conventional $NiMo/Al_2O_3$ catalyst by a factor of about two.[26]

The initial pilot plant runs with these catalysts were performed at unequal liquid hourly space velocities (volumetric flow rate of oil per volume of catalyst, LHSV).[26] A comparison of catalysts at the same LHSV is necessary for assessing the scale-up to commercial reactors. The catalytic performance of a second generation of unsupported WC and Mo_2N and supported catalysts--Mo_2N/AMOCAT™ and Mo_2C/AMOCAT™--is compared with that of Shell 324 at the same LHSV (except for tungsten carbide, WC). As before, the feedstocks included coal gas oil and resid. An additional feedstock consisting of coal gas oil spiked with CS_2 was used to assess the sulfur tolerance of the catalysts.

The catalysts used in this study were characterized before and after use in the pilot plant by x-ray photoelectron spectroscopy (XPS) to determine the extent of sulfiding of the surface. The catalysts were also characterized by N_2 adsorption/desorption to measure surface areas and pore size distributions. The latter measurements were critical in assessing the novelty of the carbide catalysts. Finally, chemisorption of carbon monoxide was used in an attempt to count active sites on the surface of the carbide and nitride.

EXPERIMENTAL

Preparation of Catalysts

High-surface-area WC, Mo_2N, Mo_2C (not tested in the pilot plant), Mo_2N/AMOCAT™, and Mo_2C/AMOCAT™ were prepared at Clarkson University by Professor Ted Oyama as part of a subcontract to this contract. Preparation methods involved temperature programmed nitriding and carburizing of MoO_3 with high flow rates of NH_3/H_2 and CH_4/H_2 mixtures, respectively. Details of the preparation methods have been described elsewhere.[19]

Pilot Plant Operation

As with the previous runs, the mini-ager pilot plant, AU-126L, was used. Table 149 shows the catalyst loadings of the five reactors. With the exception of WC, all catalysts were loaded with the same volume of catalysts. Shell 324 was loaded into Reactor A. Insufficient WC was available to load 10 cc; instead, the maximum available amount of 6 cc was loaded into Reactor B. Mo_2N was used in Reactor C. AMOCAT™-supported Mo_2N and Mo_2C were used in Reactors D and E. Process conditions are given in the bottom portion of Table 149. Note that they are different for the coal gas oil and resid, and they involve changing the space velocity during the gas oil portion of the run. Feedstock properties are given in Table 150.

The feeds shown in Table 150 were run sequentially, i.e., the coal gas oil (FSN-100) was used first at the process conditions shown in Table 149. A

flow rate of 5 cc/h (0.5 LHSV) was used for 72 hours, at which time samples were taken for measurements of product quality. The feed rate was then increased to 10 cc/h (1 LHSV). After 28 hours (120 hours total on oil), samples were again taken for analysis. It was necessary to refill the pumps with coal gas oil from a new drum. This feedstock is referred to as FSN-100 NEW in Table 150. The flow rate was then increased to 20 cc/h (2 LHSV) for 72 hours (192 hours total on oil), and a sample was taken for analysis. To check for deactivation, the flow rates were then returned to 10 cc/h (1 LHSV) and a sample taken after an additional 72 hours on oil (264 total hours).

At this point, a switch was made to the coal gas oil spiked with CS_2, referred to as FSN-100+CS_2. This feed was used to assess the sulfur sensitivity of the catalysts. A sufficient amount of CS_2 was added to increase the sulfur concentration by about a factor of 7-9. The CS_2-spiked feed was used at 10 cc/h (1 LHSV) for an additional 72 hours (336 hours total on oil), at which time a sample was taken for analysis.

The final portion of the run was devoted to assessing the performance of the catalysts on a resid-containing feed. Reactor temperatures were increased to 760°F, flow rates decreased to 5 cc/h, and the coal resid/Panasol blend (Table 150) used for an additional 240 hours (576 hours on oil total), at which time the final product sample was taken for analysis.

RESULTS

Characterization of Catalysts by CO Chemisorption

CO chemisorption results are shown in Table 151.

Characterization of Catalysts by XRD

Figures 30-32 show the x-ray diffraction patterns on WC, Mo_2N, and Mo_2C. The materials were identified by their characteristic diffraction lines: WC (2θ = 31.6, 35.8, 48.7, 65.7, 73.1), Mo_2N (37.3, 43.5, 63.2, 75.4, 79.9), and Mo_2C (34.5, 37.9, 39.5).

XPS Analysis of Fresh Catalysts

Mo_2N and Alumina-Supported Mo_2N

Tables 152 and 153 summarize the surface compositions of the fresh catalysts as measured by XPS (atom percent) and binding energies (BE's). For unsupported Mo_2N, the Mo/N ratios are 1.0 and 1.5 before and after reduction, respectively, at 790°F in flowing H_2 for four hours. As shown in Table 153, two nitrogen species are detected at N 1s BE's of 397.4 ± 0.2 and 400.3 ± 0.1 eV, attributable to a nitride and an organic amine species. While the as-received sample yields the Mo 3d5/2 BE's of 228.7 and 231.8 eV, the reduced sample gives two components at the Mo 3d5/2 of 228.8 and 230.8 eV. The Mo species at ≈ 228.8 eV is attributed to Mo(IV) associated with Mo_2N; the species at 231.8 and 230.8 eV are likely due to more oxidized forms of molybdenum, namely, Mo(V) and Mo(VI), respectively.

The presence of Mo(V) species is probably due to partial reduction of Mo(VI) at 790°F.

For alumina-supported Mo_2N, the Mo/N and Mo/Al ratios are 2.0 and 0.067, respectively. The Mo/N ratio obtained by XPS is consistent with the nominal stoichiometry of Mo_2N. Also notable is that these ratios remain essentially unchanged upon reduction at 790°F for 4 hours. There are two molybdenum species detected by XPS at the Mo3d5/2 BE's of 229.8 and 232.3 ± 0.3 eV, attributable to Mo(IV) in Mo_2N and Mo(VI), respectively. One nitrogen species is observed at the N 1s BE of 397.0 ± 0.2 eV, which is assigned to a nitride species. No changes are detected upon the reduction in both the XPS BE's for Mo and N species, suggesting that ≈ 26% of Mo_2N is partially oxidized to Mo(VI) during exposure to ambient air and that this Mo(VI) was not reduced at 790°F in H_2 for 4 hours. While it is not possible to identify exactly the chemical nature of this Mo(VI) species, the lower degree of reduction compared with the unsupported sample is probably a result of Mo-alumina interaction.

<u>Mo_2C and Alumina-Supported Mo_2C</u>

XPS data for these samples are also summarized in Tables 152 and 153. For Mo_2C/Al_2O_3, no substantial change on Mo/Al ratio is observed on reduction. For unsupported Mo_2C, only one Mo species is detected at the Mo 3d5/2 BE of ≈ 229.0 eV, characteristic of Mo(IV) carbide. However, for the supported Mo_2C sample, an additional Mo species (32-40%) is observed at the Mo 3d5/2 BE of 231.8 eV, indicative of Mo(VI). Like Mo_2C/Al_2O_3, very little change is seen in the Mo speciation upon reduction at 790°F for supported Mo_2C sample. It is clear that the presence of alumina inhibits

reduction of Mo(VI) at 790°F for both Mo_2C and Mo_2N samples, presumably due to Mo-alumina interactions.

Unsupported WC

The sample yields an XPS atom ratio of W/C of 0.49, and two W species at the W 4f7/2 BE's of 31.8 and 35.7 eV, respectively, for W(IV) in WC and W(VI) in WO_3 (Table 153). No reduction was performed on this sample.

XPS Analysis of Used Catalysts

Table 154 summarizes the XPS surface compositions (atom percent) of the five catalysts after they have been removed from the reactor, Soxhlet-extracted with tetrahydrofuran overnight, and then dried under vacuum at room temperature overnight.

As shown in Table 154, the unsupported Mo_2N catalyst experiences a decrease (from fresh catalyst) in N/Mo ratio on the used catalyst, whereas the Mo_2N/Al_2O_3 yields a higher N/Mo ratio after use. Moreover, the S/Mo ratio on the used catalysts is higher for the alumina-supported catalyst than that for the unsupported catalyst.

Table 155 summarizes the XPS binding energies (BE's) of C1s, Mo3d5/2, W4f7/2, N1s, and S2p. Shell 324 yields a Mo3d5/2 BE of 229.1 eV and a S2p BE of 162.1 eV, attributable, respectively, to molybdenum in a tetravalent state (probably MoS_2, Mo/S = 0.5) and a S^{-2} species. A N1s BE of 400.6 eV suggests that nitrogen is in a form of organic amines. Not included in this table is the XPS BE of the Ni2p3/2 line. According to the data, the

sample yields a Ni2p3/2 BE of 853.9 eV, which is due to NiO without interaction with the alumina support.

Used WC gives two components in a W4f7/2 line at 31.9 and 35.6 eV, which are assigned to W(IV) and W(VI) species, respectively. There are also two S species observed at 162.3 and 169.2 eV, due to S^{-2} and a sulfate species. Judging from the atom composition, it is suggested that W(IV) is present as both sulfide and carbide on this used sample. Some organic amine species were also observed on this sample at the N1s BE of 400.6 eV.

Both unsupported and alumina-supported Mo_2N samples show two Mo species in the Mo3d5/2 region at 228.9 and 232.1 eV, indicative of Mo(IV) and Mo(VI) species, respectively. While the unsupported sample shows a nitride (N1s 397.4 eV) and a sulfide (S2p = 161.8 eV), the sulfide and the amine species are detected on the alumina-supported sample. The absence of the nitride (N1s = 397.4 eV) for Mo_2N/AMOCAT™ suggests that most Mo_2N on alumina has been converted to MoS_2 and other Mo species during reactions. Based on the atom ratio between Mo+4 and the sum of S^{-2} and nitride, it is suggested that in addition to MoS_2, some other Mo(IV) species may also be present on these samples. Thus, the supported Mo_2N has a greater tendency to form a sulfide than the unsupported catalyst. In contrast, the low S/Mo ratio of 0.53 (Table 154) for the Mo_2N catalyst, coupled with the presence of nitrogen as a nitride (Table 155) suggests much of the Mo remains as Mo_2N and is not converted to a sulfide.

Sample Mo_2C/AMOCAT™ gives two Mo species at the Mo3d5/2 BE's of 228.9 (Mo(IV)) and 231.9 (Mo(VI)) eV and a sulfide species having the S2p BE of 162.2 eV. Again, judging from the Mo/S ratio, it is suggested that some

of the Mo_2C has been converted to MoS_2 during reactions. No nitrogen is detected on this sample.

Pore Size Distribution and BET Surface Area Measurements

Pore volumes and average pore diameters as measured by N_2 desorption and BET surface areas are shown in Table 156 for fresh Shell 324, WC, Mo_2N, and Mo_2C. The surface area of 96 m^2/g for Mo_2N is exceptionally high for an unsupported catalyst. Lower surface areas of 30 m^2/g were obtained for WC and Mo_2C.

There is a substantial difference between the exceptionally high pore volume of 0.537 cm^3/g, which exceeds that of Shell 324 for Mo_2C, and the order-of-magnitude lower values of 0.068 and 0.075 cm^3/g obtained for WC and Mo_2N.

Figures 33 and 34 show pore size distribution for the catalysts. Pore volume distributions for each catalyst in Figure 33 were normalized and graphed in Figure 34. Differences in pore volume are clearly revealed by the differences in the areas beneath the curves for each catalyst in Figure 33. Figure 34, on the other hand, emphasizes differences in pore size distributions.

In general, the pore size for WC, Mo_2C, and Mo_2N are shifted to substantially lower pore diameters (~ 40Å) compared with Shell 324. Both WC and, particularly, Mo_2C have a substantial fraction of their pore volume present within pores with diameters greater than 200Å.

Product Yields and Qualities

Table 157 shows product properties and conversions after 72 hours on the coal gas oil feed and at a feed rate of 5 cc/h. The product from Shell 324 had the highest H/C ratio and the greatest reduction in aromaticity as measured by C^{13} NMR. The increase in H/C ratio and corresponding reduction in aromatics measured by C^{13} NMR was about the same for WC and Mo_2N, while the Mo_2N/AMOCAT™ and Mo_2C/AMOCAT™ were less active than WC and Mo_2N.

Denitrogenation and removal of oxygen were slightly lower for WC and Mo_2N than Shell 324. Mo_2N/AMOCAT™ and Mo_2C/AMOCAT™ were comparable for these two functions and less active for denitrogenation than WC and Mo_2N.

It is interesting to note that WC, Mo_2N, Mo_2N/AMOCAT™, and Mo_2C/AMOCAT™ exhibited little desulfurization despite the former two catalysts being almost as active as Shell 324 for hydrogenation, denitrogenation, and removal of oxygen.

Table 158 shows product properties and conversions after 120 hours on oil, the last 28 hours at an increased feed rate of 10 cc/h. The ranking of the catalysts for hydrogenation, denitrogenation, and desulfurization is the same as it was in Table 157.

Table 159 gives product properties and conversions after 192 total hours on oil, the last 72 hours at a 20 cc/h feed rate. An additional difference between the conditions at which product was collected for Tables 157 and 158 is that the feed used for Table 159 was from a

different drum. Ostensibly, the feeds should not have been different; however, a comparison of properties in Table 159 indicates a slightly lower nitrogen content for this feed.

Product qualities and conversions after 264 hours on oil are shown in Table 160. The feed rate was restored to 10 cc/h for the last 72 hours. A comparison with the conversions in Table 157 indicates that deactivation occurred for denitrogenation, desulfurization, and deoxygenation and, although to a lesser degree, for hydrogenation.

Table 161 gives product qualities and conversions after a switch was made to the feed containing 0.2% of sulfur (CS_2-spiked feed shown in Table 150). Notable is an increase in denitrogenation. Hydrogenation decreased slightly while desulfurization was uniformly high for all the catalysts due to the easy removal of sulfur from CS_2 in the liquid product (due to either its vaporization or hydrogenation).

Figures 35-36 and 38-40 summarize the data of Tables 157-161 in the form of graphs of the ln (1-conversion) vs. 1/LHSV for desulfurization, aromatics saturation, and denitrogenation. A straight line would be observed if first-order kinetics were applicable. It can be seen that this is true for aromatics saturation, but not for denitrogenation. Figure 37 shows a plot of 1/[product sulfur] vs. 1/LHSV. The data fall along a straight line indicative of second-order kinetics. In all the graphs, the numbers above the data points indicate the order that the data were obtained.

Table 162 shows product properties after a switch to the feed containing coal resid. A comparison with Table 157 (start of run with gas oil feed) shows the hydrogenation of this feed was, in general, greater for the resid feed than for the gas oil. Denitrogenation was comparable for both feeds, while oxygen removal was lower for the resid feed. Figures 36-40 also show data for the resid feedstock. It is interesting to note the carbides and nitrides now exhibit substantial desulfurization activity, whereas they did not for the gas oil feed (Tables 157 to 160).

Shell 324 outperformed the other catalysts for hydrogenation, denitrogenation, desulfurization, and oxygen removal. The nitrides and carbides performed as well as Shell 324 for resid conversion. The remarkably low value of 37.8% resid conversion for Mo_2N may have been due to a faulty distillation.

Table 162 also indicates the AMOCAT™-supported Mo_2N and Mo_2C now perform better than WC and Mo_2N. The opposite ranking was observed for the coal gas oil feed (Tables 157 to 161).

DISCUSSION

XPS Analysis of Fresh and Used Catalysts

A number of observations may be made of the XPS results on the fresh catalyst. There is a decrease in the surface concentration of carbon (Table 152) after reduction of the fresh catalysts in flowing nitrogen at 790°F. This may be explained by the removal of hydrocarbons adsorbed during exposure to ambient air.

It is apparent, from the ratio of N to Mo in the case of the molybdenum nitrides and C to Mo and W in the case of carbides, that the surface composition is different from our nominal compositions of Mo_2N, Mo_2C, and WC. For bulk molybdenum nitride, the surface is best represented by $Mo_{1.5}N$ after reduction; for bulk molybdenum carbide, $Mo_{0.7}C$ represents the surface composition. In the case of the alumina-supported samples, $Mo_{1.4}N$ and $Mo_{2.9}C$ are better representations.

A substantial amount of molybdenum and tungsten, even in the bulk compounds and after reduction in hydrogen at 790°F, exists in a valence state greater than four. For example, for reduced Mo_2N, 68% of the molybdenum is present as Mo(IV) while 32% is in a higher valence state.

In the case of the supported samples, a comparatively greater proportion of molybdenum and tungsten is present in a valence state exceeding four. Consequently, it appears that the supported catalysts were not as extensively nitrided (carbided) as the bulk compounds.

XPS of the used catalysts removed from the reactor showed an increase in the carbon level on each catalyst. This is undoubtedly due to the buildup of coke on the catalyst's surface. Of particular importance is that the sulfur-to-Mo (and W, in the case of tungsten carbide) is well below 2, the value expected for molybdenum disulfide had formed. In the case of Shell 324, however, the sulfur-to-molybdenum ratio is equal to 2. Further evidence against extensive sulfiding of the nitride's surface is that the nitrogen-to-molybdenum ratio for bulk Mo_2N is reduced from 0.66 to only 0.51 after reaction.

Unfortunately, it is not possible to use the information on binding energies (Table 155) to distinguish molybdenum (or tungsten) nitride (or carbide) from molybdenum (or tungsten) sulfide because the metal is in the same valence state in all of these compounds. This is apparent from noting that the binding energy of molybdenum in Shell 324 (229.1 eV) and bulk Mo_2N (228.6 eV) is comparable (Table 155). However, for the Mo_2N/AMOCAT™, it appears that most of the molybdenum has been converted to MoS_2 and other Mo species because of the absence of nitrogen in a nitride (BE = 397.4 eV) state.

It is notable, however, that the nitrogen in the case of bulk Mo_2N remains in the valence state expected of that for molybdenum nitride (Table 155). This further supports the contention that molybdenum nitride is present on the surface of bulk compounds.

Despite exposure to practical hydrotreating process conditions, the Mo_2N and WC bulk catalysts exhibited remarkable resistance to sulfiding, as confirmed by the XPS in Table 154. This is consistent with recently published work[27] also showing these compounds to be sulfur-tolerant despite the presence of a large thermodynamic driving force for conversion to molybdenum disulfide.[25]

Finally, a comparison of Tables 153 and 155 indicates the molybdenum in the supported samples is more extensively reduced after use in the pilot plant. This has been noticed in the previous study of these materials and is attributable to the extensive exposure to reducing conditions (576 hours at 700-760°F at hydrogen partial pressures exceeding 1000 psig

vs. 5 hours at 780°F and atmospheric pressure hydrogen as for the pretreatment used for the samples shown in Table 153).

Pore Size Distribution and Surface Area Measurements

The preparation of the bulk Mo_2N was quite successful because a surface of 96 m^2/g was achieved. Lower surface areas of 30 m^2/g were obtained for WC and Mo_2C. Notable is that the pore volumes for Mo_2N and WC, the catalysts tested in the pilot plant, were much lower than that for Shell 324. This is also apparent in Figure 33 by comparing the relative areas under the curves for the catalysts. Also notable from Figures 33 and 34 is that the pore radii of the Mo_2N and WC catalysts are substantially lower than those for Shell 324. In view of the fact that a considerable effort has been expended on tailoring the pore structure of commercial catalysts, one would expect the Mo_2N and WC to perform poorly as hydrotreating catalysts due to severe diffusional restrictions.

Pilot Plant Results

Aromatics Saturation

Figures 35-37 summarize performance of Shell 324 in the pilot plant. Figure 35 shows the percent reduction of aromatics as measured by C^{13} NMR plotted against 1/LHSV. A straight line on this graph indicates the kinetics are pseudo-first-order. The dashed line is through the data points taken with the gas oil feedstock (including when it was spiked with CS_2). The solid line is for the resid-containing feedstock. The data

points are numbered in the order in which the data were obtained. The same nomenclature is used for Figures 35-41.

Notable in Figure 35 is that aromatics saturation indeed follows first-order kinetics when the coal gas oil is used as the feedstock. Too few data points were collected with the resid-containing feedstock to make a similar conclusion. Figure 35 also indicates that there was little deactivation for aromatics saturation and that the presence of carbon sulfide, which is rapidly converted to H_2S, does not alter the aromatic saturation activity. Indeed, the same conclusions may be made for WC, Mo_2N, Mo_2N/AMOCAT™, and Mo_2C/AMOCAT™ on the basis of Figures 38A, 39A, 40A, and 41A. In addition, it is also notable that the slope of the line for the resid feedstock is greater than for the gas oil feedstock. At first glance, this suggests that the resid constituents are easier to hydrogenate than those in the gas oil. A more likely explanation is that the hydrogenation of methyl naphthalenes in Panasol is instead responsible for most of the reduction in aromatics shown in these figures and that the naphthalene compounds are easier to hydrogenate than the aromatic compounds present in the gas oil.

Desulfurization

Figure 37 presents a graph of the desulfurization data for Shell 324. The data are expected to fall along a line if second-order kinetics are obeyed. Furthermore, the intercept of the line should be the reciprocal of the feed sulfur concentration if second-order kinetics are being followed. It can be seen that second-order kinetics are indeed followed for the gas oil feed; however, there are too few data points for the resid

feedstock for a similar conclusion to be made. Similar graphs are not shown for the carbide and nitride catalysts because of their surprisingly low desulfurization activity.

Denitrogenation

Figures 36, 38B, 39B, 40B, and 41B show first-order graphs for denitrogenation. Note that a straight line is not drawn through the data points for the coal gas oil. This is because it does not appear that first-order kinetics were followed for any of the catalysts. Alternatively, it may be that the catalytic activity of the catalysts for denitrogenation, unlike for aromatics saturations and desulfurization, was continuously changing throughout the run. It is, however, apparent from each of these figures that the presence of CS_2 did not significantly alter the activity of the catalysts.

Deoxygenation

Graphs are not given for deoxygenation because of the potential inaccuracy of the analysis of the oxygen contents in feeds and products.

Relative Catalytic Activities of Catalysts

In addition to product qualities, Tables 157-161 also show rate constants for denitrogenation (HDN), desulfurization (HDS), deoxygenation (HDO), and hydrogenation (HYD) of aromatic rings. First-order kinetics were assumed for HDN, HDO, and HYD, while second-order kinetics were used for HDS.

Rate constants are given on a volume and weight basis. For ease of comparison, the rate constants are normalized relative to Shell 324.

A number of observations may be made concerning the rate constants in Tables 157-162:

At the start of the run, the carbides and nitrides have little to no activity for HDS compared with Shell 324.

The volume-based rate constants for HDN, HDO, and HYD by WC and Mo_2N are often equal and, for WC, frequently exceed that of Shell 324.

The Mo_2N/AMOCAT™ and Mo_2C/AMOCAT™ volume-based rate constants for HDN, HDS, HDO, and HYD are always lower than either Shell 324 or Mo_2N and WC.

The weight-based rate constants for Mo_2N/AMOCAT™ and Mo_2C/AMOCAT™ frequently exceed that of Shell 324 and Mo_2N and WC.

The weight-based rate constants for Mo_2N and WC are generally lower than either Shell 324 or the AMOCAT™-based catalysts.

One can speculate that the lack of HDS activity of the carbides and nitrides indicates catalytic sites that are distinct from those on Shell 324. Alternatively, the small pores present in the Mo_2N and WC may lead to strong diffusion restrictions for HDS.

For the five catalysts of this study, Table 163 shows the relative reactivities of sulfur and nitrogen removal expressed as the ratio of k_{hds}/k_{hdn} for three feeds: coal gas oil, coal gas oil spiked with CS_2, and coal resid.

The quantity k_{hds}/k_{hdn} for coal-derived feeds is about 100 or more using Shell 324 catalyst, as seen in Table 163. This may be due to the higher reactivities of the sulfur components in the coal-derived feeds of this study. These feeds were obtained from the second stage of the two-stage coal liquefaction process at Wilsonville and may have undergone significant partial cracking to form lower molecular weight, higher reactivity sulfur compounds. Having higher reactivities, the coal-derived sulfur compounds of these feeds may be more subject to diffusional constraints where pore size restrictions dominate. These diffusional constraints manifest themselves in the unusually low sulfur conversions observed for many of the novel catalysts, especially the bulk unsupported materials.

The comparable volume-based rate constants for WC, Mo_2N, and Shell 324 has implications for commercial reactors because they are sized on this basis. The high density of the bulk Mo_2N and WC catalysts, however, requires a substantially greater weight (Table 149) to be packed into the reactors using these catalysts. This, along with the likely greater cost of bulk Mo_2N and WC, probably restricts their commercial use.

The comparatively large rate constants for Mo_2N/AMOCAT™ and Mo_2C/AMOCAT™ on a weight basis are promising despite the low values for k_v. This

result suggests that the values of k_v may be improved by using an alumina support that has a higher skeletal density than AMOCAT™ alumina.

Table 161 shows the result of adding CS_2 to the feed. CS_2 is frequently used to sulfide conventional hydrotreating catalysts. It was used here to measure the sulfur sensitivity of the nitride and carbide catalysts.

Notable from Table 161 is that CS_2 did not poison the carbide and nitride catalysts. A comparison with Tables 157-160 does indicate that the HDN and HDO reactions of Mo_2N and W decreased relative to Shell 324, while they were increased for the AMOCAT™-based catalysts. Relative hydrogenation activities were unaffected. No comment can be made about HDS activities because it is impossible to determine if sulfur concentrations in the product were due to the removal of sulfur in the feed or CS_2.

Table 162 shows that the carbides and nitrides are active even for coal resid. This is surprising in the case of WC and Mo_2N considering their small pores (Figures 33-34). Notable too is that the performance of WC, as was often the case with coal gas oil, exceeds that of Shell 324, as can be seen from its values of k_v. It is also apparent that the AMOCAT™-based catalysts exhibit values of k_v that exceed those for Mo_2N and, for some reactions, equal that of WC. This may be due to the pore structure of AMOCAT™ alumina reducing intraparticle diffusion limitations, while diffusion limitations play an even greater role in the small-pore WC and Mo_2N catalysts.

Supported Molybdenum Carbides and Nitrides

While the bulk nitride and carbide catalysts showed remarkable sulfur tolerance under hydrotreating conditions, the supported materials underwent partial conversion to molybdenum sulfide. A strategy to minimize the conversion of supported nitrides and carbides to sulfides during reactions includes the use of different supports that combine surface area stability (necessary because of the high temperatures required for the synthesis of the carbides and nitrides) with minimal Mo-support interactions.

Table 152 suggests that strong Mo-alumina interactions may have inhibited the complete reduction of the supported molybdenum oxide prior to the high-temperature carbiding or nitriding process. Incomplete nitriding or carbiding may render the supported molybdenum more susceptible to sulfidation during reaction.

Several laboratories have found that temperatures at least as high as 1470°F were necessary to reduce completely the molybdenum dispersed on a gamma-alumina support,[28-30] temperatures that are significantly higher than for other supports such as silica or carbon,[31] indicating the latter supports interact only weakly with Mo. There is also an indication that some of these supports undergo very little loss in surface area as a result of the high-temperature reduction.[28] The aluminas used in these studies were highly pure PHF-type aluminas. Other type aluminas (such as AMOCAT™) might not retain their surface area under the extreme high-temperature reduction conditions required above.[32] Thus, the type of

support material must be considered for preparation of the supported nitrides and carbides.

Since the goal of future work is to develop new supports that minimize molybdenum-support interactions during reduction and subsequent sulfiding and nitriding, such supports must also exhibit surface area stability under these conditions. Mo-support interactions may be reduced by choosing supports besides alumina that more closely match the relatively acidic isoelectric point of MoO_3.[33,34]

Candidate materials include silica-stabilized aluminas[35-38] because they show both good surface area retention with temperature and can be prepared with varying degrees of acidity. In addition, one may choose alumina doped with various stabilizing metals to impart the desired surface acidity and surface area stability.[32,35,39]

By using these different materials, one may be able to reduce the supported molybdenum completely and at lower reduction temperatures. This may ensure complete nitriding or carbiding of the molybdenum and, consequently, significantly enhance the sulfur tolerance of the supported catalyst in real hydrotreating conditions.

SUMMARY

Bulk WC and Mo_2N have aromatic saturation and denitrogenation activities approaching that of Shell 324 when the catalysts are compared on a volume basis. This is surprising in view of the small pore volume and pores of WC and Mo_2N. It appears that there are

catalytic sites present on WC and Mo_2N that are intrinsically more active than those of a conventional $NiMo/Al_2O_3$ catalyst.

The unsupported carbide and nitride catalysts were not extensively sulfided under the hydroprocessing conditions encountered in this study, as confirmed by XPS analyses of the spent catalyst. The addition of CS_2 did not significantly alter their catalytic activity.

XPS of the molybdenum carbide and nitride supported on AMOCAT™ alumina indicated the molybdenum was not as extensively reduced as the bulk compounds due to strong Mo/Al_2O_3 interactions. This may have them more extensively sulfided and therefore resulted in lower activities compared with the bulk compounds. Future research on these materials should include using high density supports, which only weakly interact with Mo. These preparations may make it possible to prepare catalysts in which the active sites present at the surface of the supported carbide and nitride crystallites are made more accessible by taking advantage of the tailored pore structure of the support.

CONCLUSIONS FROM TASK 3.2.2

Many NiMo catalysts have equivalent activities for resid conversion, where high initial activities are balanced by increased rates of deactivation. Similarly to petroleum refining, it is difficult to develop resid conversion catalysts primarily due to rapid deactivation by coke and asphaltene adsorption. Large pore, bimodal catalysts are more resistant to pore plugging, but have poorer product upgrading capability, whereas,

small pore, unimodal catalysts have high initial activity and good product upgrading but poor long-term stability. Mo promoted by Ni seems to be the best combination; Ir, Pt and Rh are poisoned by sulfur in the feed. Molybdenum and tungsten carbides and nitrides have good initial activity on active site basis, however, low activity on volume basis.

Task 3.2.3: Hydrous Metal Oxide Catalysts

1. Mini-Ager Testing

INTRODUCTION

The mini-ager testing of hydrous metal oxide catalysts was done in Runs 7, 8 and 9. The purpose of these runs was to compare the performance of a catalyst series based on hydrous titanate oxide (HTO) support materials, developed at Sandia National Laboratories[40,41], to commercial hydrotreating catalysts. The commercial catalysts are considered to be those currently available for use at demonstration-scale or even larger facilities. With the exception of AMOCAT™ series of catalysts, all the other commercial catalysts that were used in this study have been developed and utilized in petroleum refining.

EXPERIMENTAL

Catalysts

The Sandia prepared catalysts included hydrous titanate oxide (HTO) supports with CoMo, PdNiMo, Pd and NiMo promoters. The commercial catalysts in this report included NiMo-containing AMOCAT™ 1C with bimodal pore structure, NiMo-containing Shell 324 (extensively used at Wilsonville) and Shell 411, both with unimodal pore structure. Shell 411 is typically recommended for use as a hydrotreating catalyst for petroleum gas oils (materials with a boiling point range of 650-1000°F) and distillates (boiling range of 350-650°F). While the molecular constituents of these light feeds are undoubtedly different from coal residuums (1000°F+ boiling point), it was reasoned that coal residuums are made up of molecules that are smaller than those in petroleum residuum and so this catalyst might prove to be promising in this work. A detailed description of the available catalyst properties is given in Table Nos. 164-166. Most of the properties of the Sandia catalysts are also available in Sandia reports.

RESULTS

The testing was done with the same reference feedstock, pilot plant and operating conditions as was used in the second stage catalyst testing program. The feedstock properties, catalysts and testing conditions are in Table Nos. 167-170.

Product Qualities

The product qualities from Run No. 7 are in Tables 171-172. After 357 hours on oil (Table 171), the Sandia catalysts, NiMo/HTO and PdNiMo/HTO show comparable denitrogenation and ramscarbon conversion, but slightly better desulfurization and oxygen removal compared to AMOCAT™ 1C. Both Pd #1 and Pd #2 indicate considerably worse product quality, except for oxygen removal by Pd #2 catalyst, than for any of the previous catalysts. At 574 hours on oil (Table 172), the NiMo/HTO and AMOCAT™ 1C show comparable product quality. Desulfurization is slightly lower for PdNiMo/HTO compared to the other two catalysts. As before, the Pd #1 and Pd #2 catalysts have poor product quality (note oxygen removal by Pd #2 again).

The product qualities from Run No. 8 are in Tables 173-174. After 168 hrs on oil (Table 173), the denitrogenation and desulfurization are comparable for AMOCAT™ 1C, and CoMo/HTO. Pd containing catalyst (Pd #3) again shows poorer product quality. The ramscarbon conversion is higher for AMOCAT™ 1C than for CoMo/HTO and Pd #3. After 336 hours on oil (Table 174), the AMOCAT™ 1C shows nominally higher nitrogen and sulfur content in the product than any of the other catalysts, except Pd #3. Oxygen content is also higher for AMOCAT™ 1C than for the other catalysts including Pd #3. The ramscarbon conversion is best for AMOCAT™ 1C, and worst for CoMo/HTO and Pd #3. The other catalysts have ramscarbon conversion that fall in-between.

Tables 175-177 show the product qualities for Run 9. The two Sandia preparations for this run are NiMo promoted HTO catalysts, one with

typical commercial catalyst promoter levels (NiMo/HTO(F)), and the other with half the promoter levels (NiMo/HTO(L)). After 470 hours on oil (Table 175), AMOCAT™ 1C, NiMo/HTO(F) and NiMo/HTO(L) show comparable nitrogen, sulfur, oxygen and ramscarbon in the products. The product from Shell 324 has slightly lower nitrogen, comparable sulfur but higher oxygen than those of the previous three catalysts, and Shell 411 product has even lower nitrogen and comparable oxygen. The sulfur analysis showing high content in the Shell 411 product is questionable. Both Shell catalysts indicate better ramscarbon conversion than that of the three other catalysts. Similar product quality trends can be seen after 779 hours on oil (Table 176) for ramscarbon and sulfur, except that Shell 411 now has low sulfur content also, which points out again the questionable earlier sulfur analysis. The product oxygen content is comparable for AMOCAT™ 1C and Shell 324, but lower for the Sandia and Shell 411 catalysts. After 876 hours on oil (Table 177), the product quality for AMOCAT™ 1C is poorer than for any of the other catalysts. Both Shell 324 and 411 have lower product nitrogen and ramscarbon contents compared to the Sandia catalysts. Oxygen content is comparable with the Shell 411 and high promoter level NiMo/HTO, and again similar for Shell 324 and low promoter level NiMo/HTO. Sulfur content is similar for all the catalysts within experimental error.

The product nitrogen vs time on oil for Run 9 and the various catalysts is graphed in Figures 42-45.

The conversions for nitrogen, ramscarbon and resid for various catalysts at 20, 32 and 37 days on-oil in Run 9 are graphed in Figures 46-48 respectively. At 20 days-on-oil (Figure 46), denitrogenation is similar

for AMOCAT™ 1C, and Sandia NiMo/HTO catalysts, but slightly better for Shell 324 and 411; ramscarbon conversion is similar for all the catalysts, and resid conversion is about 20% for the AMOCAT™ 1C, whereas NiMo/HTO(L) and Shell 411 have about 40% resid conversion. At 32 days-on-oil (Figure 47), AMOCAT™ 1C and NiMo/HTO(F) have comparable nitrogen conversion, about 30%; Shell 324 and NiMo/HTO(L) have about 40% conversion of nitrogen and Shell 411 has about 50% conversion. The ramscarbon conversion is between 25 and about 40% for all the catalysts. The resid conversion is similar for both Shell catalyst and NiMo/HTO(L), but slightly lower for NiMO/HTO(F) and even lower for AMOCAT™ 1C. At 37 days-on-oil (Figure 48), AMOCAT™ 1C catalyst has lower conversions for nitrogen, ramscarbon and resid than the other catalysts. Shell 411 has good nitrogen and ramscarbon conversion, and NiMo/HTO has the best resid conversion. Figure 49 shows conversions from earlier runs, where both Shell 324 and AMOCAT™ 1C have similar ramscarbon and resid conversions, Shell 324 has a slightly better nitrogen conversion. The thermal process, as expected, shows the lowest conversions.

DISCUSSION

Sandia prepared NiMo promoted hydrous titanate oxide (HTO) catalysts performed on par with the commercial catalysts. The catalyst designated NiMo/HTO(L) was especially interesting because it contained roughly half the promoters that were in the NiMo/HTO(F), however, it still had good performance. This points to the possibility that the dispersion of Ni and Mo onto the HTO surface is extremely good. CoMo/HTO showed also reasonable denitrogenation and desulfurization but poorer ramscarbon conversion. The product hydrogen content was lower for the CoMo catalyst,

indicating an inferior hydrogenation function for CoMo compared to NiMo, which is well-known in petroleum hydrotreating.

The Pd catalysts (Pd #1, Pd #2 and Pd #3) all had poorer performance compared to the commercial catalysts, or NiMo/HTO and CoMo/HTO preparations. Although Pd containing catalysts are known to be good for hydrogenation, low product hydrogen contents are seen here. Pd is a noble metal and it gets poisoned easily with sulfur in the feedstock, which could be a part of the explanation for poor catalytic activity for these materials.

Observing the product nitrogen in Figures 42-45, it's very promising that the NiMo/HTO catalysts performed comparably to commercial hydrotreating catalysts. The conversions in Figures 46-48 also indicate good performance for the Sandia NiMo/HTO catalysts.

SUMMARY

The mini-ager testing results show that Sandia's NiMo/HTO catalysts look as though they are comparable to commercial hydrotreating catalysts, although the support pore structure has not been optimized. Furthermore, one of the preparations of NiMo/HTO performed remarkably well despite having a relatively low promoter loading. This points to the possibility that Ni and Mo are well dispersed onto the hydrous titanate oxide surface.

2. Continuous Testing

A powdered nickel/molybdenum version of Sandia's hydrous metal titanate catalyst was compared to a powdered nickel/molybdenum on alumina catalyst for liquefaction of Illinois No. 6 bituminous coal. The hydrous titanate catalysts showed high hydrogenation activity in Sandia's tests, which might increase resid conversion with Illinois No. 6 feed at lower reactor temperatures. Two different levels (0.1% and 0.2% catalyst/coal) of the powdered NiMo/titanate catalyst and one level (0.1% catalyst/coal) of the NiMo/alumina catalyst were tested. Molybdenum levels were 90-152 ppm Mo/coal, which is reasonable for an economic liquefaction process.

A thin-film form of Sandia's hydrous titanate catalyst on AMOCAT™ alumina with nickel and molybdenum hydrogenation metals was also tested.

Sandia's Powdered NiMo/Titanate with Illinois No. 6 Coal

EXPERIMENTAL

Catalyst powder was added directly to 33% coal 67% solvent slurry without a sulfiding agent. The NiMo/hydrous titanate powder was prepared by R. Dosch[40] at Sandia. The NiMo/alumina catalyst was prepared by separately dissolving ammonium molybdate and nickel nitrate in water, combining the two water solutions, immediately mixing with alumina powder, drying at 125°C, and calcining at 800°F for one hour. Properties of the catalyst powders are given in Table 178.

Pilot plant AU-135L was operated at 2500 psig with the first stage at 800°F and the second stage at 500°F, giving a nominal residence time of 1.5 hours. Due to the small size of the catalyst sample, the second stage was non-catalytic; thus the temperature was kept low so that little effect was seen on the product.

RESULTS

Net yields from coal are given in Table 179. For comparison, results from Molyvan L at a higher temperature (820°F) are included because they are the best to date. Resid yield was higher for NiMo on hydrous titanate powder than for NiMo on alumina (18-20% vs. 9%), at the expense of 650-935°F distillate. Yields of other distilled fractions were comparable for the two catalyst. Resid yield decreased insignificantly (2%) when twice as much of the hydrous titanate catalyst was used, but hydrogen consumption increased 1%. Lower product gas yields from the hydrous titanate catalysts may reflect lower acidity.

Elemental analyses of distilled fractions are given in Table 180. Hydrogen and heteroatom contents were comparable for the alumina- and titania-supported catalyst powders.

SUMMARY

A nickel/molybdenum/hydrous titanate catalyst powder prepared by Sandia gave comparable performance to a nickel/molybdenum/alumina catalyst powder except resid conversion was somewhat lower. Performance was good enough to warrant further testing of these novel materials.

NiMo/TiO_2 on AMOCAT™ Alumina with Illinois No. 6 Coal

EXPERIMENTAL

The NiMo/hydrous titanate on AMOCAT™ alumina was prepared by R. Dosch[42] at Sandia. Properties of the catalyst are given in Table 181. The catalyst was calcined at 800°F for 1 hour before use, and 60 cc. were loaded into each reactor of AU-51L pilot plant. The first stage was operated at 790°F and the second stage was operated at 760°F with a hydrogen pressure of 2500 psig. The catalyst was presulfided with an organic disulfide in coal liquid at reaction conditions for several hours before use.

RESULTS

Product yields and elemental analyses are summarized in Table 182. The activity of the Sandia NiMo thin film titanate on AMOCAT™ alumina for resid and asphaltene conversion was higher than that of AMOCAT™ catalysts. At 70 hours, oil (hexane soluble) yields were 78% with the Sandia catalyst compared to 65% with AMOCAT™ 1C catalyst. Net resid yields were about 30% lower with the Sandia catalyst, and distillate yields were higher. Light hydrocarbon gas yields were also higher with the Sandia catalyst, which could indicate either higher cracking activity or higher thermal severity for the Sandia catalyst. The two runs were completed in different pilot plants, which could account for some of the difference. However, previous runs in AU-51L (pilot plant for Sandia test) did show comparable or lower activity than those of AU-135L, which suggests that catalyst activity is the real reason for high product quality with the Sandia catalyst.

Elemental analyses of product from the Sandia catalyst show less hydrogenation and less heteroatom removal than with AMOCAT™ catalyst. Poorer hydrogenation activity and heteroatom removal is not desirable, but will have a small impact on process economics compared to the large benefit from the high distillate yields. It would be relatively simple to upgrade distilled fractions by fixed bed hydrotreating.

The test of the thin-film Sandia catalyst was short because of a few unit upsets, unrelated to catalyst, that forced an early shutdown of the run. Additional tests should be completed to confirm that benefits are retained at longer run lengths. High liquid yields from the Sandia catalyst are unique, and other heavy feedstocks should also be investigated.

Spent catalyst analyses are given in Tables 183-184. Spent first stage catalysts (Table 183) showed about the same amount of carbon but more hydrogen for the Sandia catalyst, which is normal for the lower age of the Sandia catalyst (7 days vs. 21 days). Difference in catalyst age could also account for the slightly higher pore volume of the Sandia catalyst. The Ni/Mo ratio is higher for both fresh and spent Sandia catalyst, and mildly acidic properties of nickel could account for the high distillate yields from the Sandia catalyst.

Spent second stage catalyst (Table 184) showed much more severe deactivation for the Sandia catalyst than for AMOCAT™ 1C catalyst, in spite of the lower age. The severe deactivation could be from undetected overheating in the second stage, or could be from the several unit upsets. The catalyst baskets were easily removed from the reactors, which would not be likely if the second stage chronically overheated. Deactivation of

second stage Sandia catalyst is probably not typical for these operating conditions.

CONCLUSIONS ON TASK 3.2.3

In the mini-ager testing, hydrous titanate catalysts were comparable to commercial hydrotreating catalysts, however lower levels of promoters could be used.

A thin film titanate catalyst on AMOCAT™ alumina with nickel and molybdenum hydrogenation metals was prepared by R. Dosch of Sandia National laboratories. With Illinois No. 6 coal feed, distillate and oil yields were higher for the Sandia catalyst than for AMOCAT™ 1C catalyst. Heteroatom contents of distilled fractions were higher, and hydrogenation was poorer for the Sandia catalyst, but this could be corrected in subsequent fixed bed hydrotreating. The high distillate yields from the Sandia catalyst are very significant, and this catalyst should be tested in the future with other heavy feedstocks in longer pilot plant runs.

Task 3.3: Additional Process Developments

The results from this section are discussed under Task 3.1 pp. 50-72. Since pretreatment and decarboxylation are coal handling procedures prior

to liquefaction and complement beneficiation, they are addressed in that section.

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FIGURE 1

SCHEMATIC OF TUBING REACTOR ON SGU-1

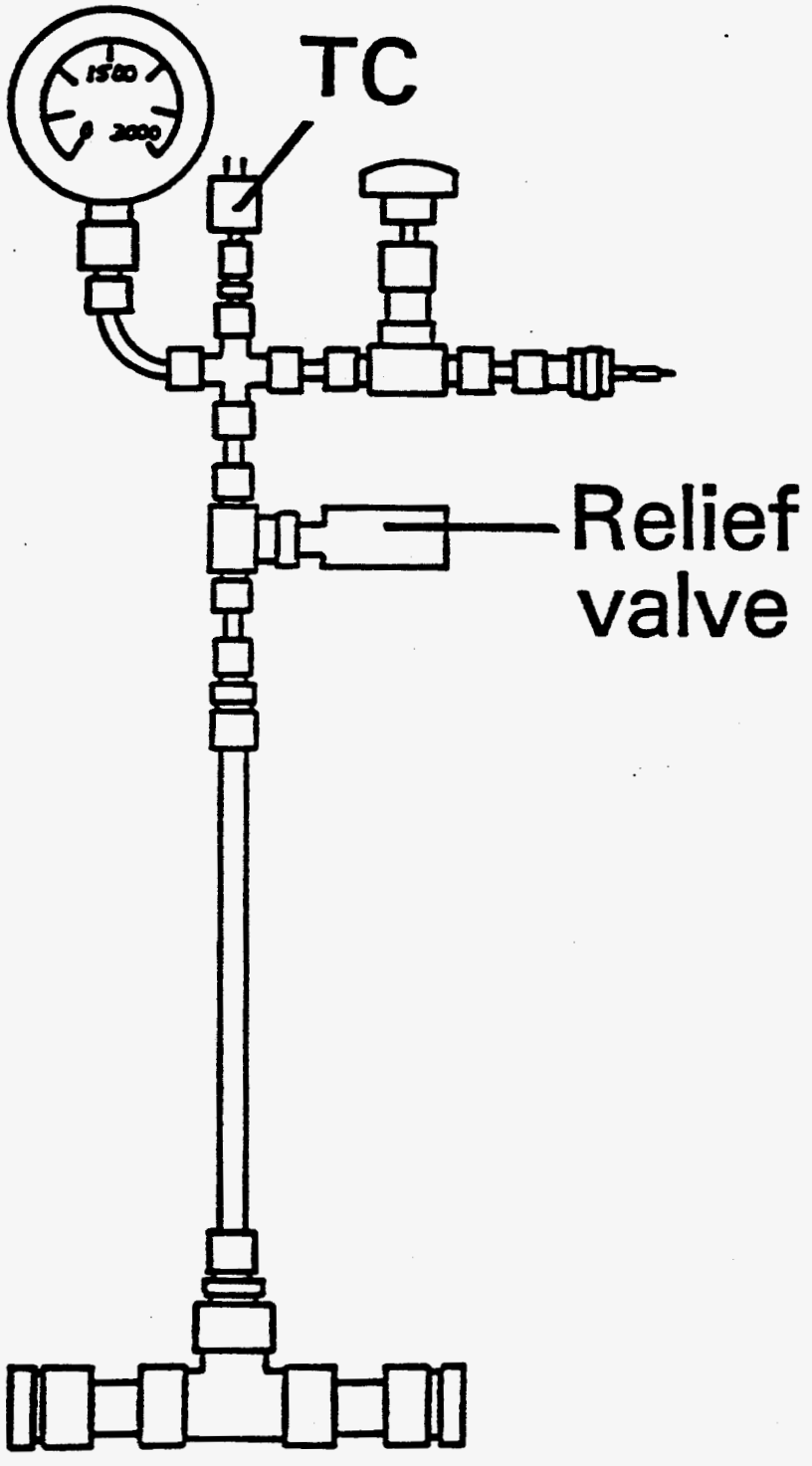

FIGURE 2

Conversion of Carboxylate Salts

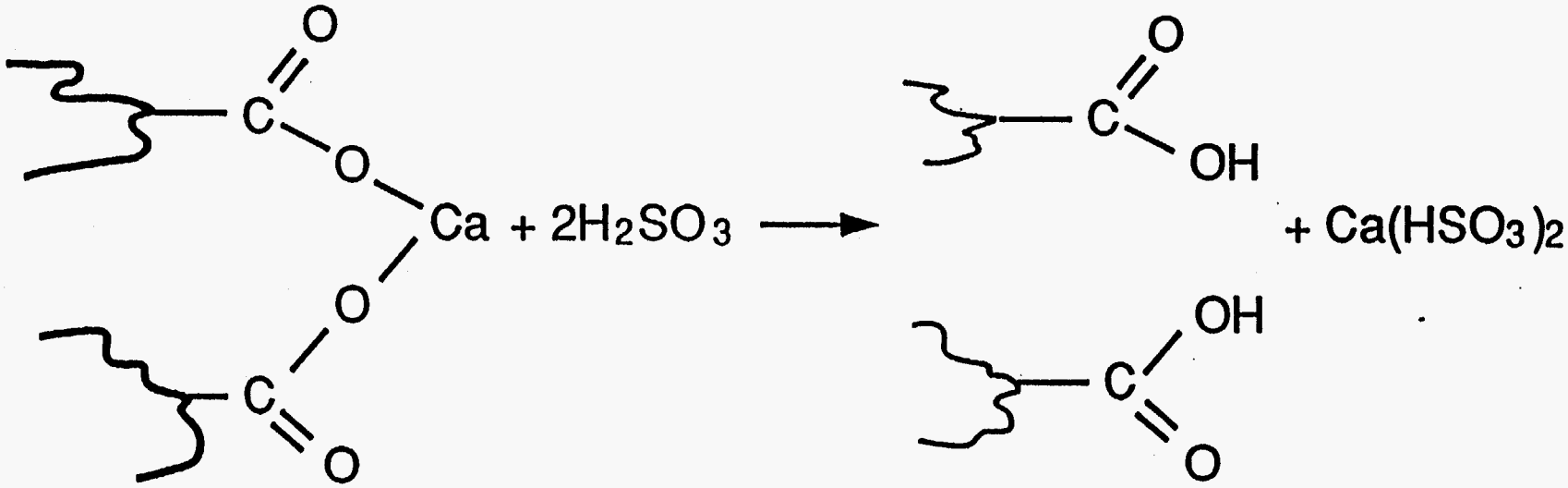

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FIGURE 3

SCHEMATIC OF THE IL NO. 6 BENEFICIATION PROCEDURE

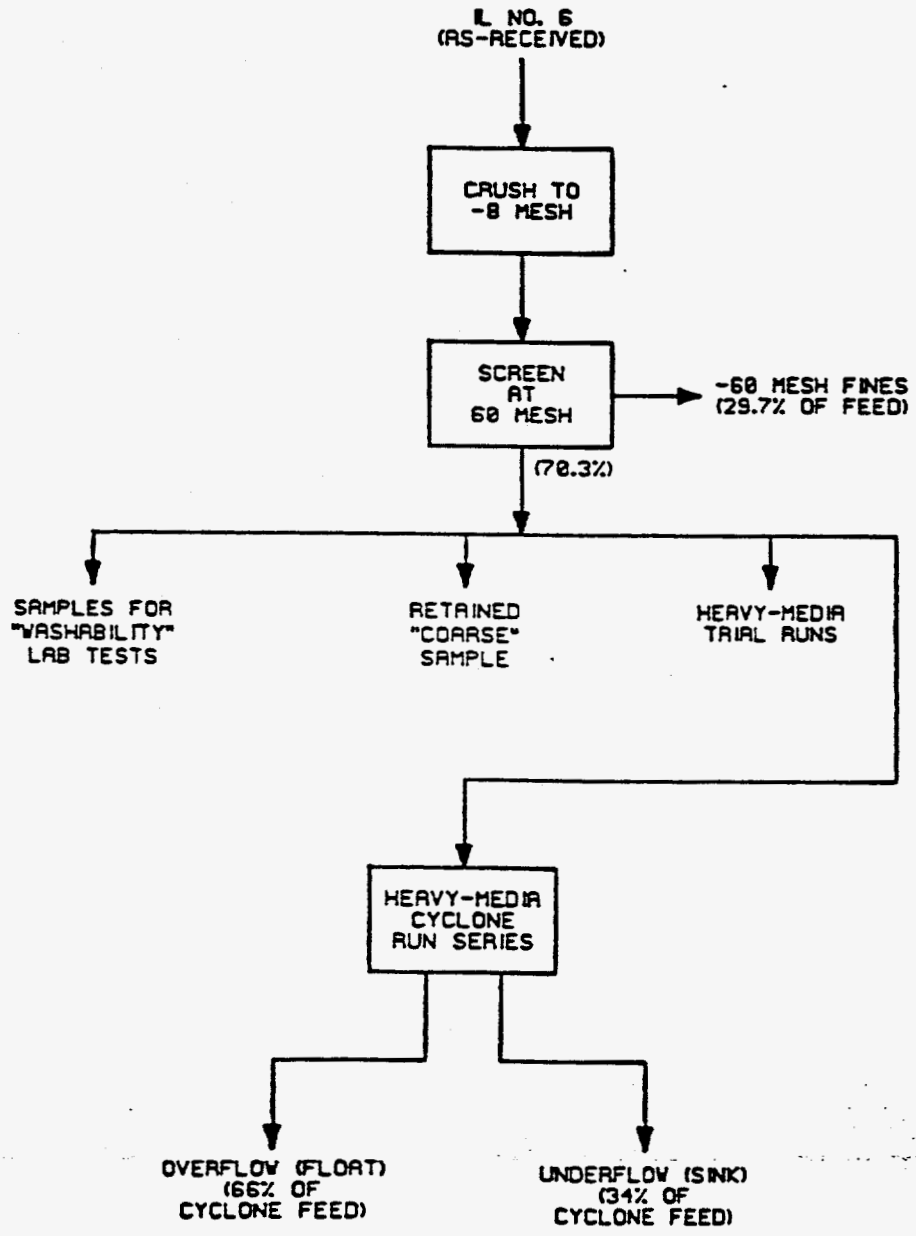
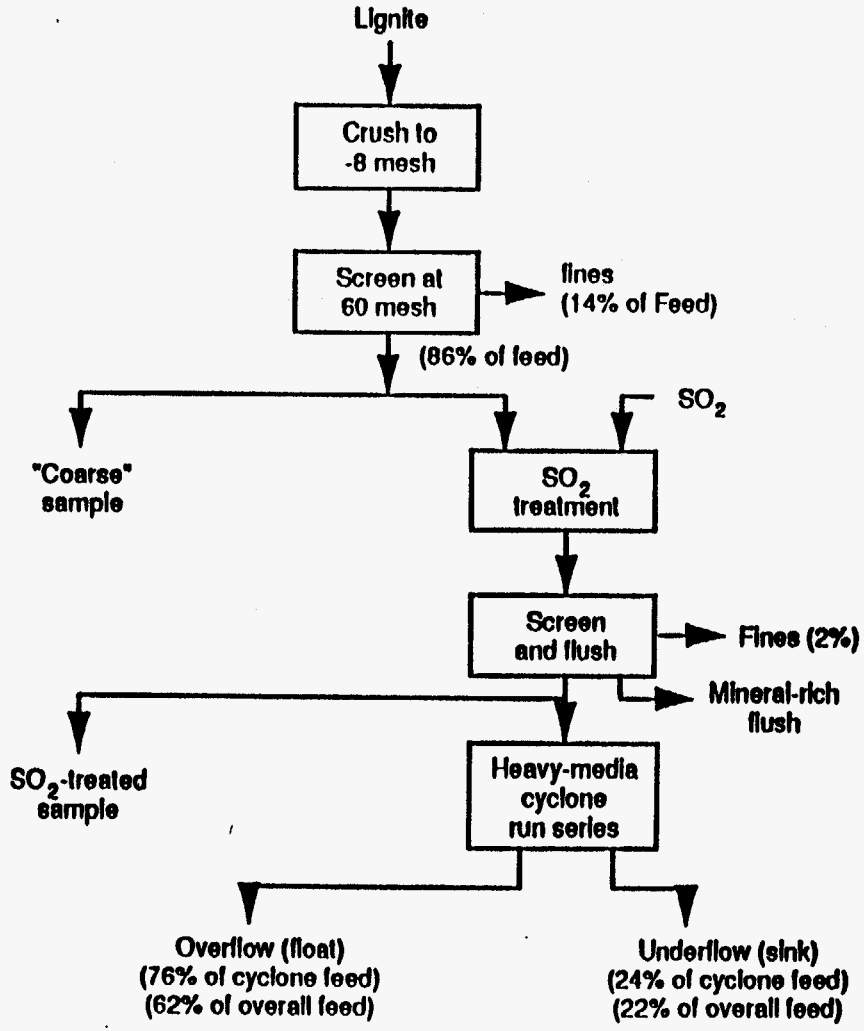


FIGURE 4

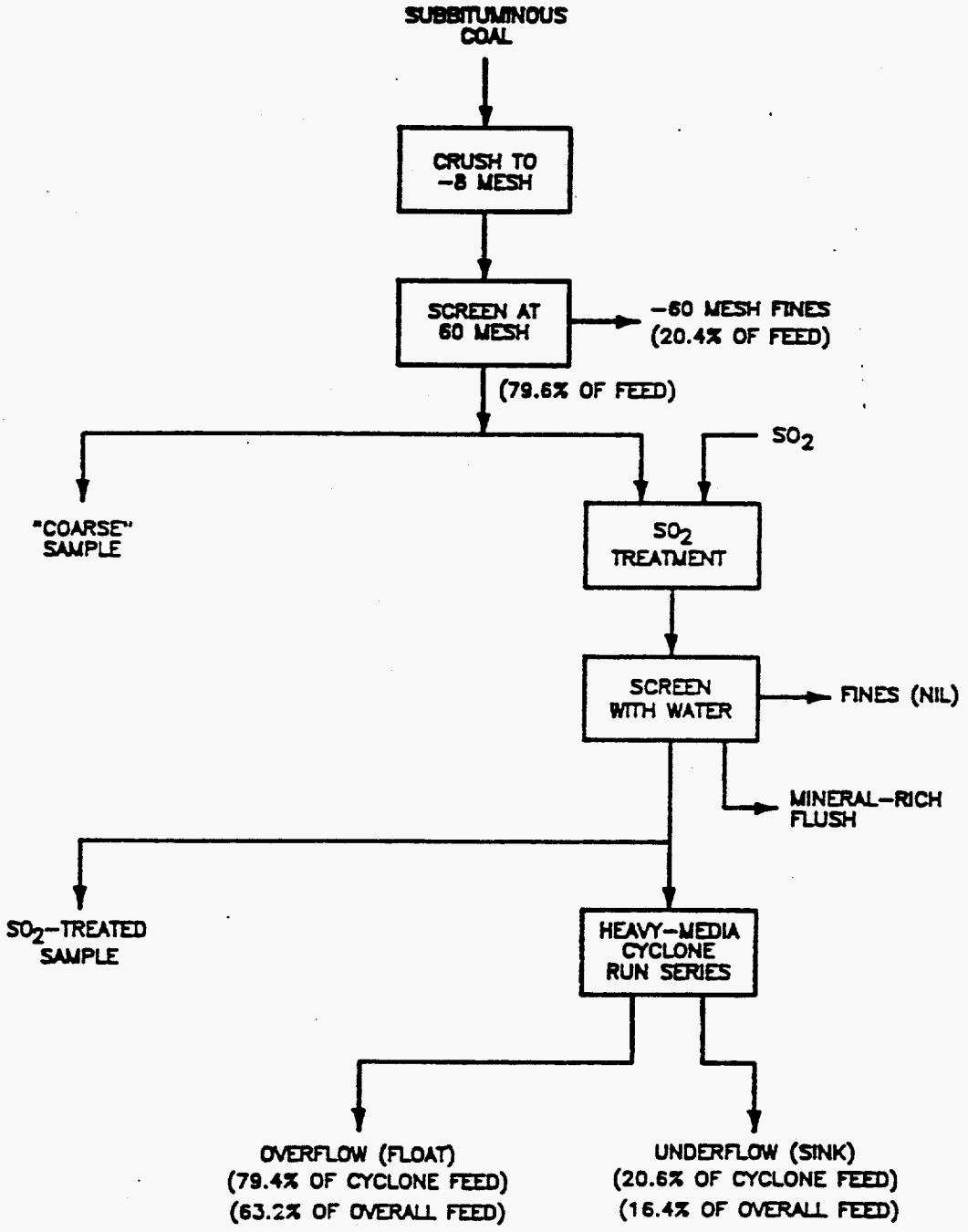
Lignite Beneficiation Procedure



d:E4486-15

FIGURE 5

SPRING CREEK COAL BENEFICIATION PROCEDURE



FI E 6

SCHEMATIC OF THE AU–44 FLOW UNIT

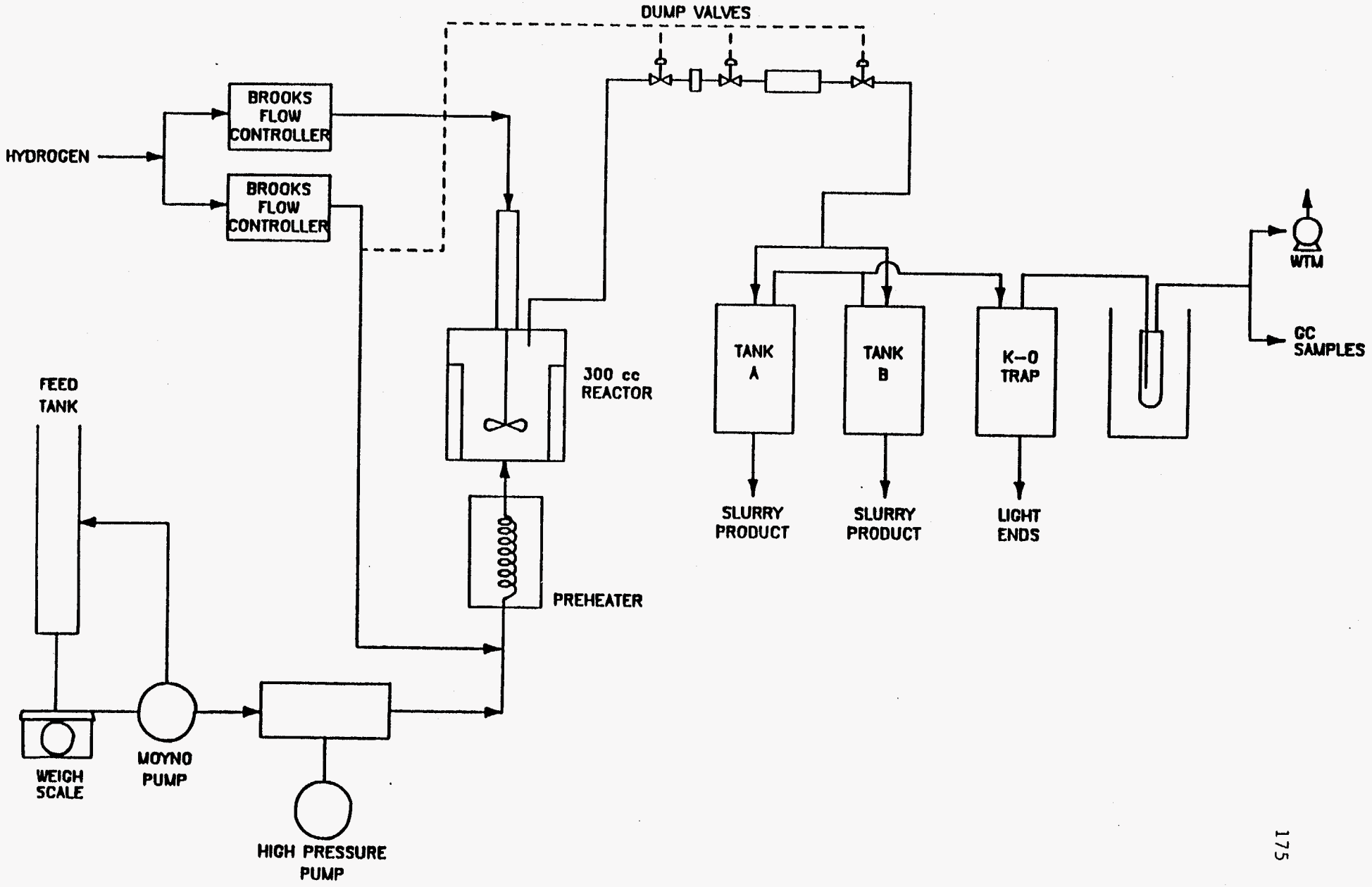


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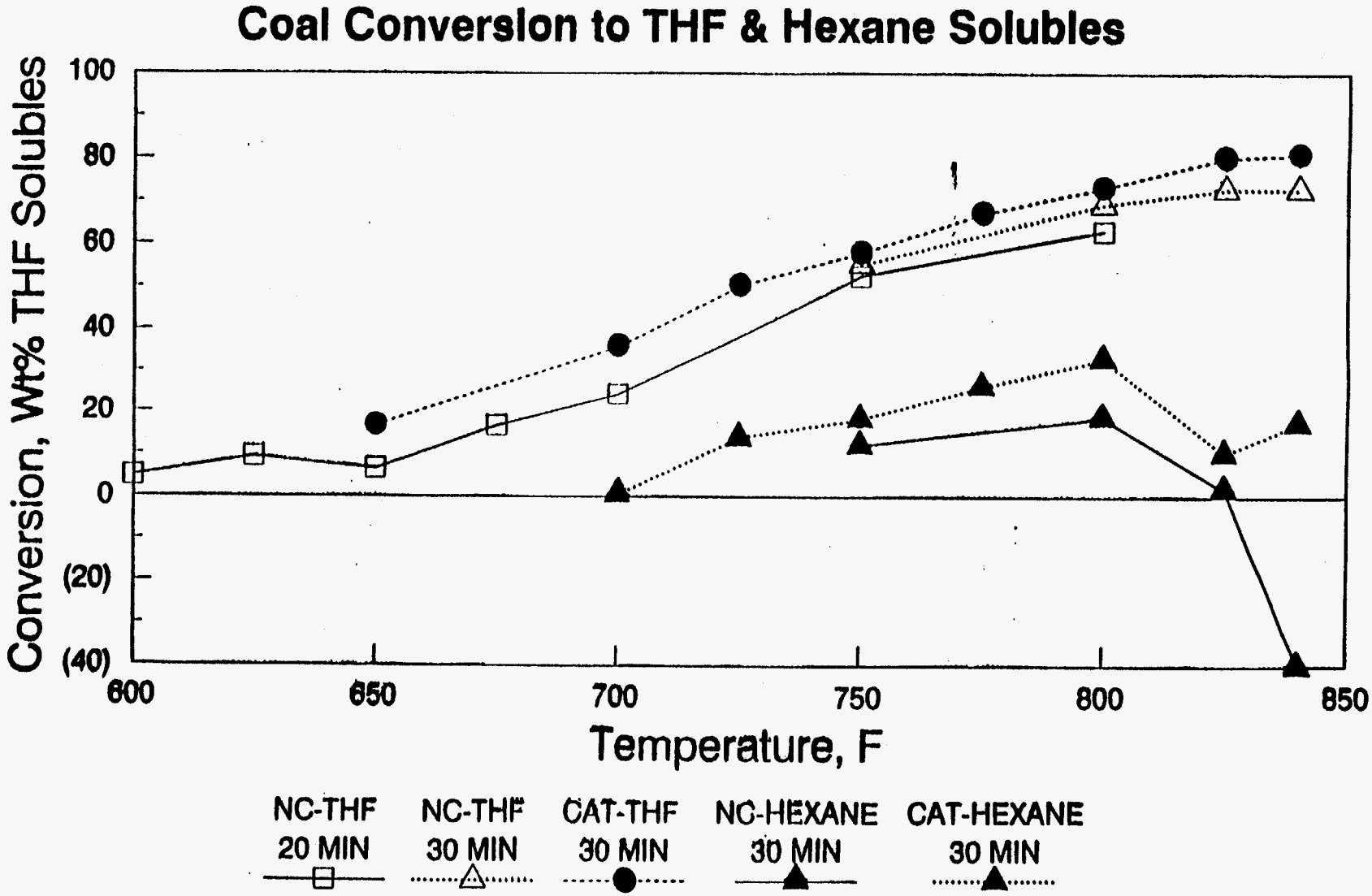
FIGURE 7



CC-CONV7

FIGURE 8

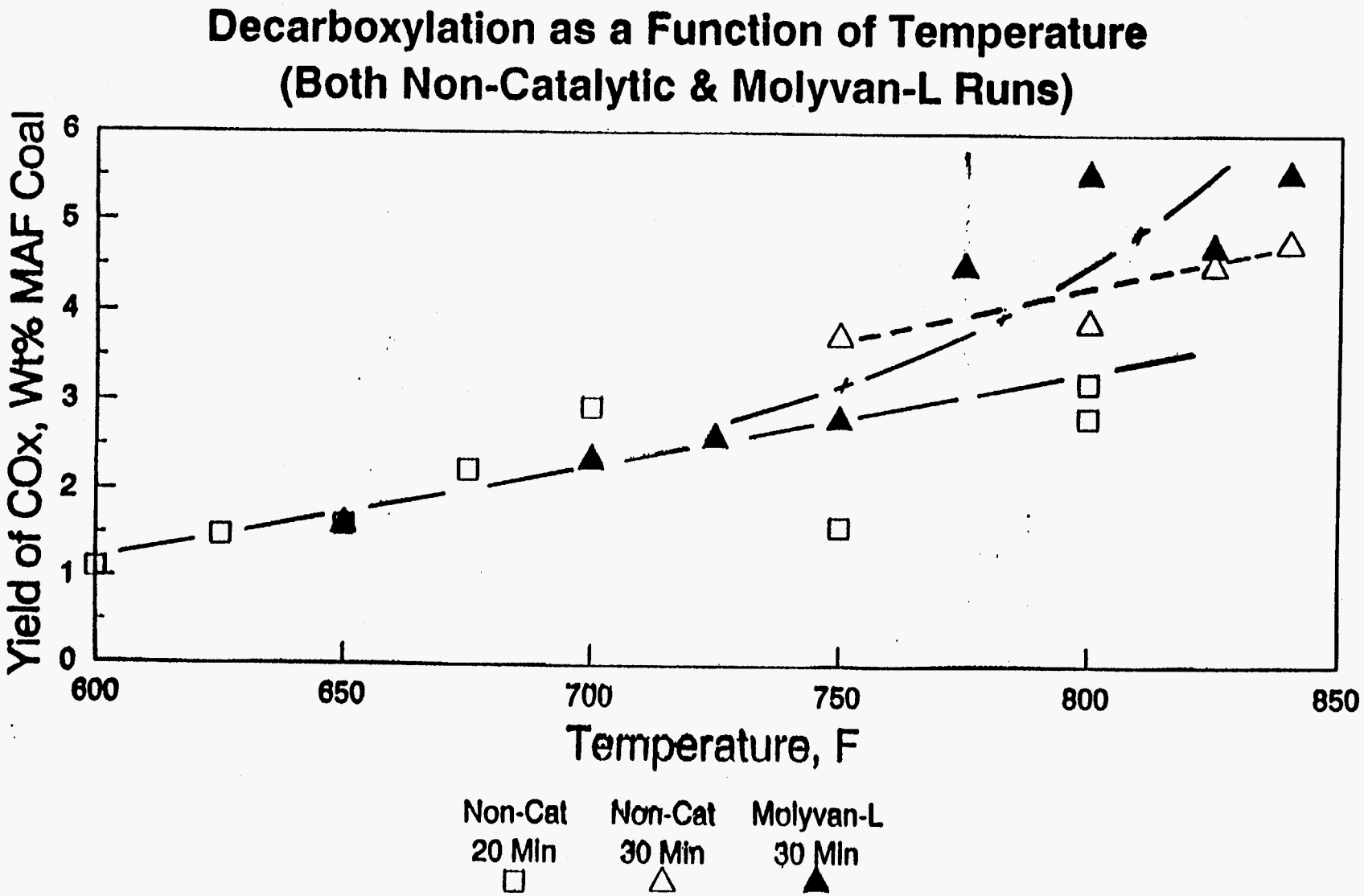
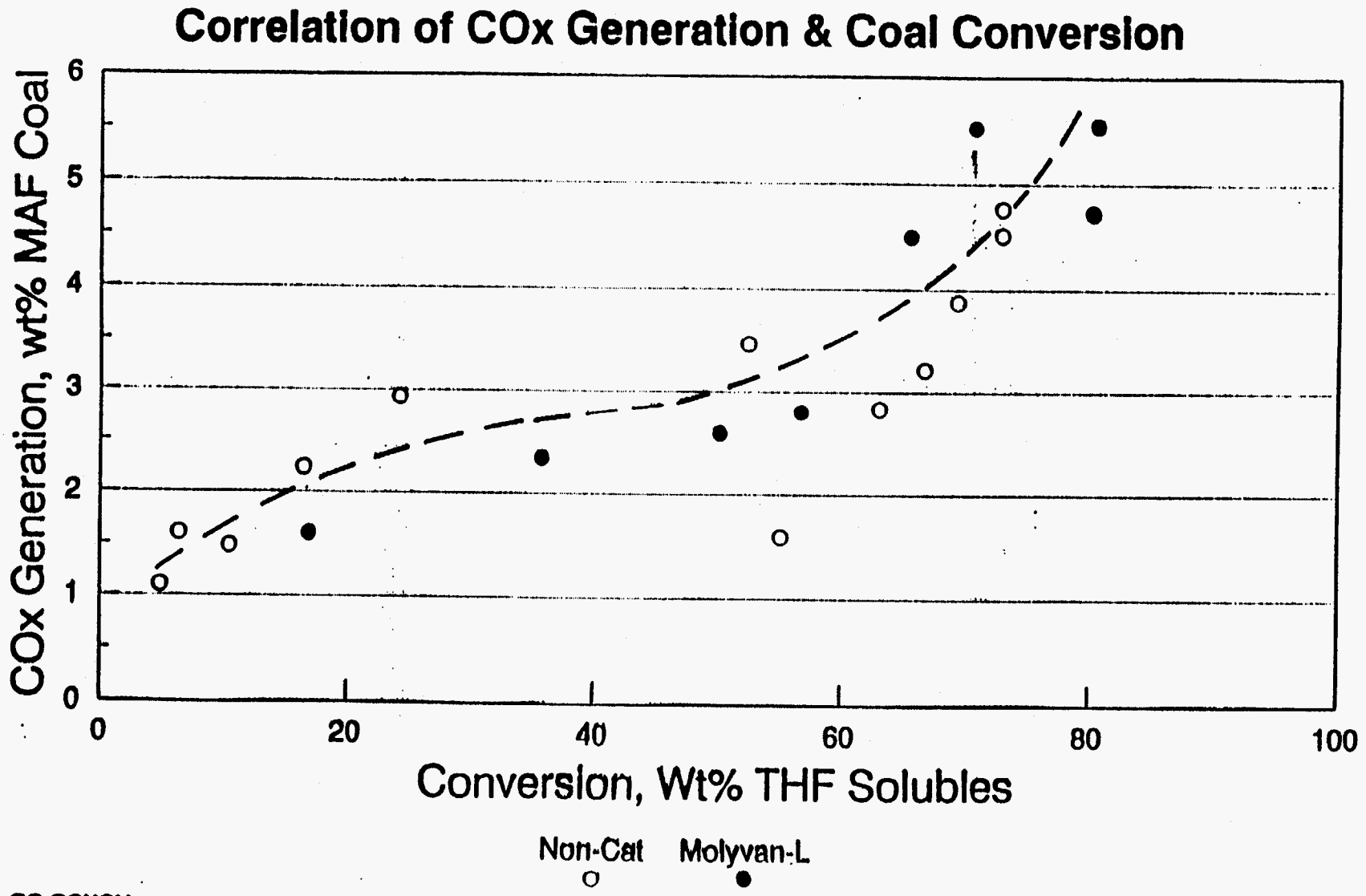

Decarboxylation as a Function of Temperature
(Both Non-Catalytic & Molyvan-L Runs)
Yield of COx, Wt% MAF Coal
0
1
2
3
4
5
6
600
650
700
750
800
850
Temperature, F
Non-Cat
20 Min
Non-Cat
30 Min
Molyvan-L
30 Min
CP_DEOX

FIGURE 9



CC-COXCN

FIGURE 10

Simplified Flow Diagram of the Continuous Aging Units

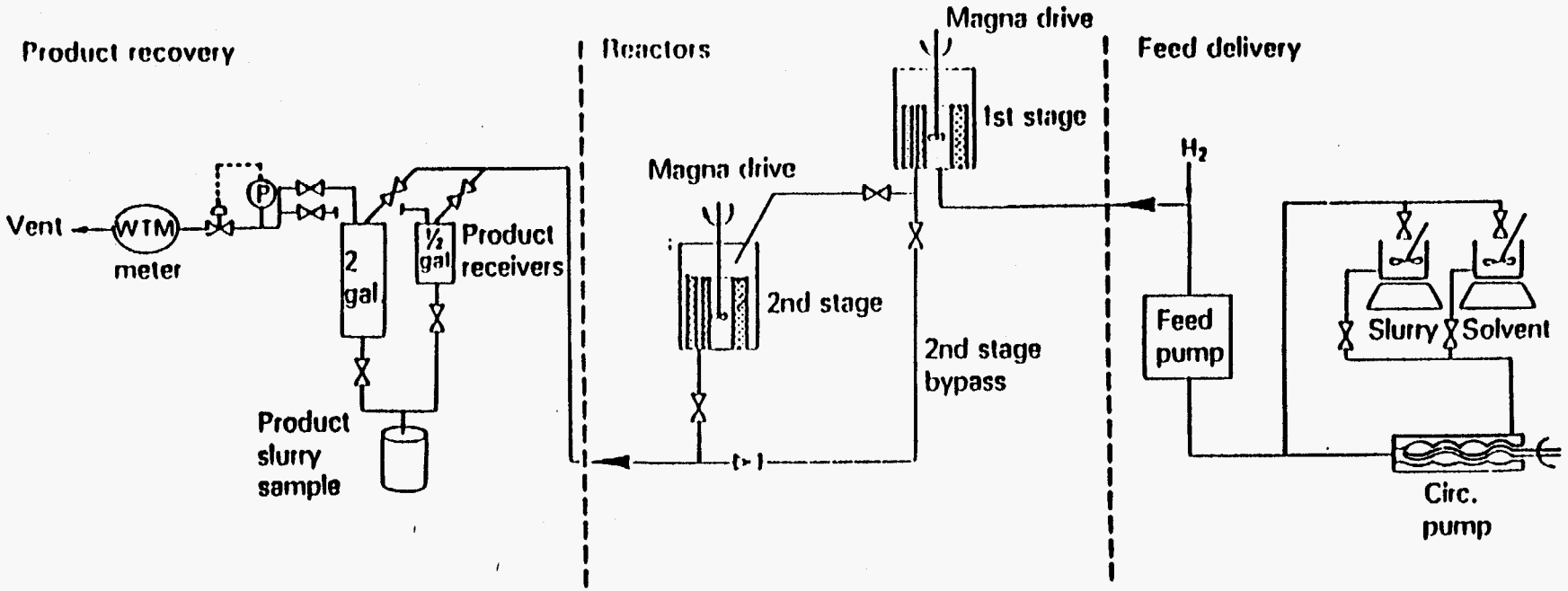


FIGURE 11

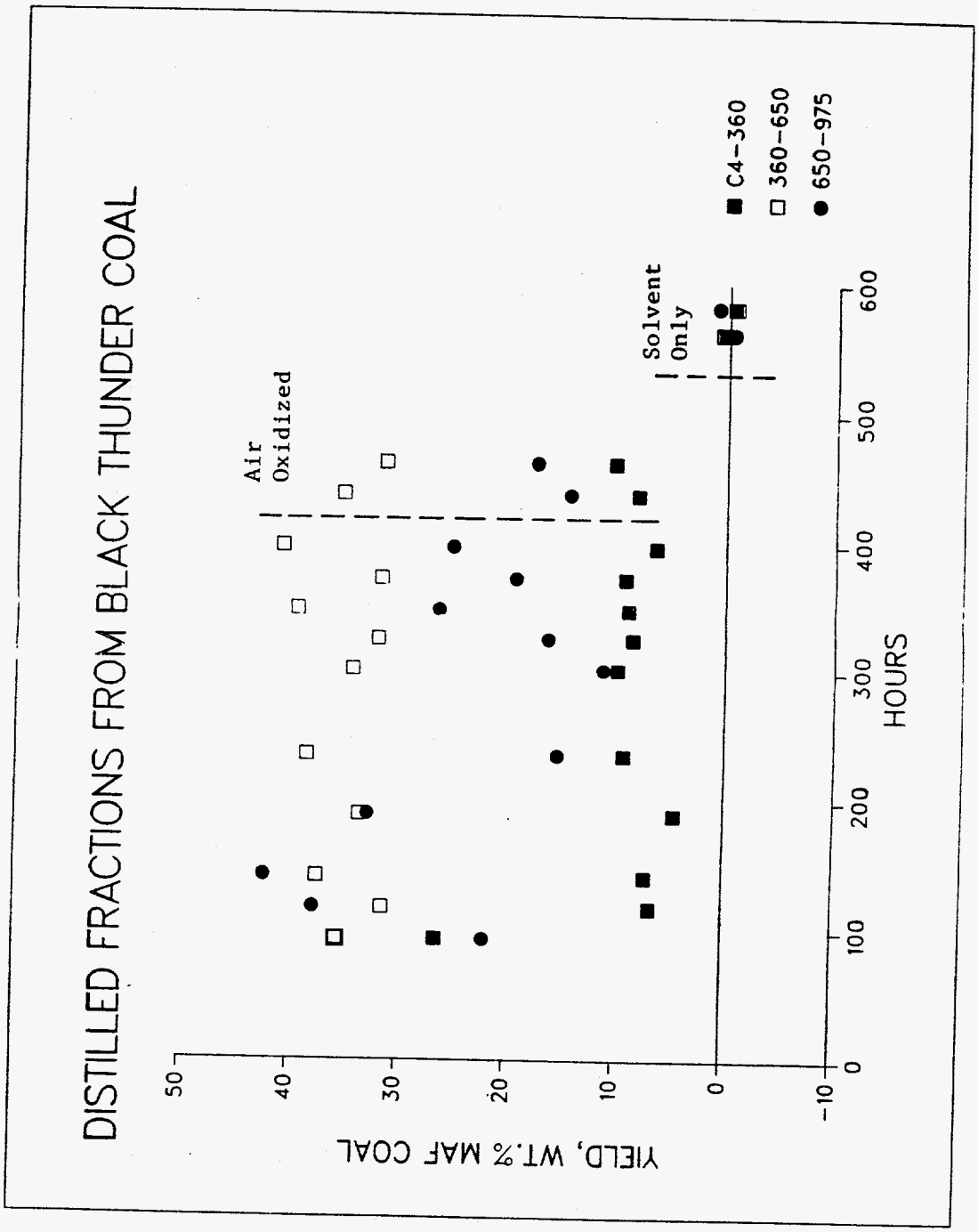

DISTILLED FRACTIONS FROM BLACK THUNDER COAL
YIELD, WT.% MAF COAL
50
40
30
20
10
0
-10
0
100
200
300
400
500
600
HOURS
Air Oxidized
Solvent Only
C4-360
360-650
650-975

FIGURE 12

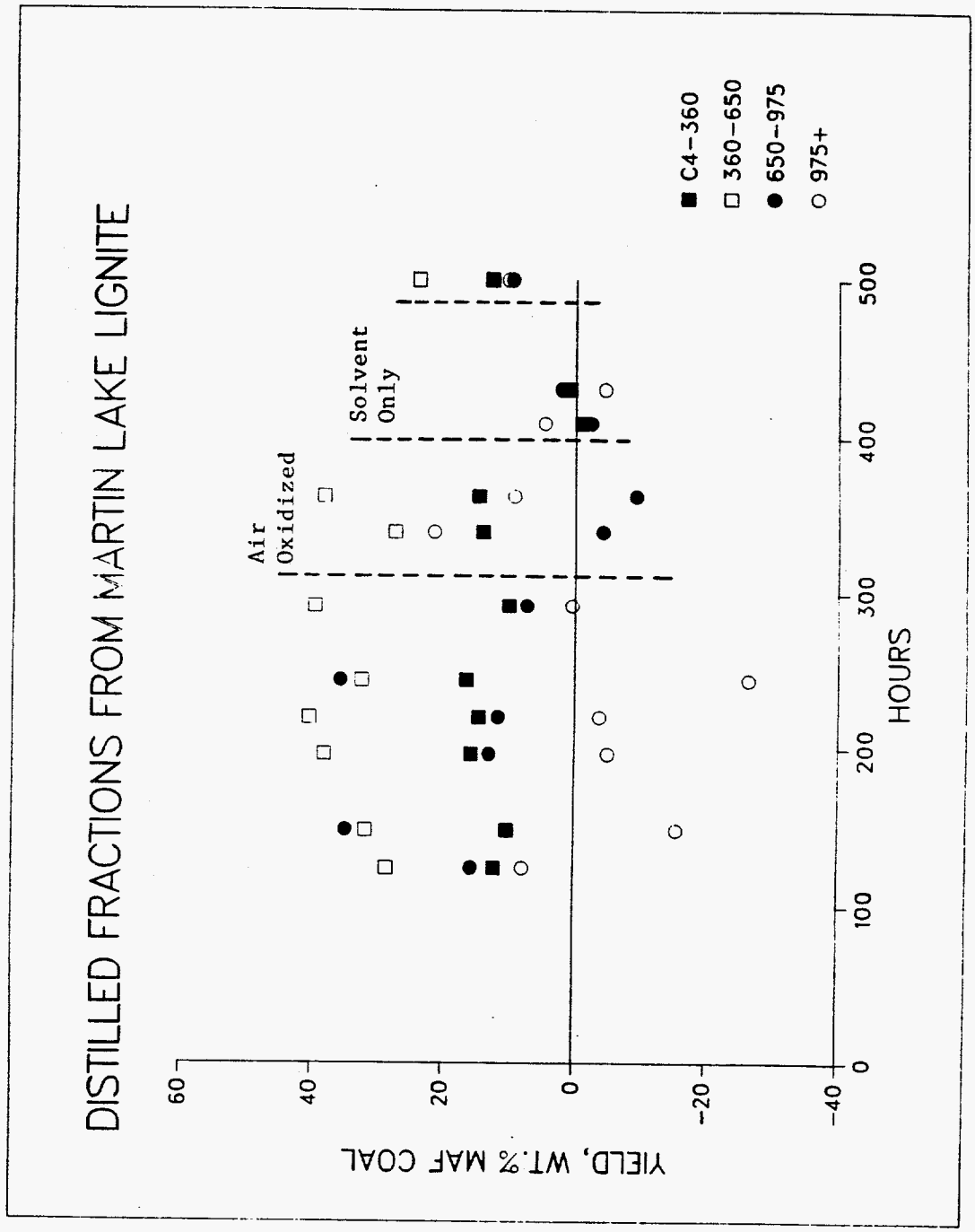

DISTILLED FRACTIONS FROM MARTIN LAKE LIGNITE
YIELD, WT.% MAF COAL
HOURS
Air Oxidized
Solvent Only
C4-360
360-650
650-975
975+
60
40
20
0
-20
-40
0
100
200
300
400
500

FIGURE 13

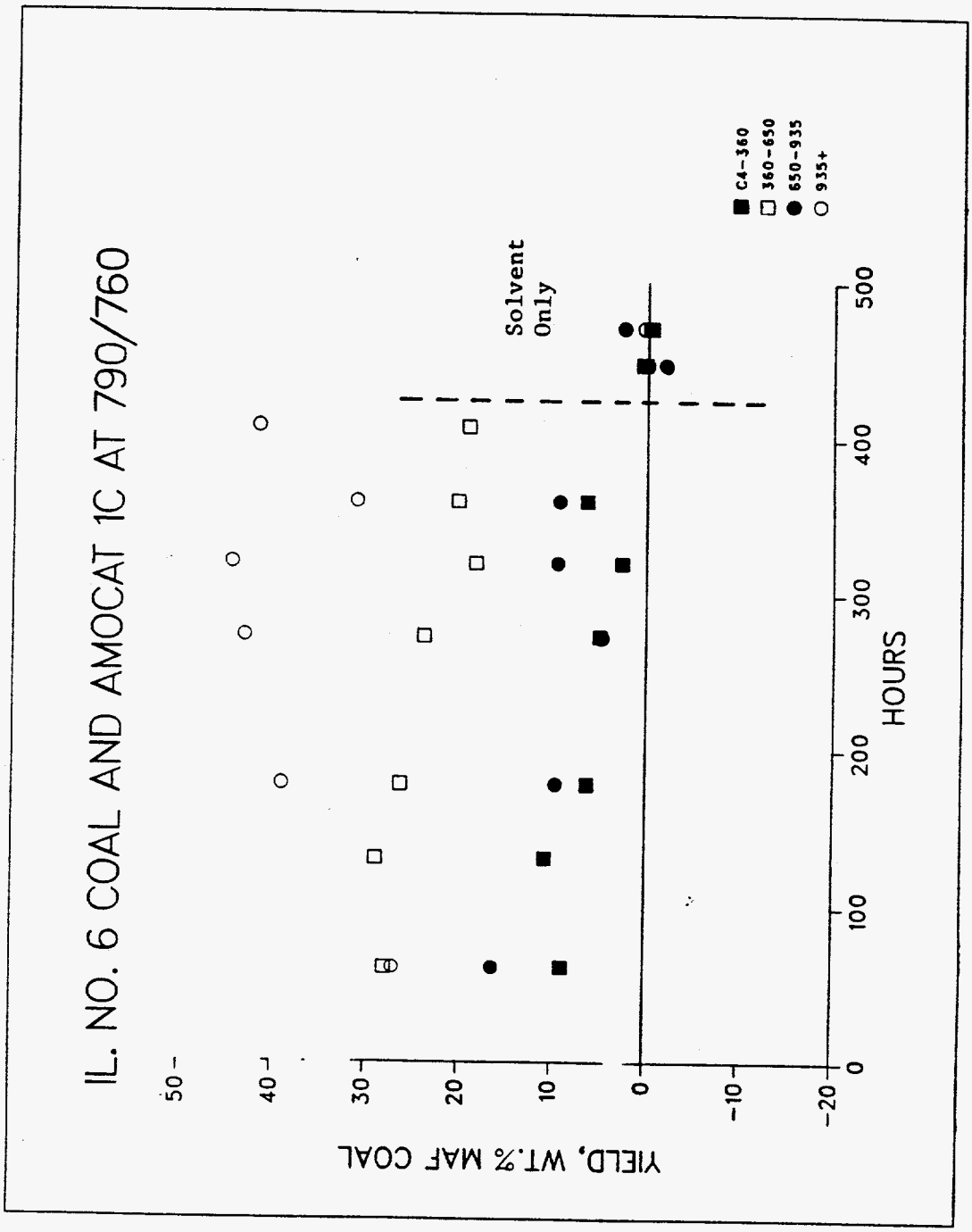
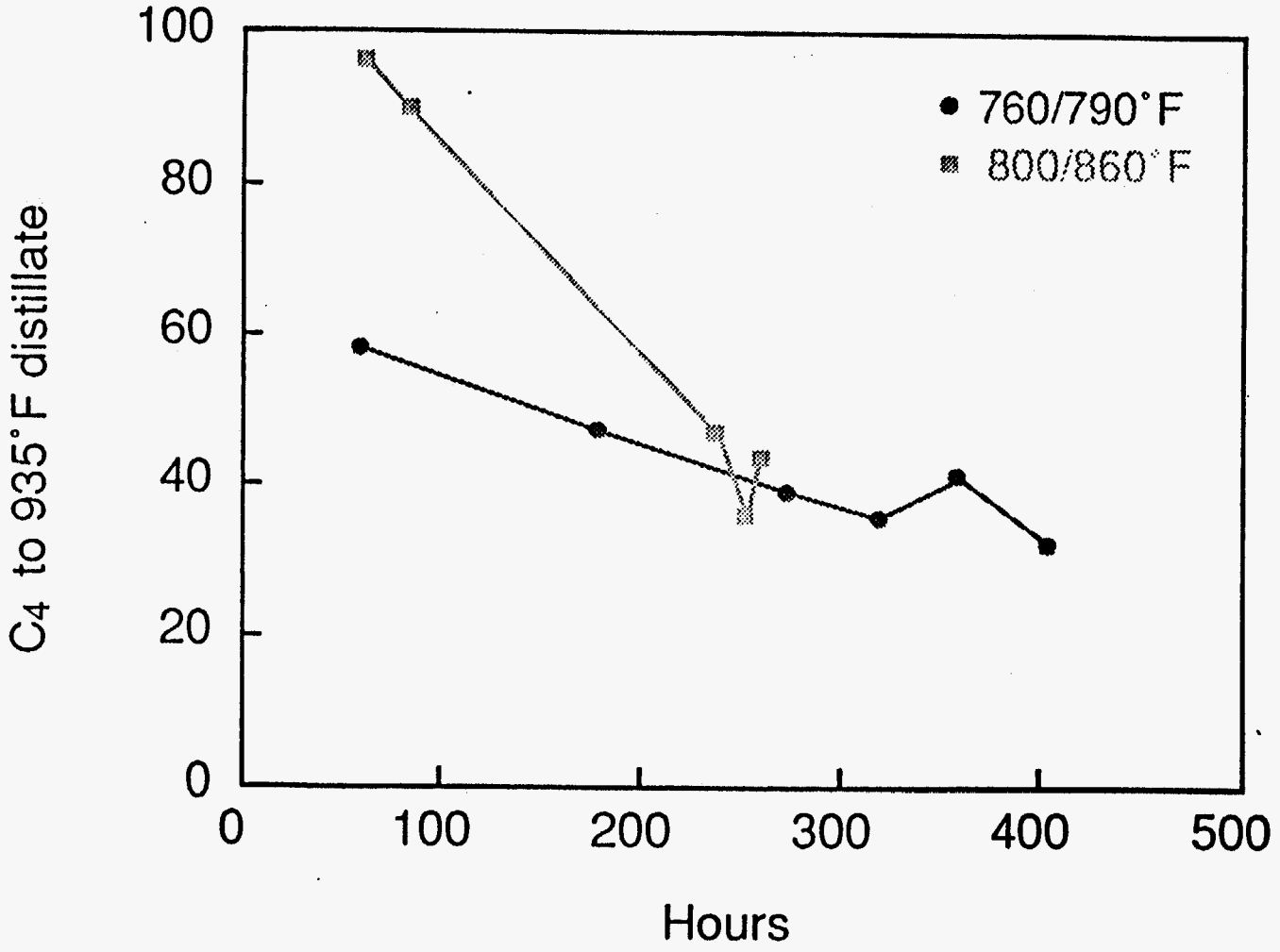

IL. NO. 6 COAL AND AMOCAT 1C AT 790/760
YIELD, WT.% MAF COAL
HOURS
Solvent Only
C4-360
360-650
650-935
935+
50
40
30
20
10
0
-10
-20
0
100
200
300
400
500

FIGURE 14

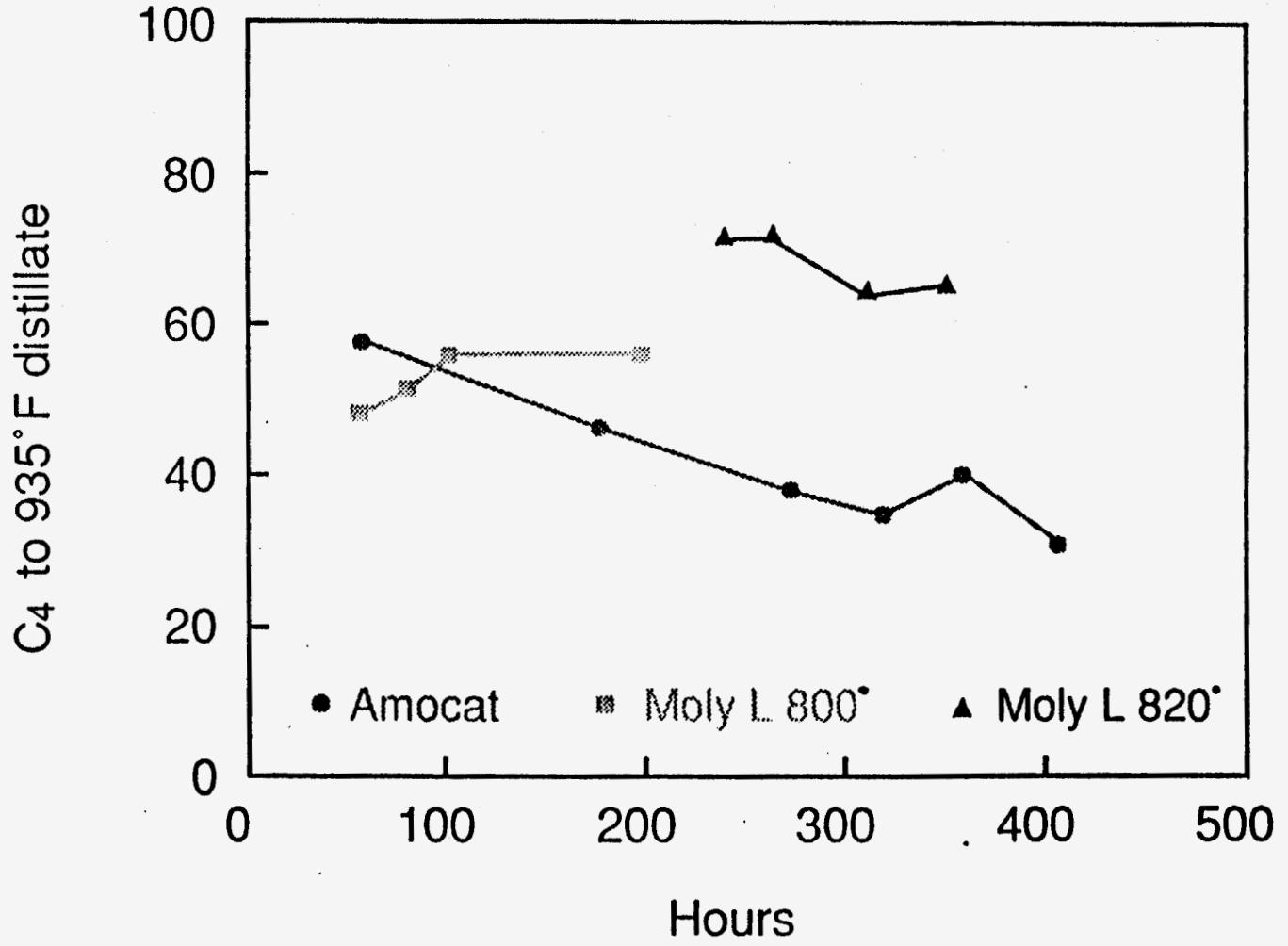
Amocat 1C Catalyst at High Temperature



F5585-22

FIGURE 15

Amocat 1C vs. Molyvan L Stage 1



F5585-18

FIGURE 16

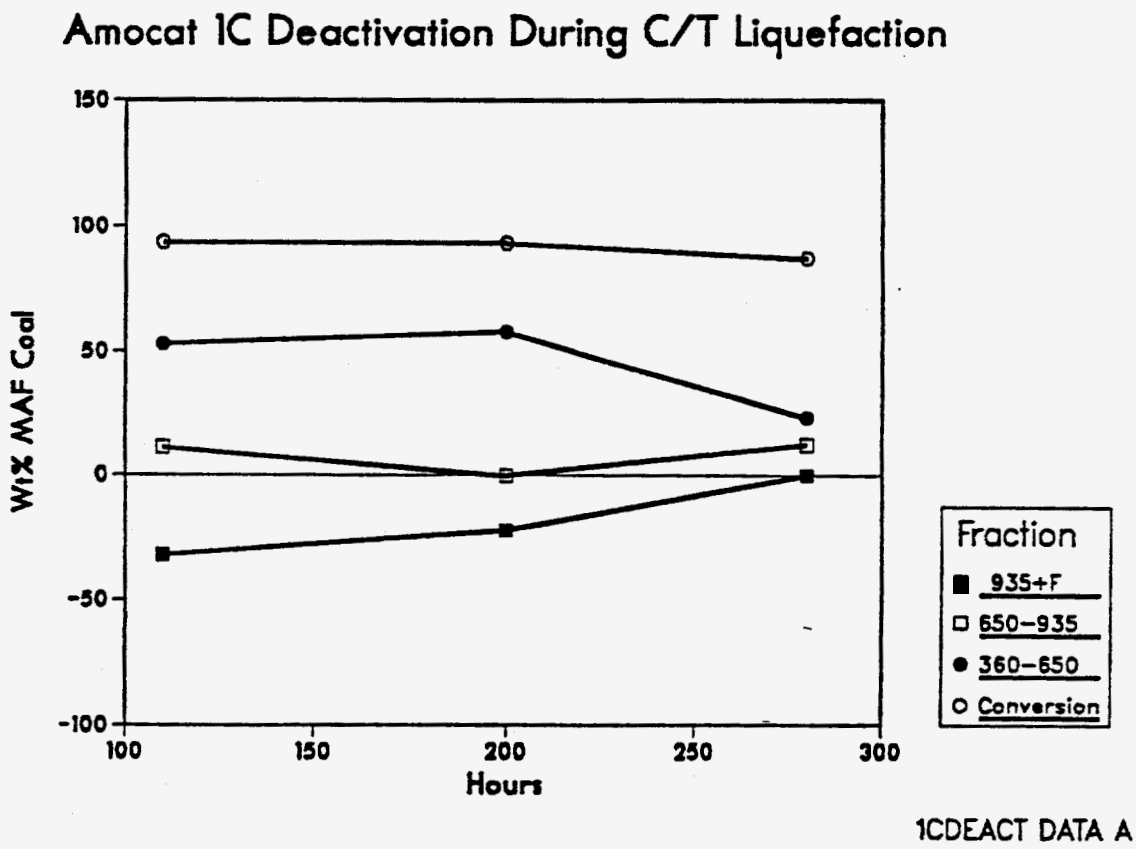

Amocat 1C Deactivation During C/T Liquefaction
Wt% MAF Coal
150
100
50
0
-50
-100
100
150
200
250
300
Hours
Fraction
935+F
650-935
360-650
Conversion
1CDEACT DATA A

FIGURE 17

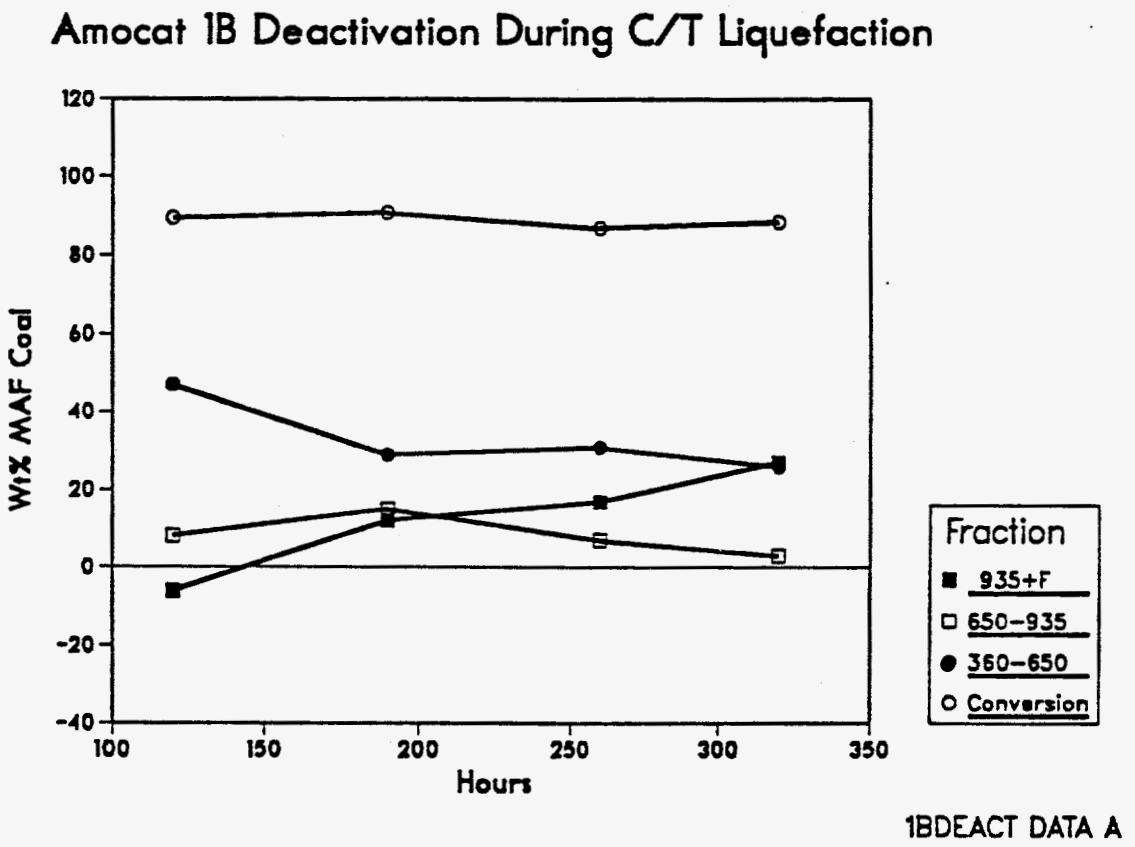

Amocat 1B Deactivation During C/T Liquefaction
Wt% MAF Coal
120
100
80
60
40
20
0
-20
-40
100
150
200
250
300
350
Hours
Fraction
935+F
650-935
360-650
Conversion
1BDEACT DATA A

FIGURE 18

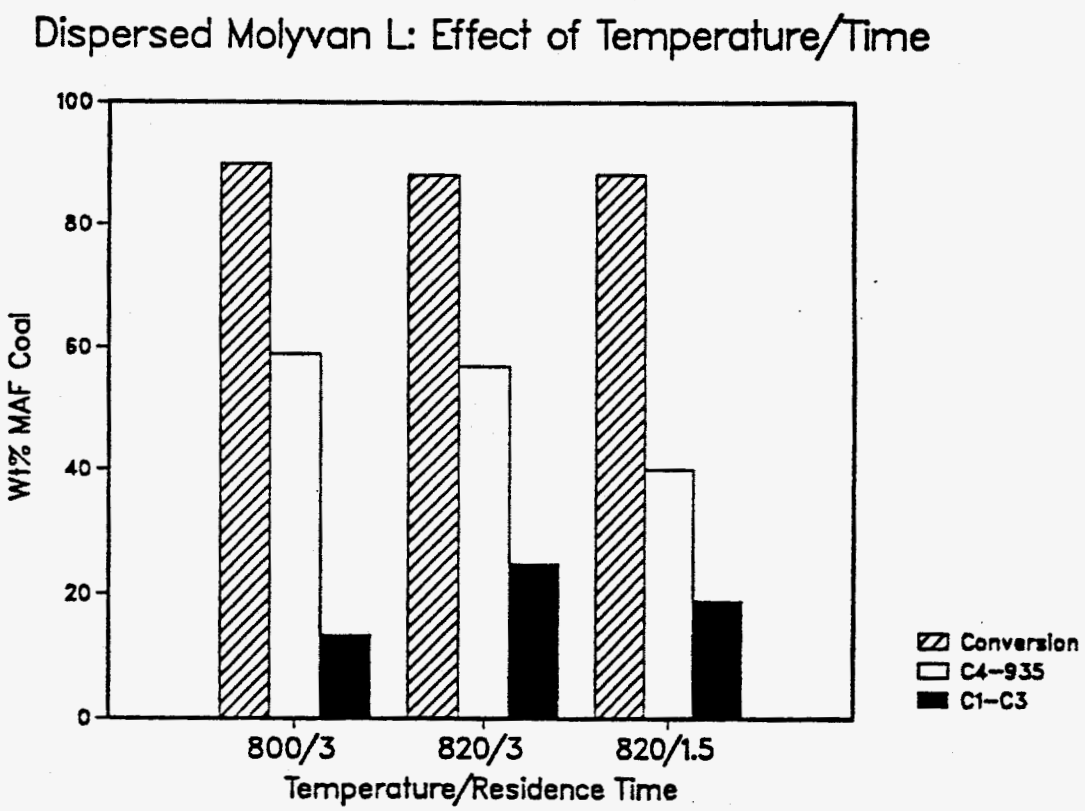

Dispersed Molyvan L: Effect of Temperature/Time
Wt% MAF Coal
100
80
60
40
20
0
800/3
820/3
820/1.5
Temperature/Residence Time
Conversion
C4–935
C1–C3

FIGURE 19

Dispersed Mo or Mo/Fe (3 Hours)

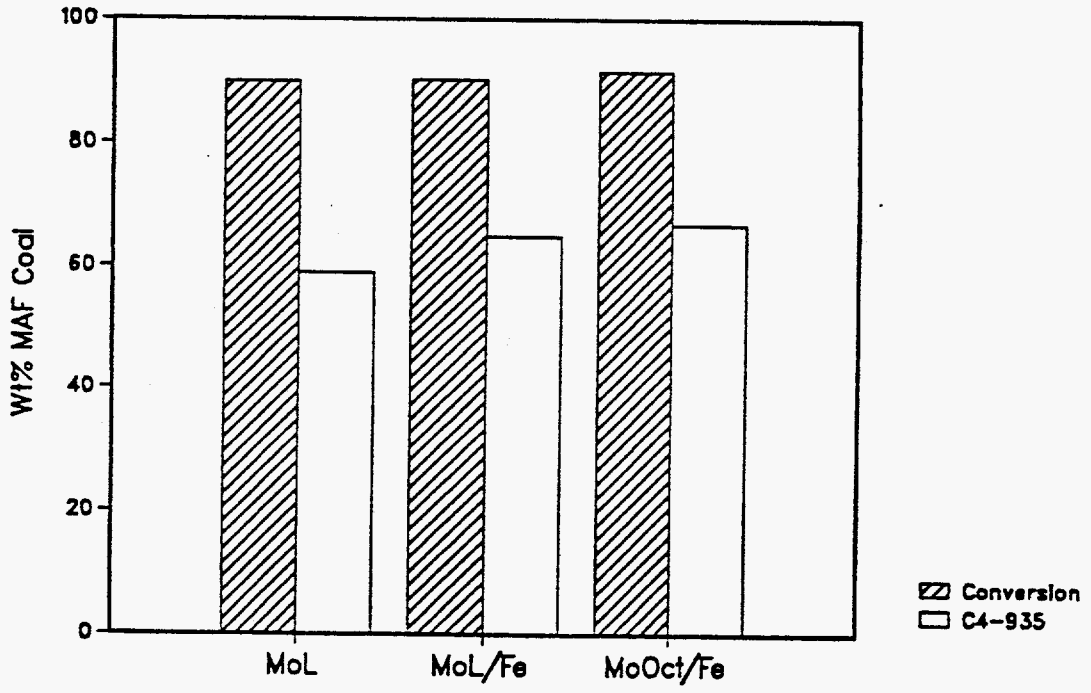


FIGURE 20

PORE SIZE DISTRIBUTION

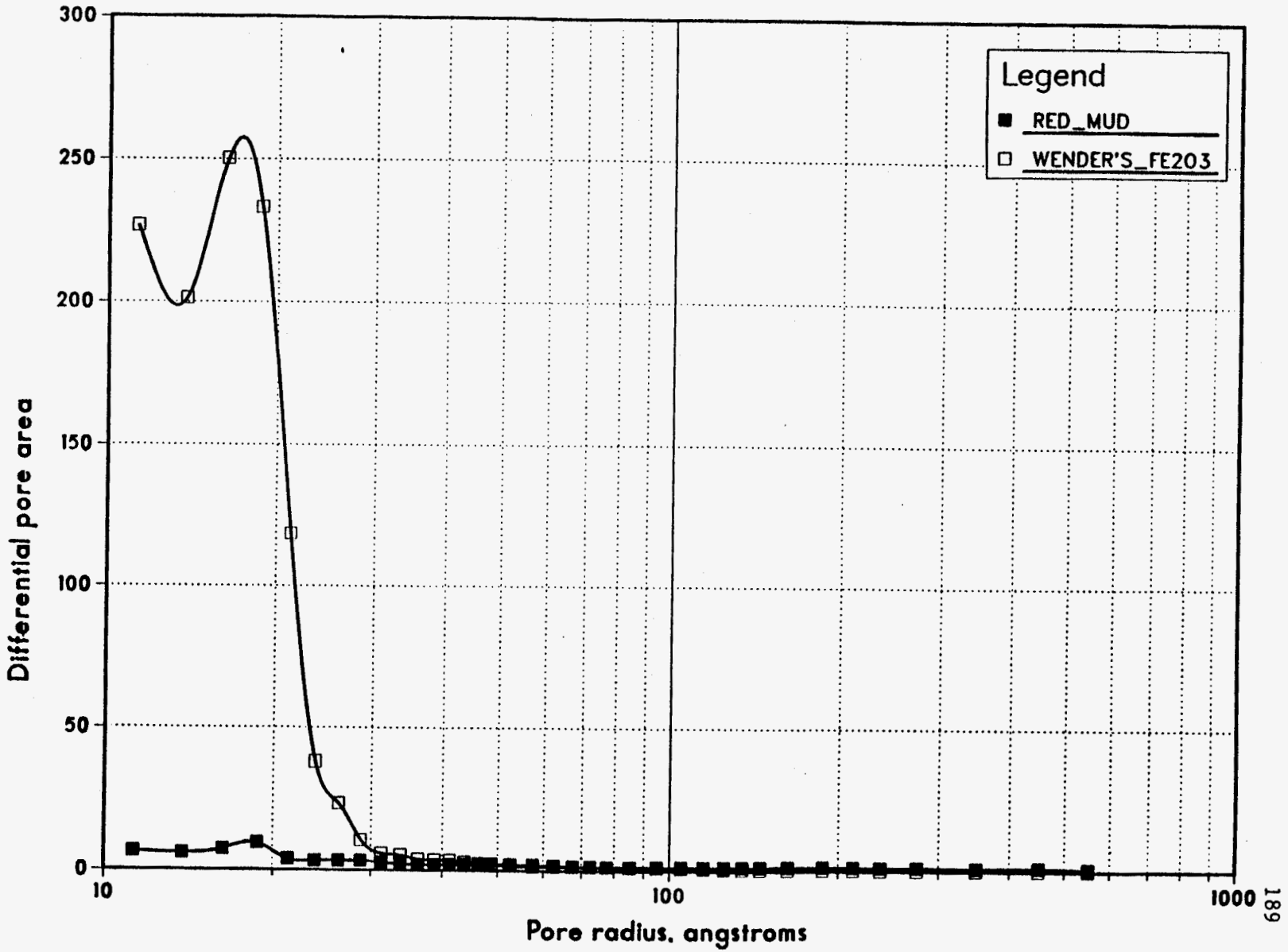


FIGURE 21

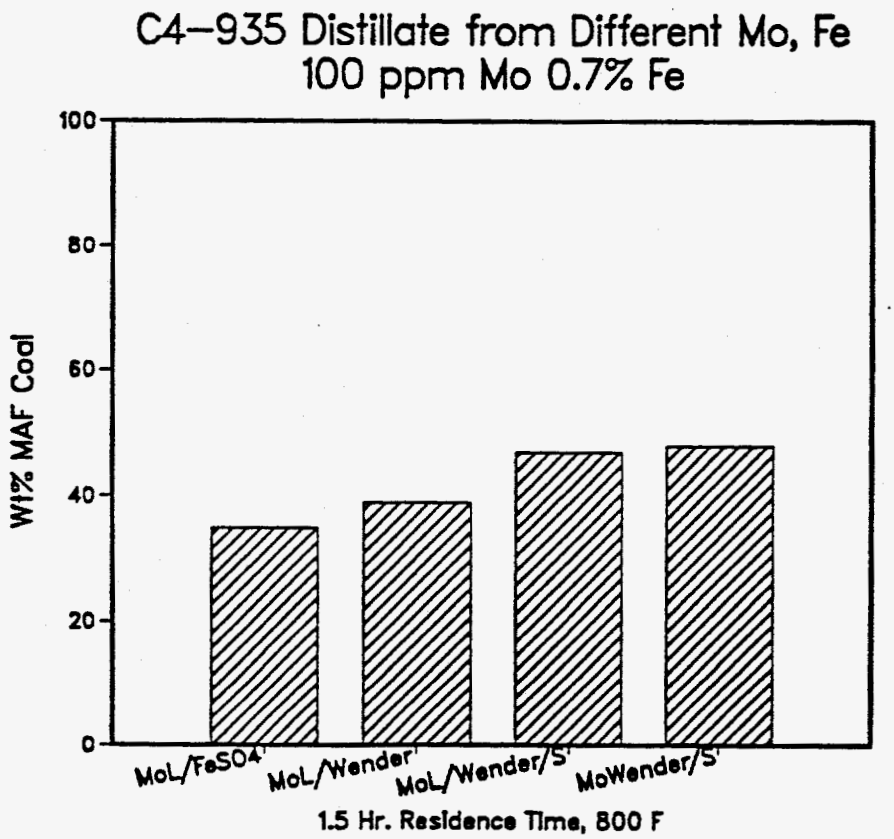
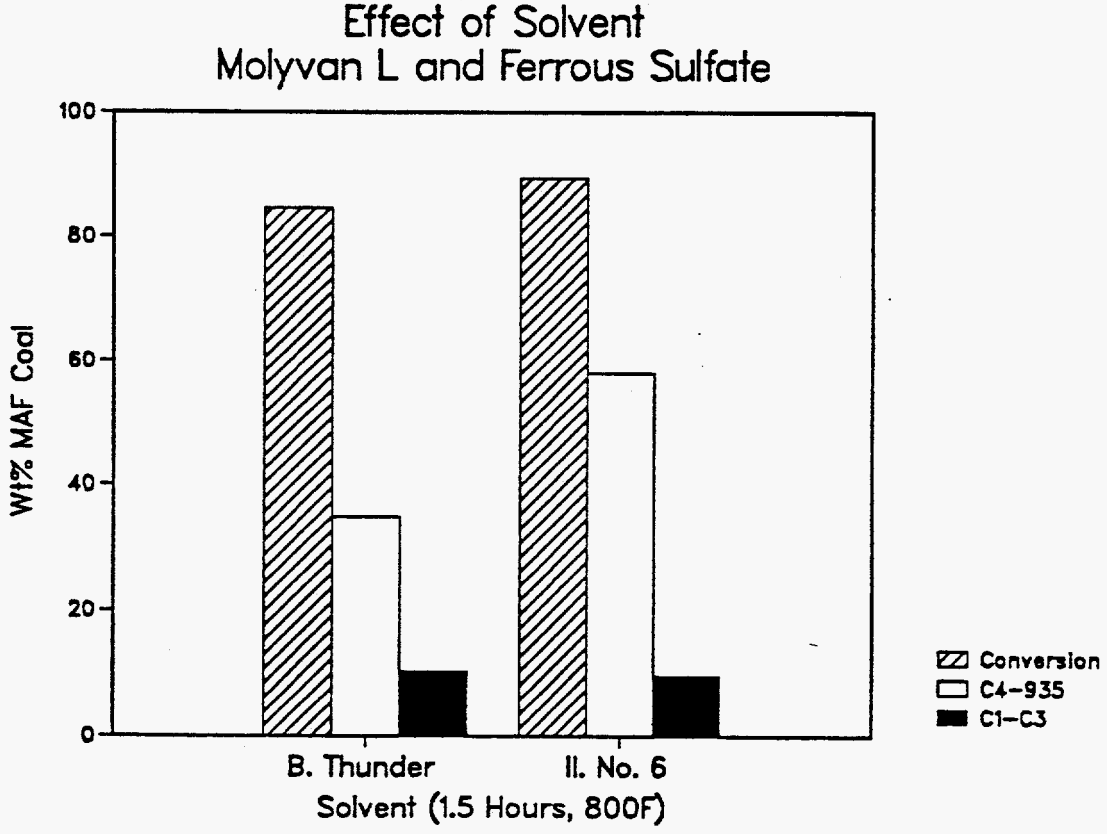
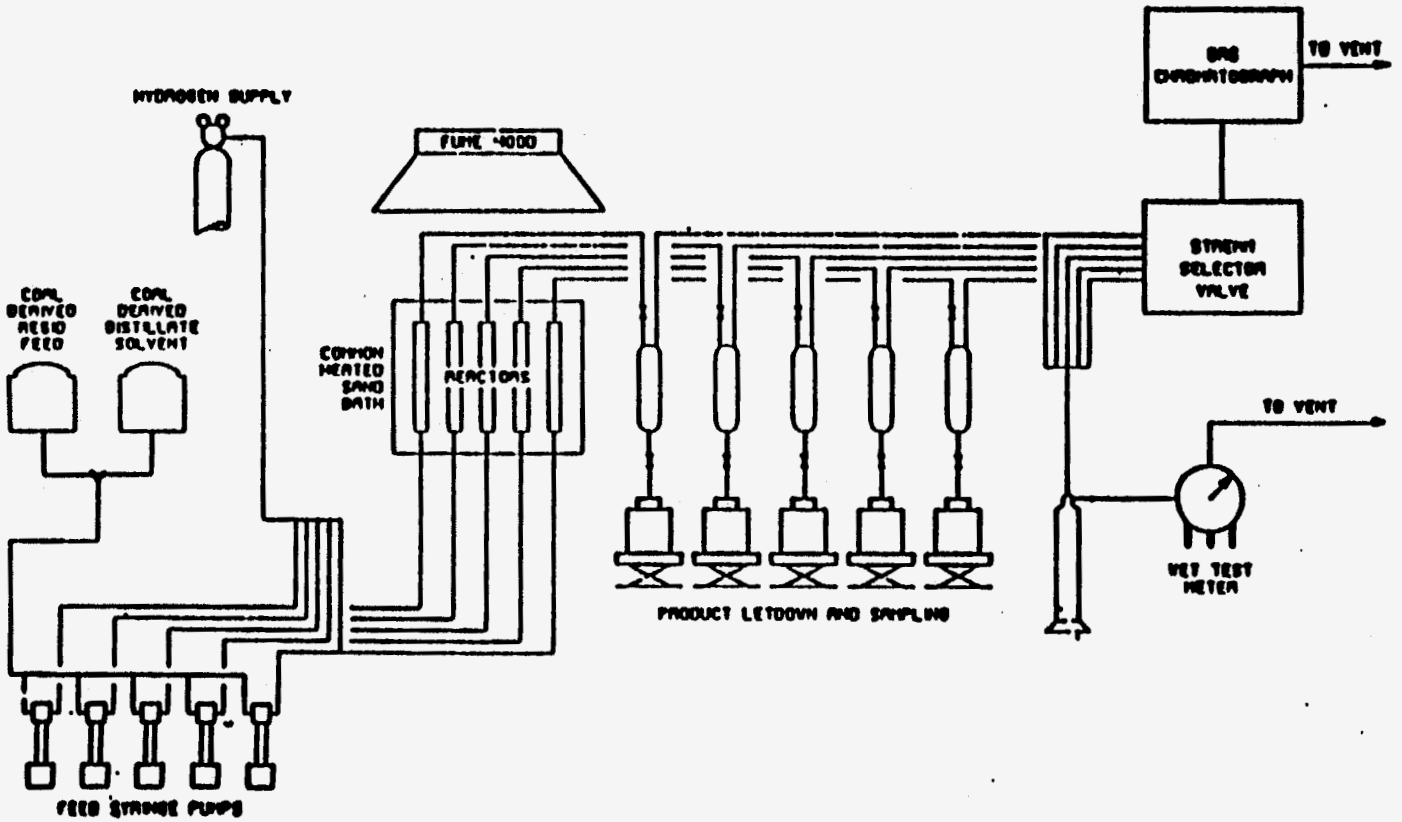

C4–935 Distillate from Different Mo, Fe
100 ppm Mo 0.7% Fe
Wt% MAF Coal
100
80
60
40
20
0
MoL/FeSO4'
MoL/Wender'
MoL/Wender/S'
MoWender/S'
1.5 Hr. Residence Time, 800 F

FIGURE 22


Effect of Solvent
Molyvan L and Ferrous Sulfate
Wt% MAF Coal
100
80
60
40
20
0
B. Thunder
Il. No. 6
Solvent (1.5 Hours, 800F)
Conversion
C4-935
C1-C3

GURE 23

SCHEMATIC OF 5-PARALLEL FIXED-BED REACTOR PILOT PLANT, AU-126



- Cont. unattended operation
- 5-fixed bed reactors
- Variable reactor volume
- Capacity < 0.4 gal/day/reactor (60 cc/hr)

FIGURE 24 Reactor Packings

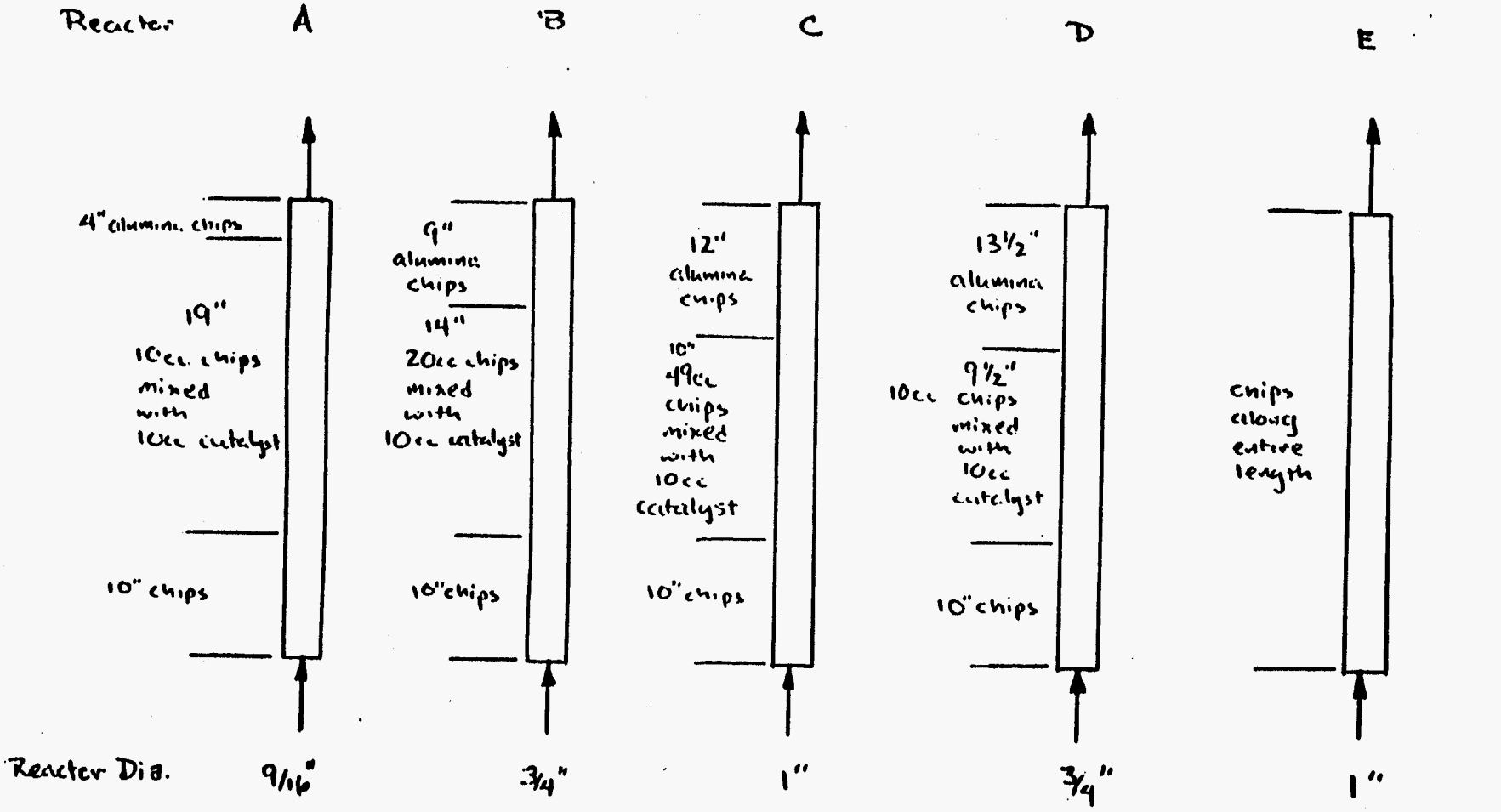


FIGURE 25

COMPARISON OF K_v VALUES FOR
RUN 3B WITH OHIO NO. 6 RESID

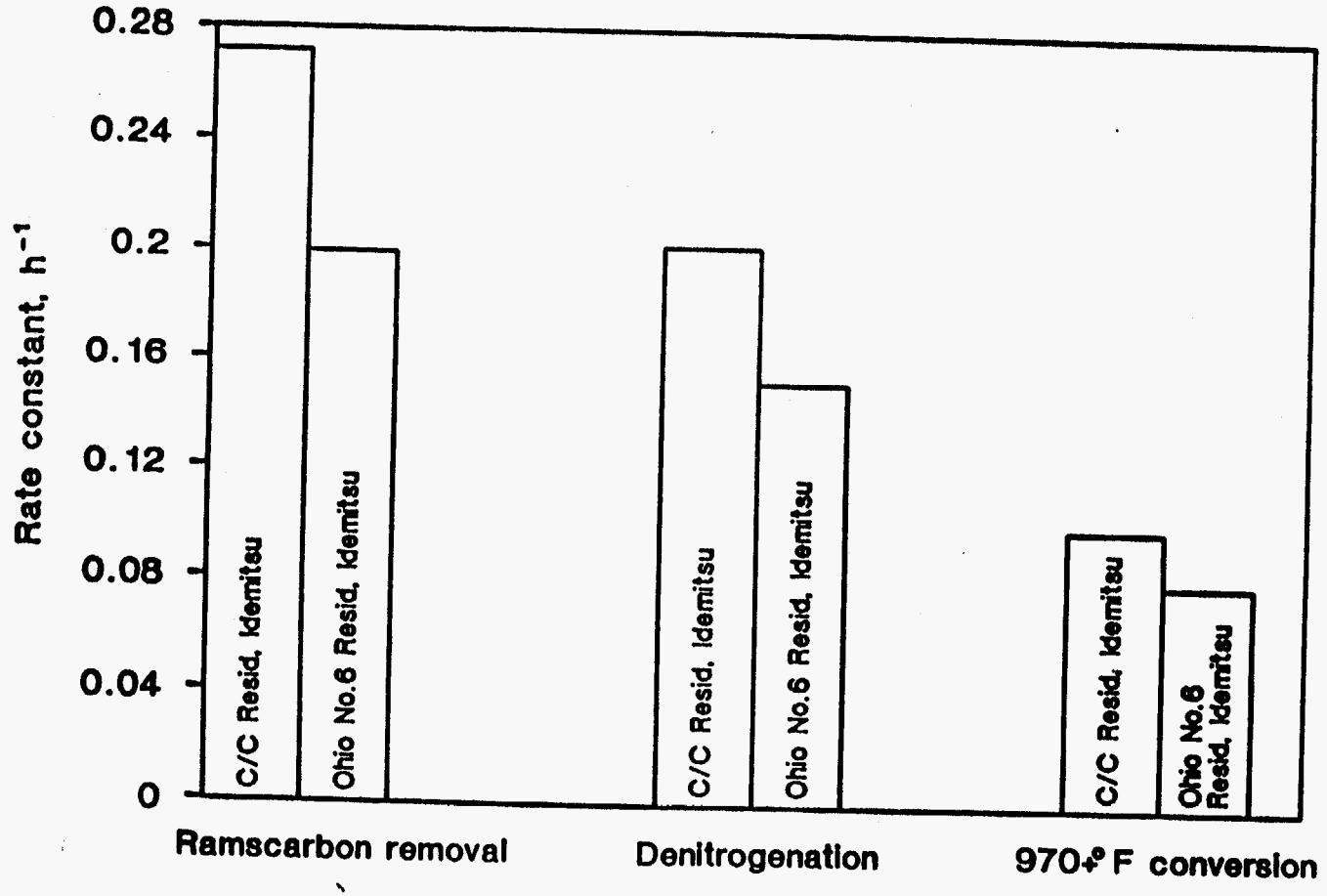


FIGURE 26

COMPARISON OF K_v VALUES FOR
RUN 3B WITH MARTIN LAKE LIGNITE RESID

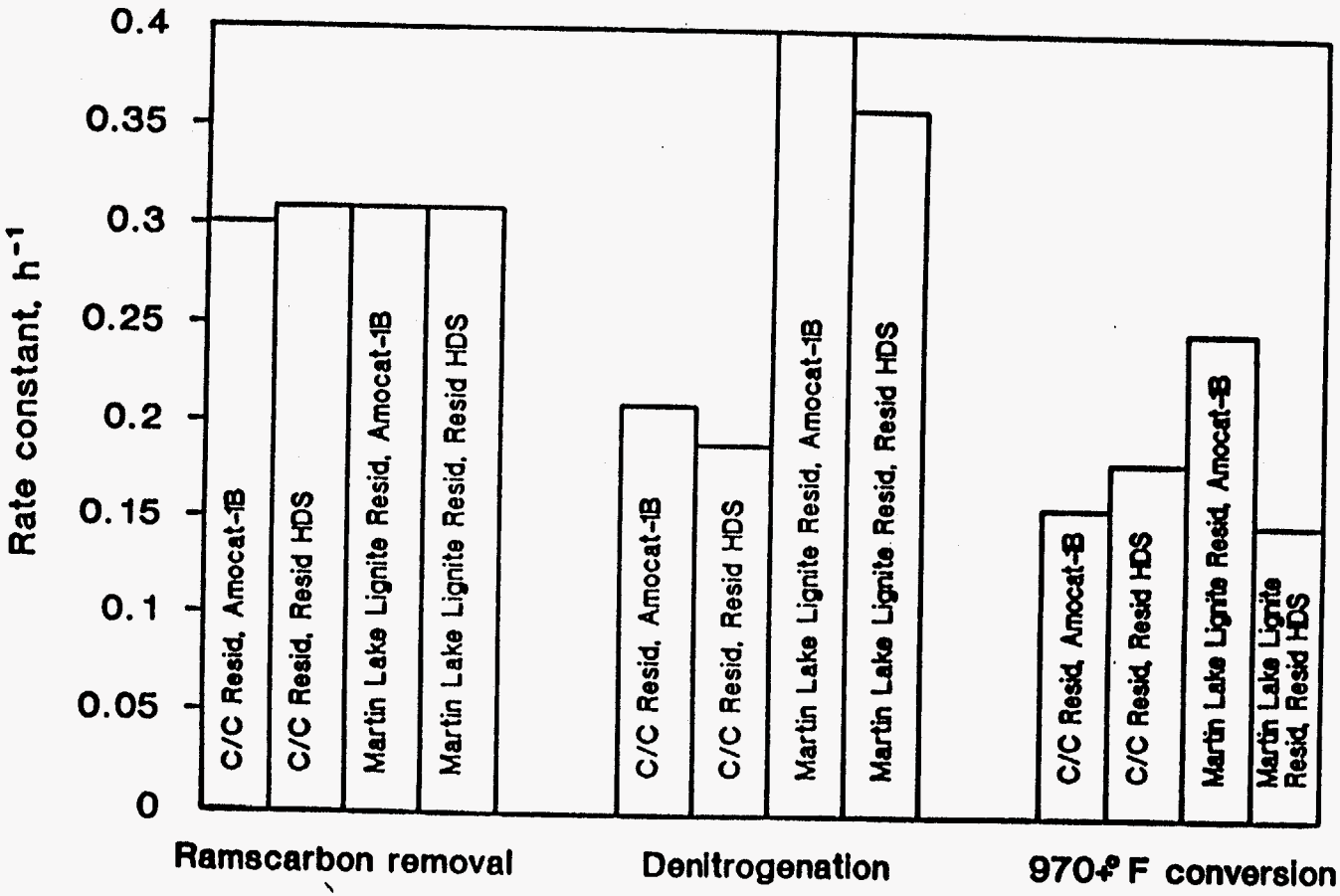


FIGURE 27

COMPARISON OF K_v VALUES FOR RUN 3B WITH RESID DERIVED FROM ILLINOIS NO. 6 COAL LIQUEFIED IN THE T/C MODE

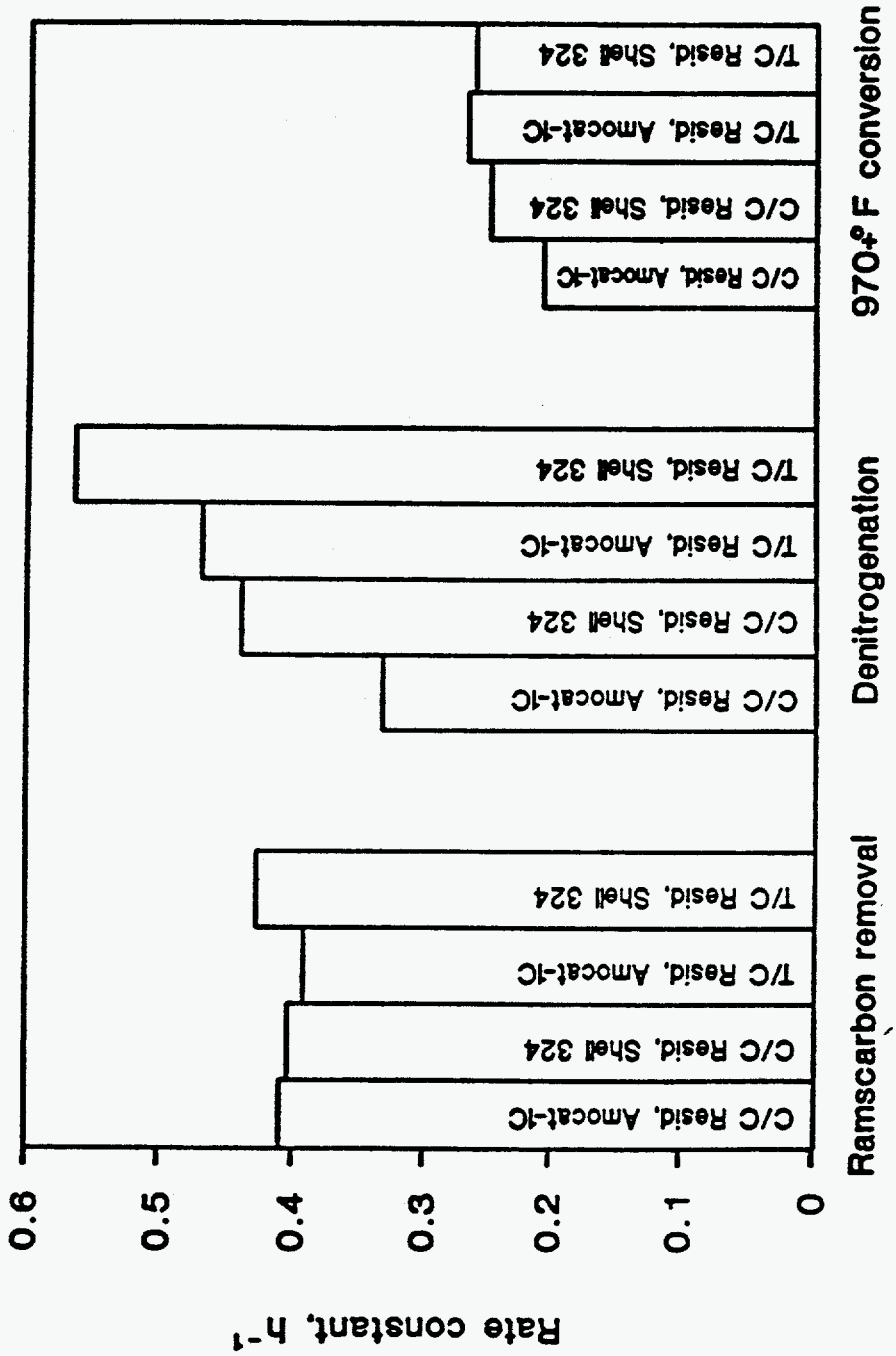


FIGURE 28

Crystal Structures of Catalysts

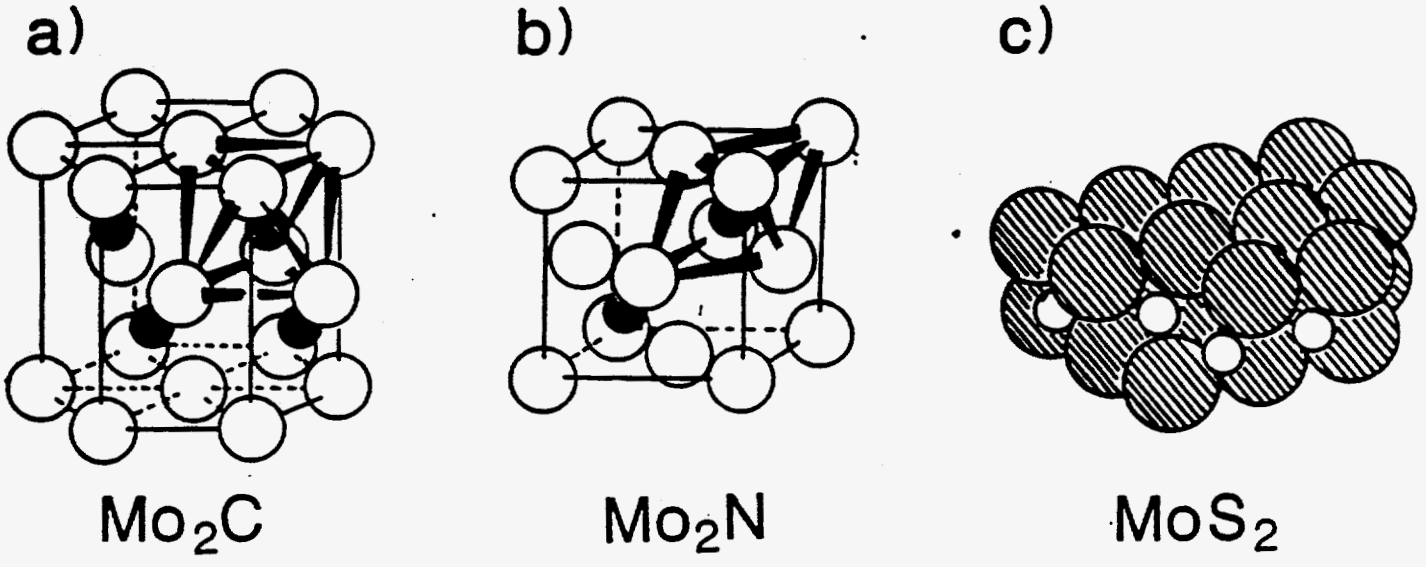


FIGURE 29

NITROGEN CONTENT OF THE PRODUCT VS.
TIME ON OIL FOR RUN 6B

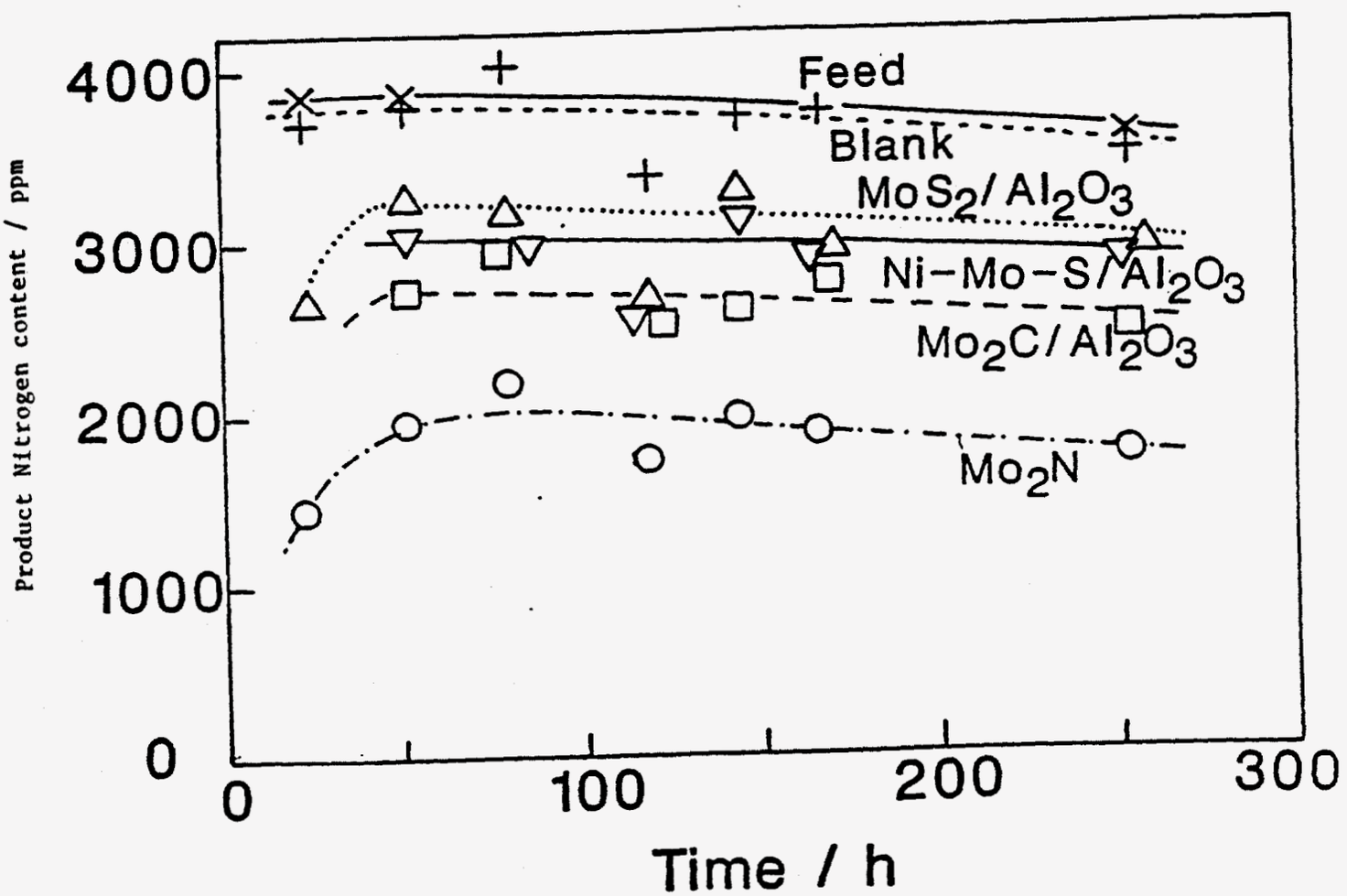


FIGURE 30

XRD PATTERN FOR WC

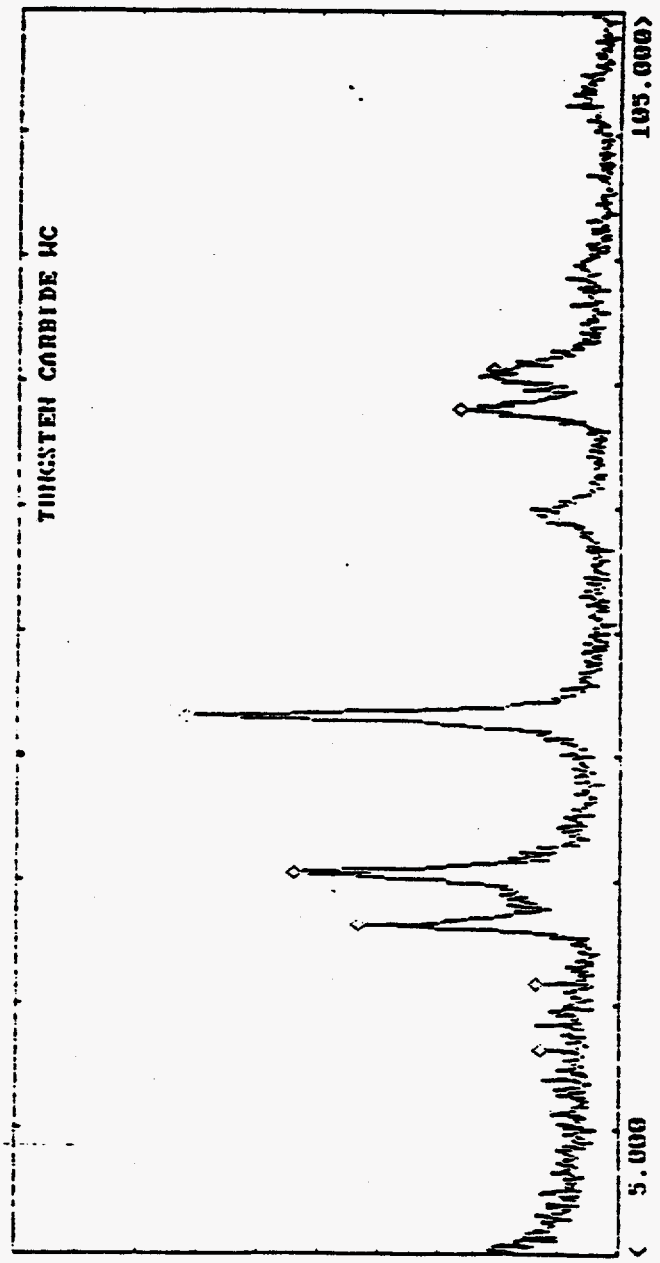


FIGURE 31

XRD PATTERN FOR Mo_2N

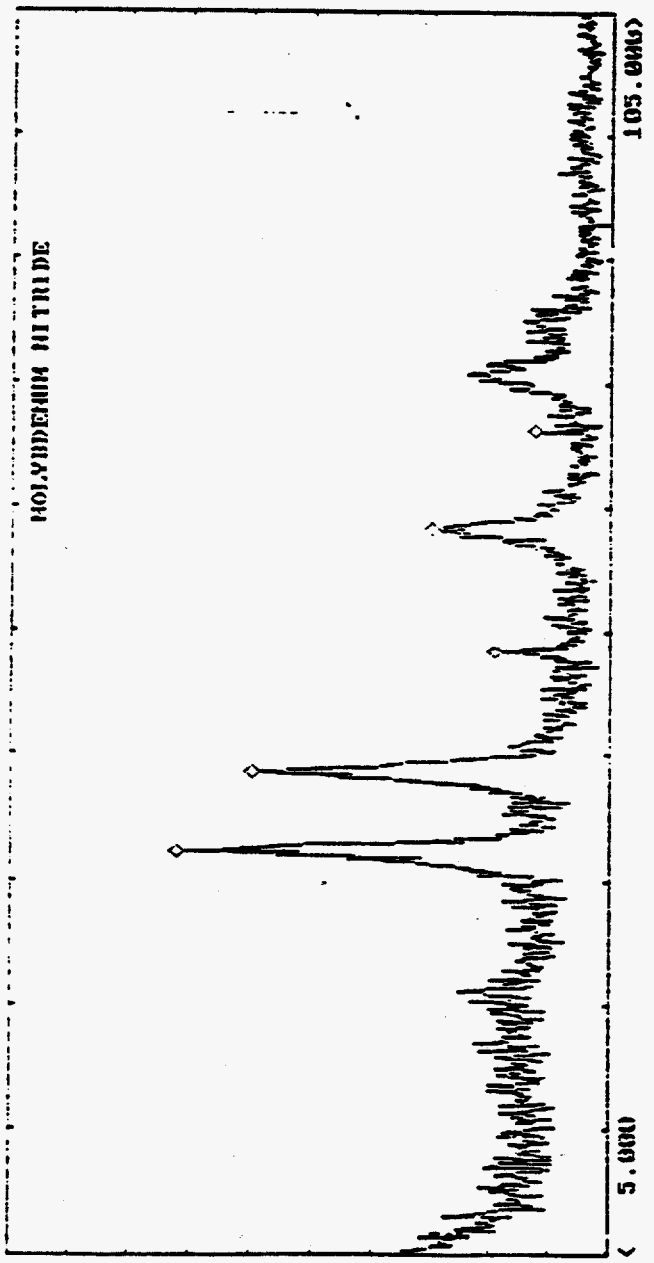


FIGURE 32

XRD PATTERN FOR Mo_2C

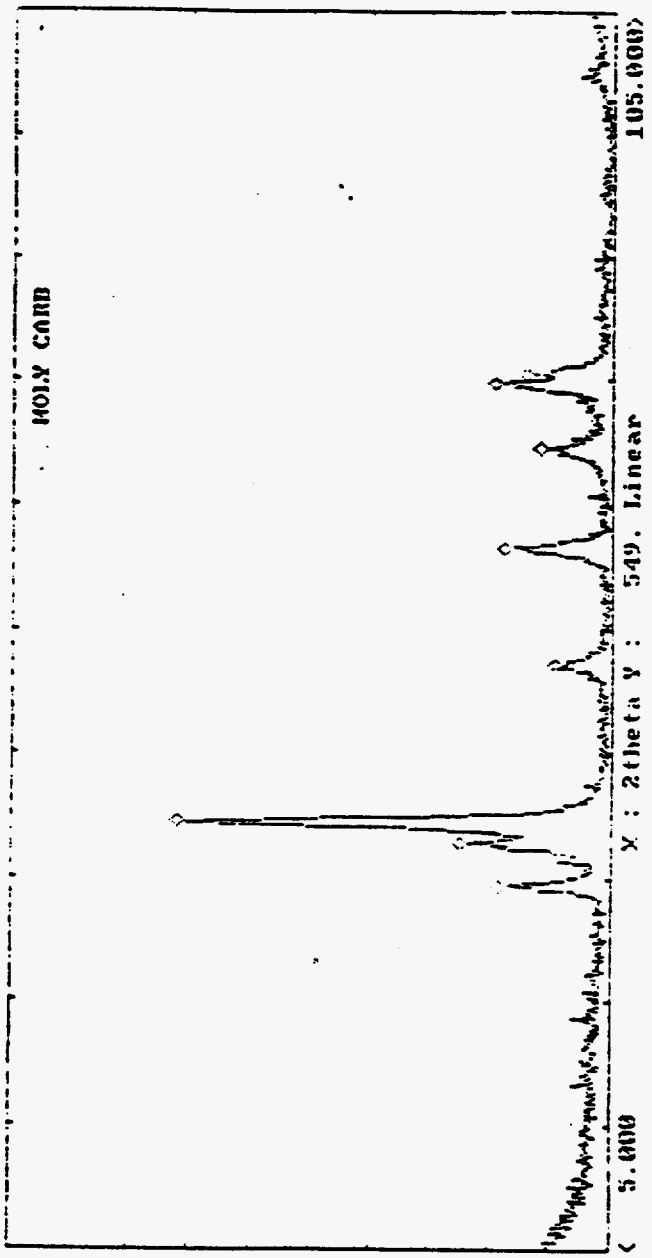


FIGURE 33

PORE SIZE DISTRIBUTIONS
OF CATALYSTS

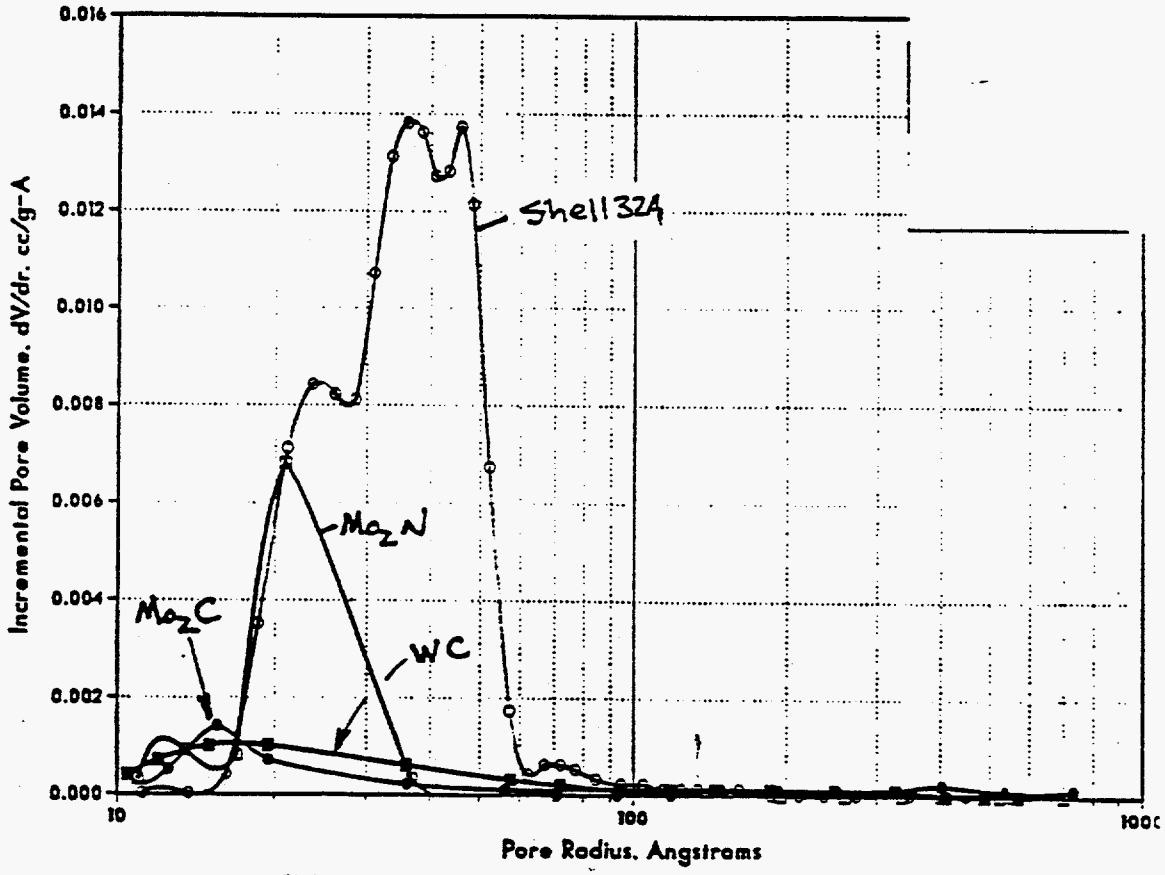


FIGURE 34

PORE SIZE DISTRIBUTIONS OF CATALYSTS. EACH DISTRIBUTION IS NORMALIZED BY ITS MAXIMUM PORE VOLUME

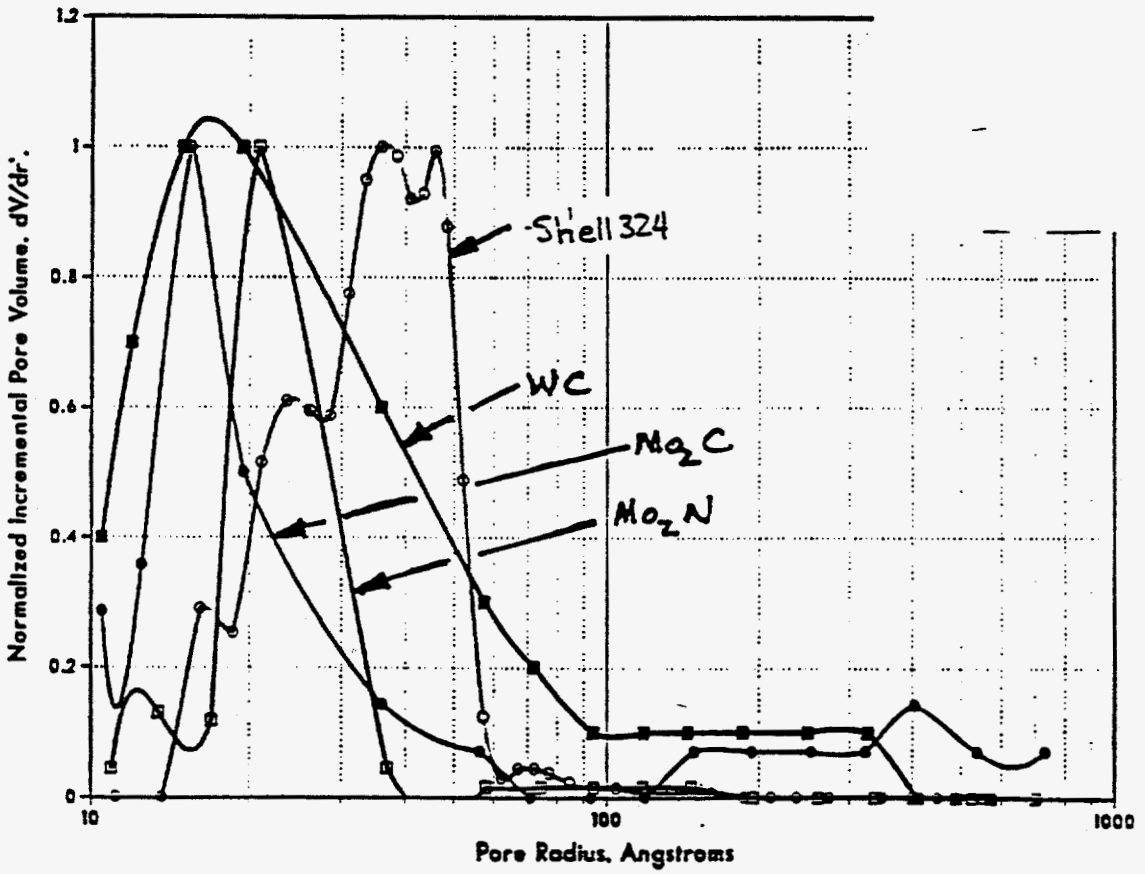


FIGURE 35

AROMATICS SATURATION
BY SHELL 324

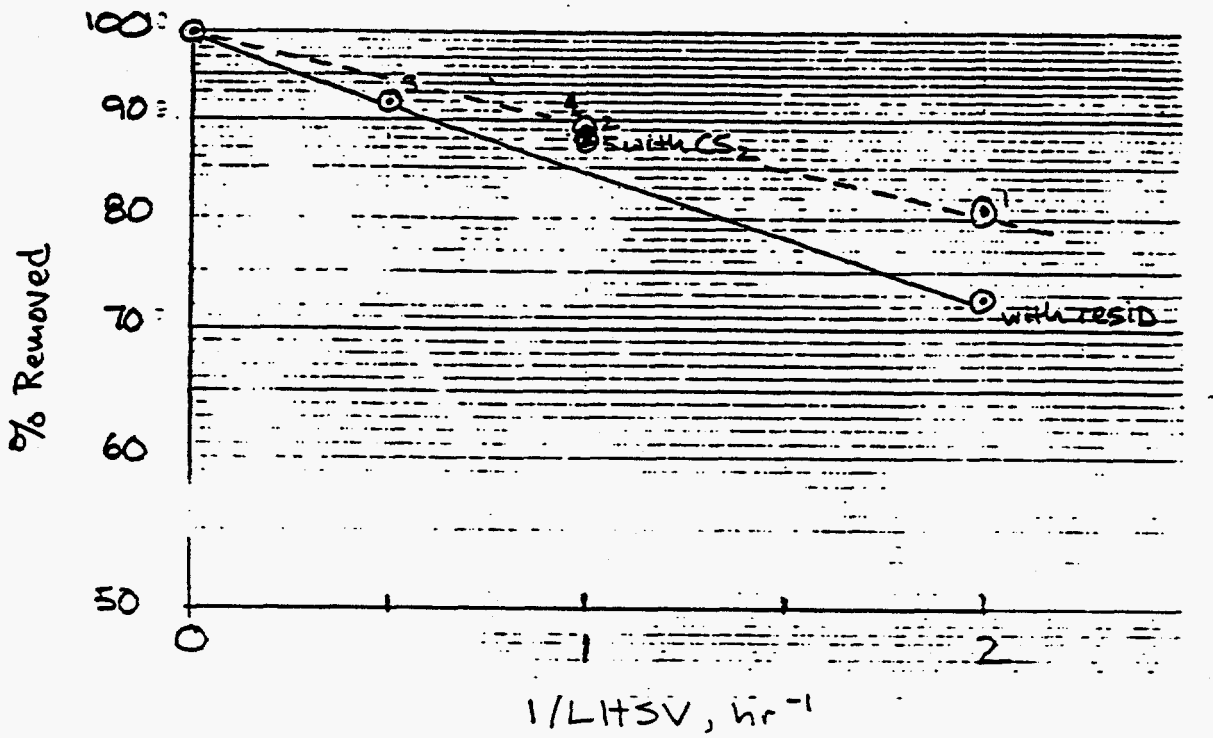


FIGURE 36

DENITROGENATION BY SHELL 324

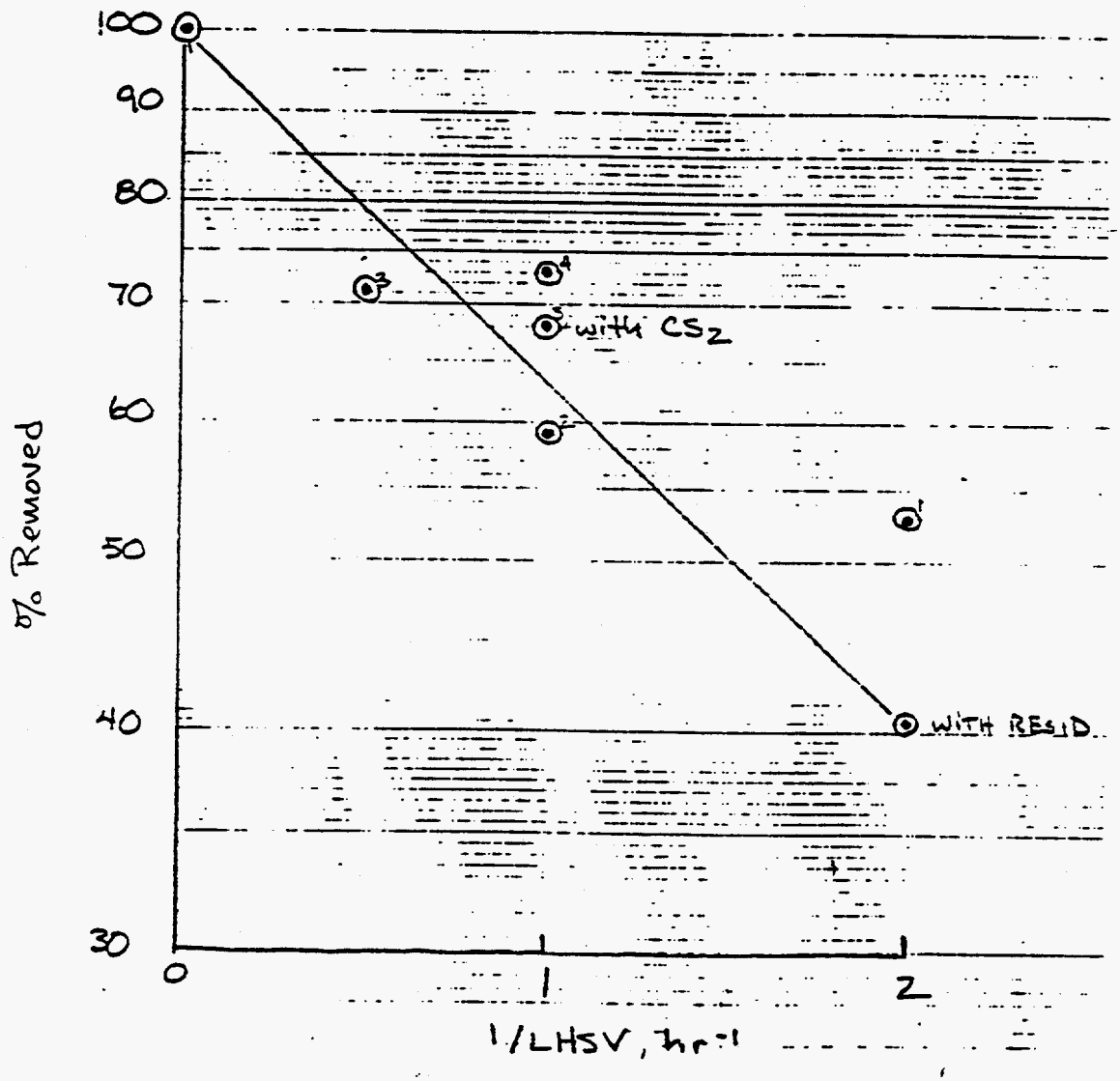


FIGURE 37

DESULFURIZATION
BY SHELL 324

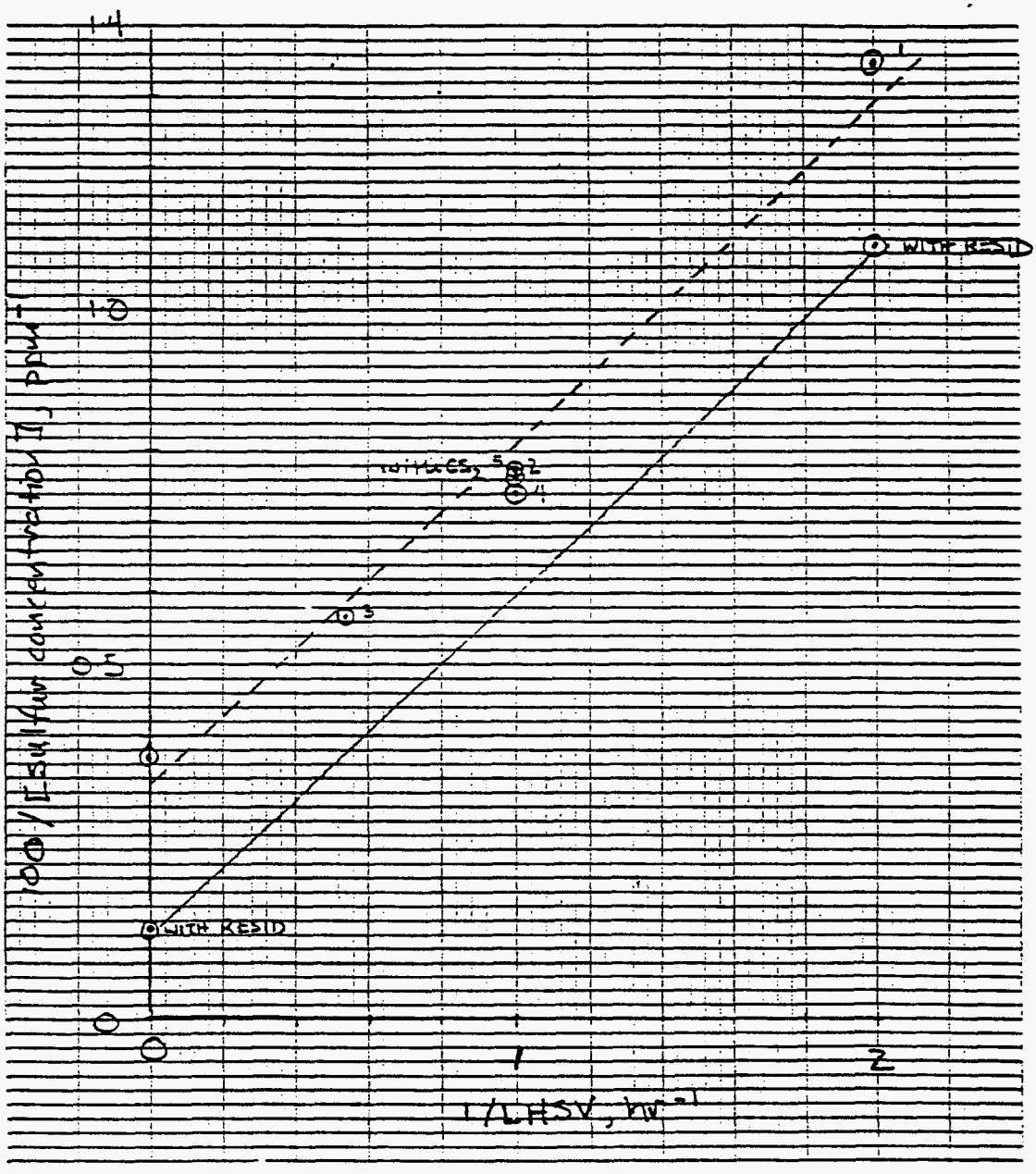


FIGURE 38A

AROMATICS SATURATION BY WC

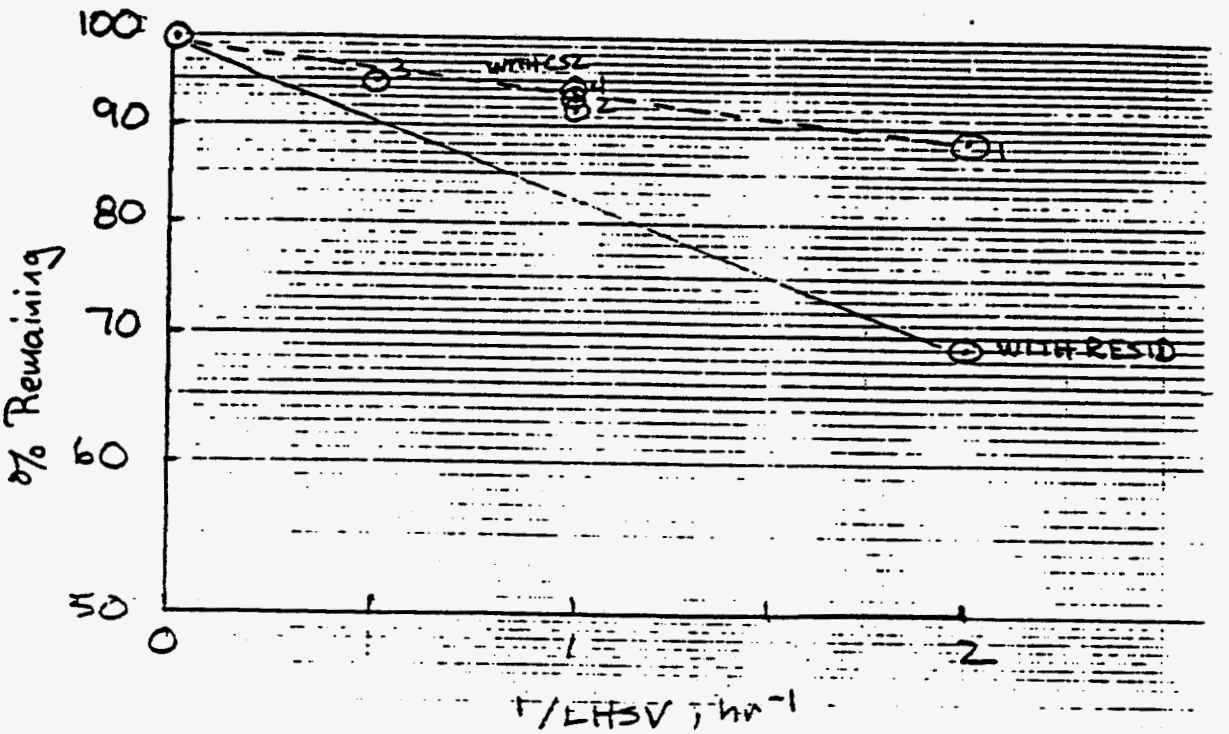


FIGURE 38B

DENITROGENATION BY WC

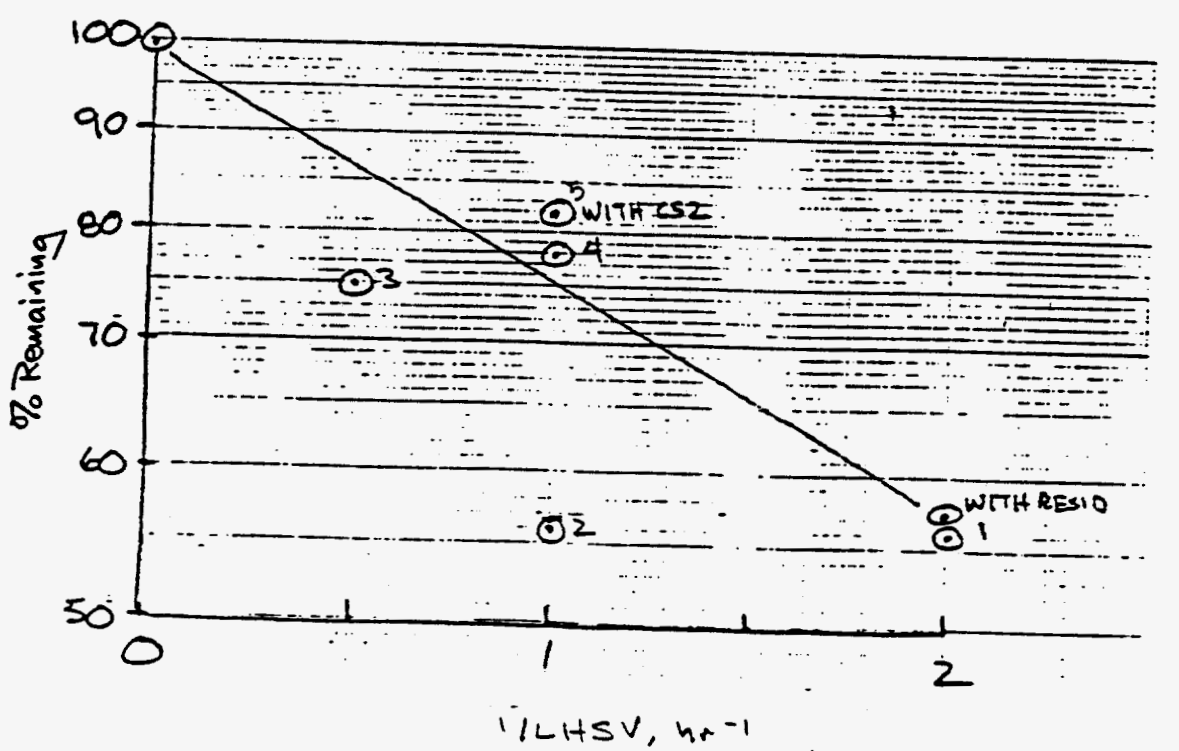


FIGURE 39A

AROMATICS SATURATION BY Mo_2N

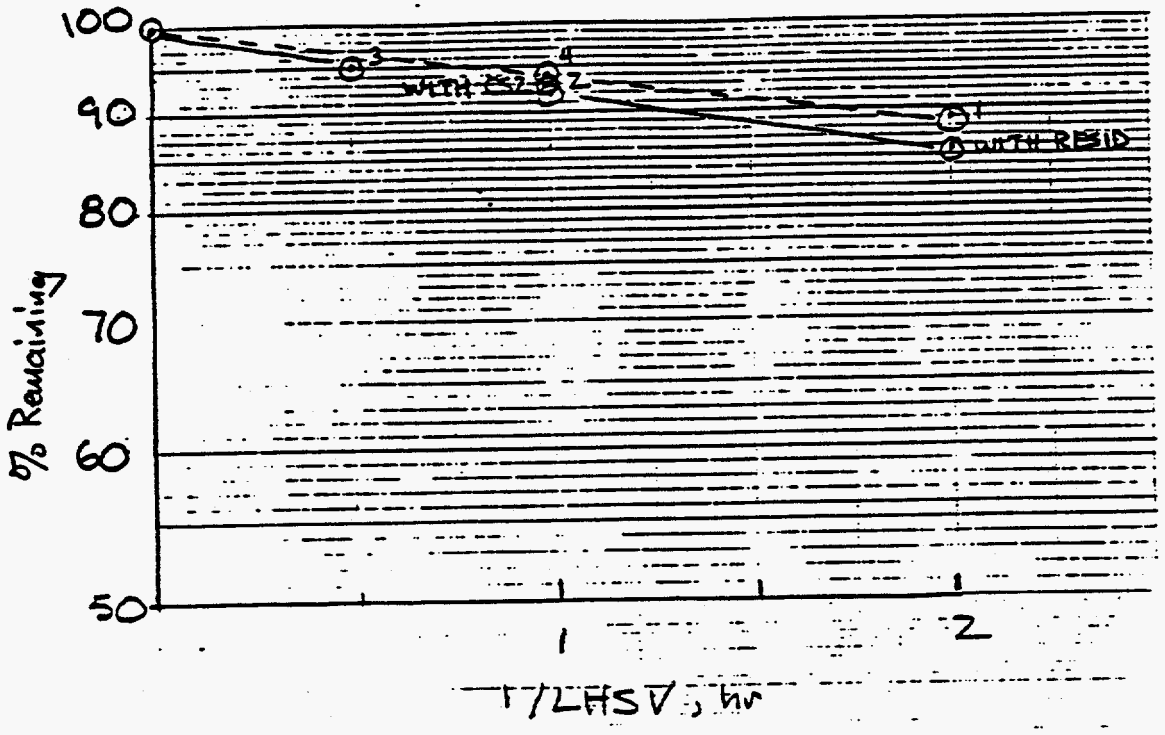


FIGURE 39B

DENITROGENATION BY Mo_2N

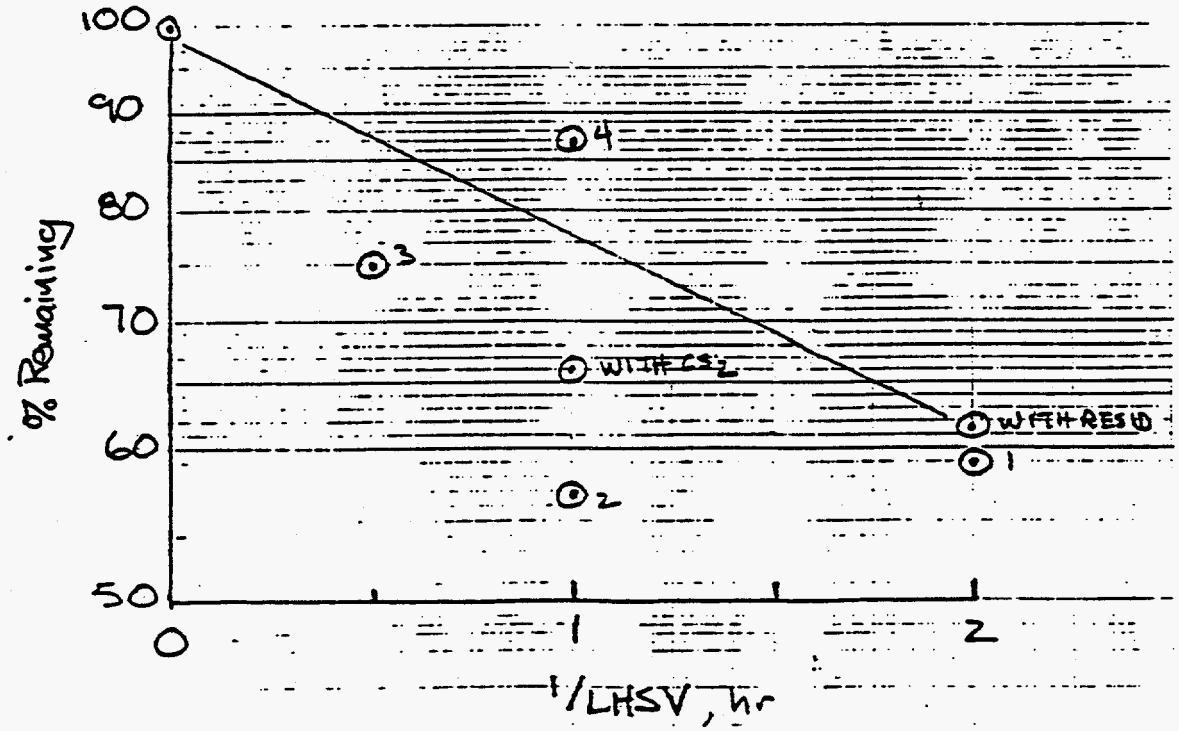


FIGURE 40A

AROMATICS SATURATION
BY Mo_2N/AMOCAT

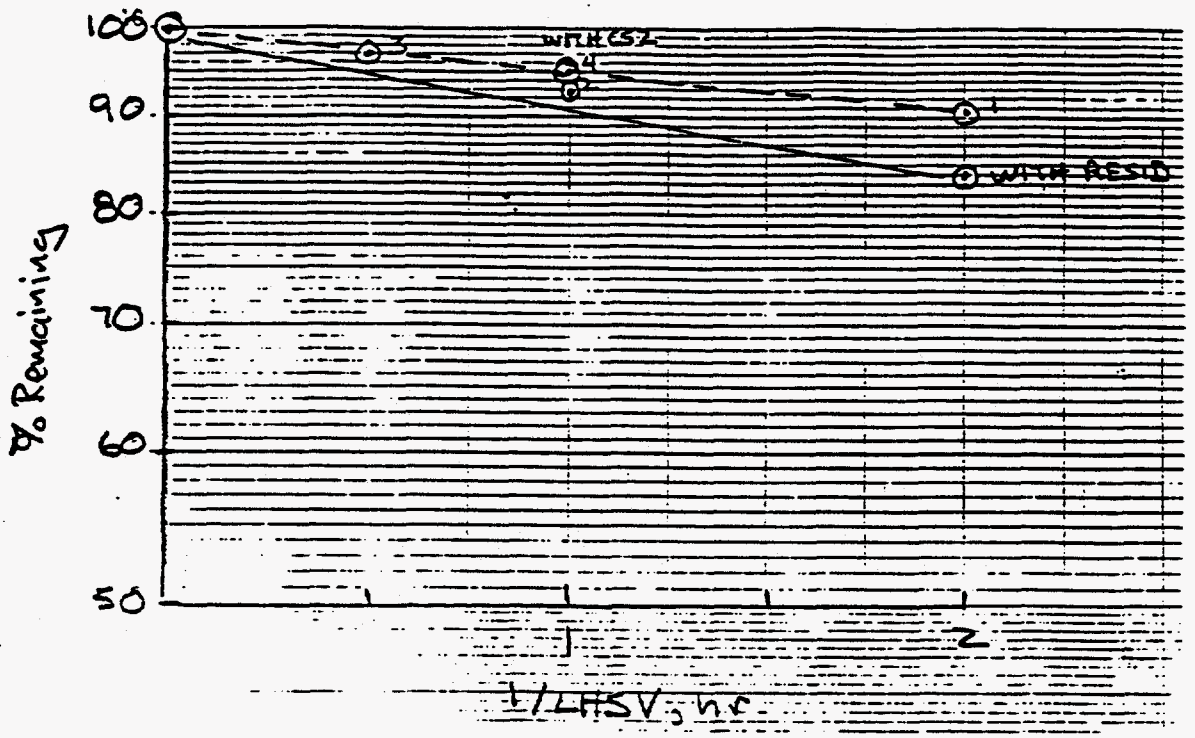


FIGURE 40B

DENITROGENATION
BY Mo_2N/AMOCAT

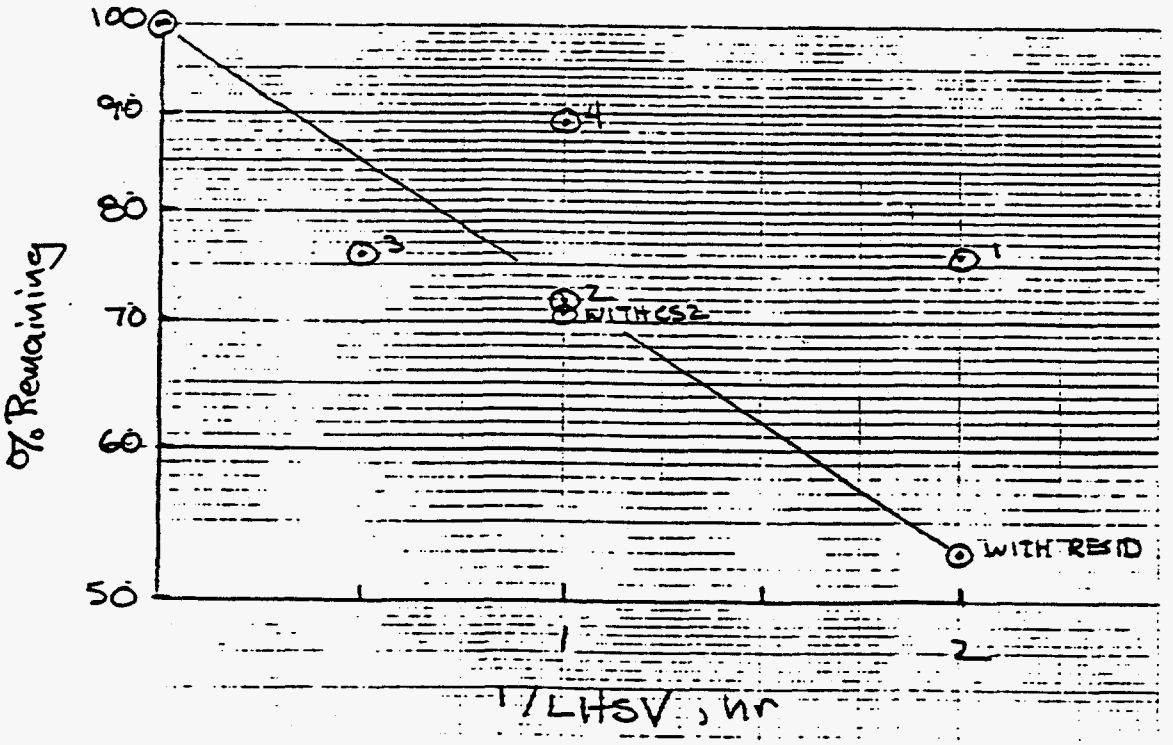


FIGURE 41A

AROMATICS SATURATION
BY Mo_2C/AMOCAT

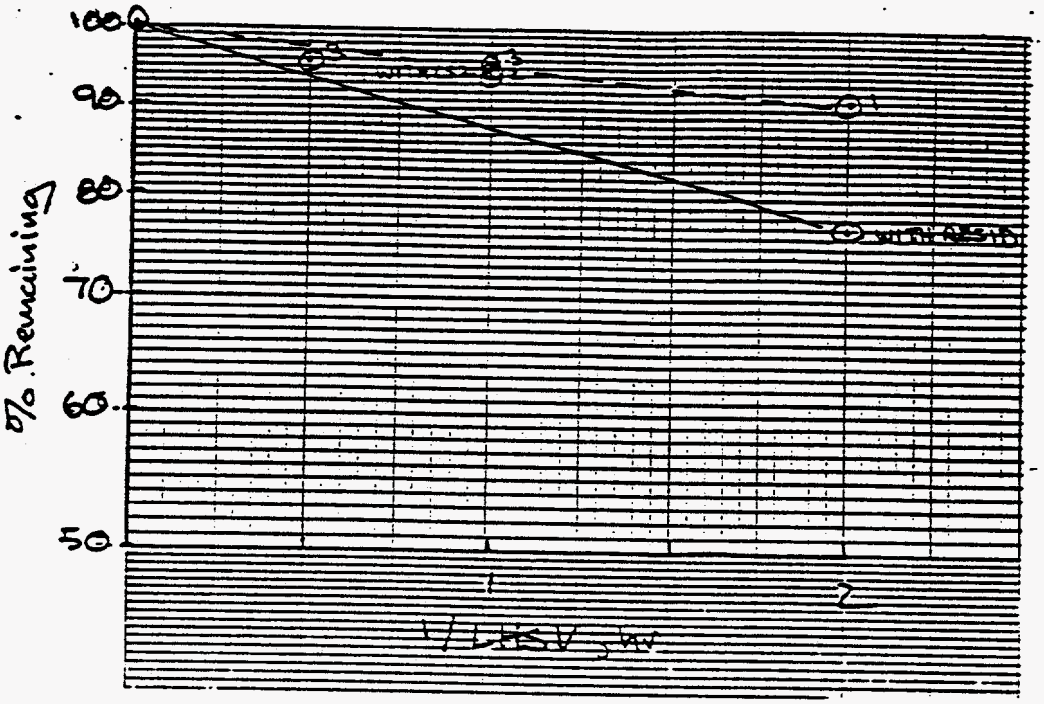


FIGURE 41B

DENITROGENATION
BY Mo_2C/AMOCAT

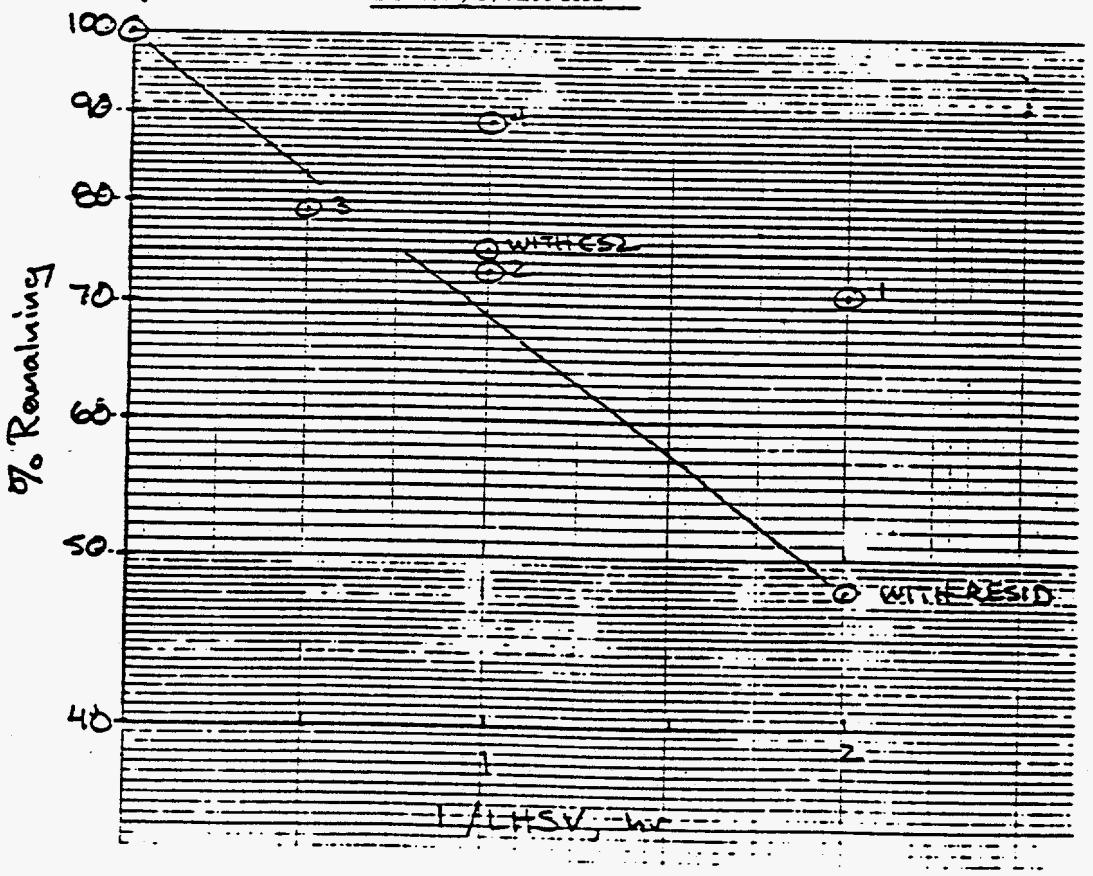


FIGURE 42

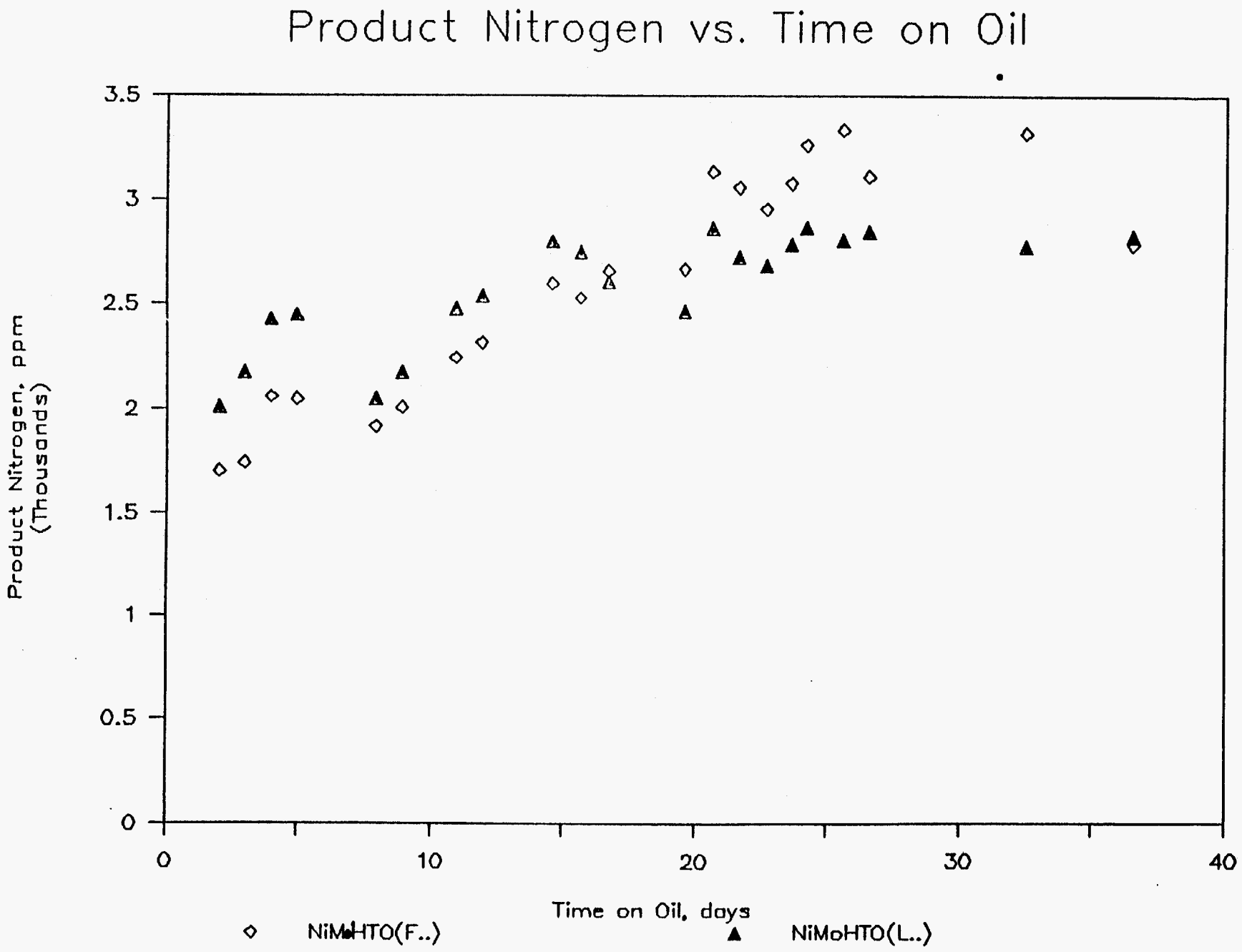

Product Nitrogen vs. Time on Oil
Product Nitrogen, ppm (Thousands)
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
Time on Oil, days
NiMoHTO(F..)
NiMoHTO(L..)

FIGURE 43

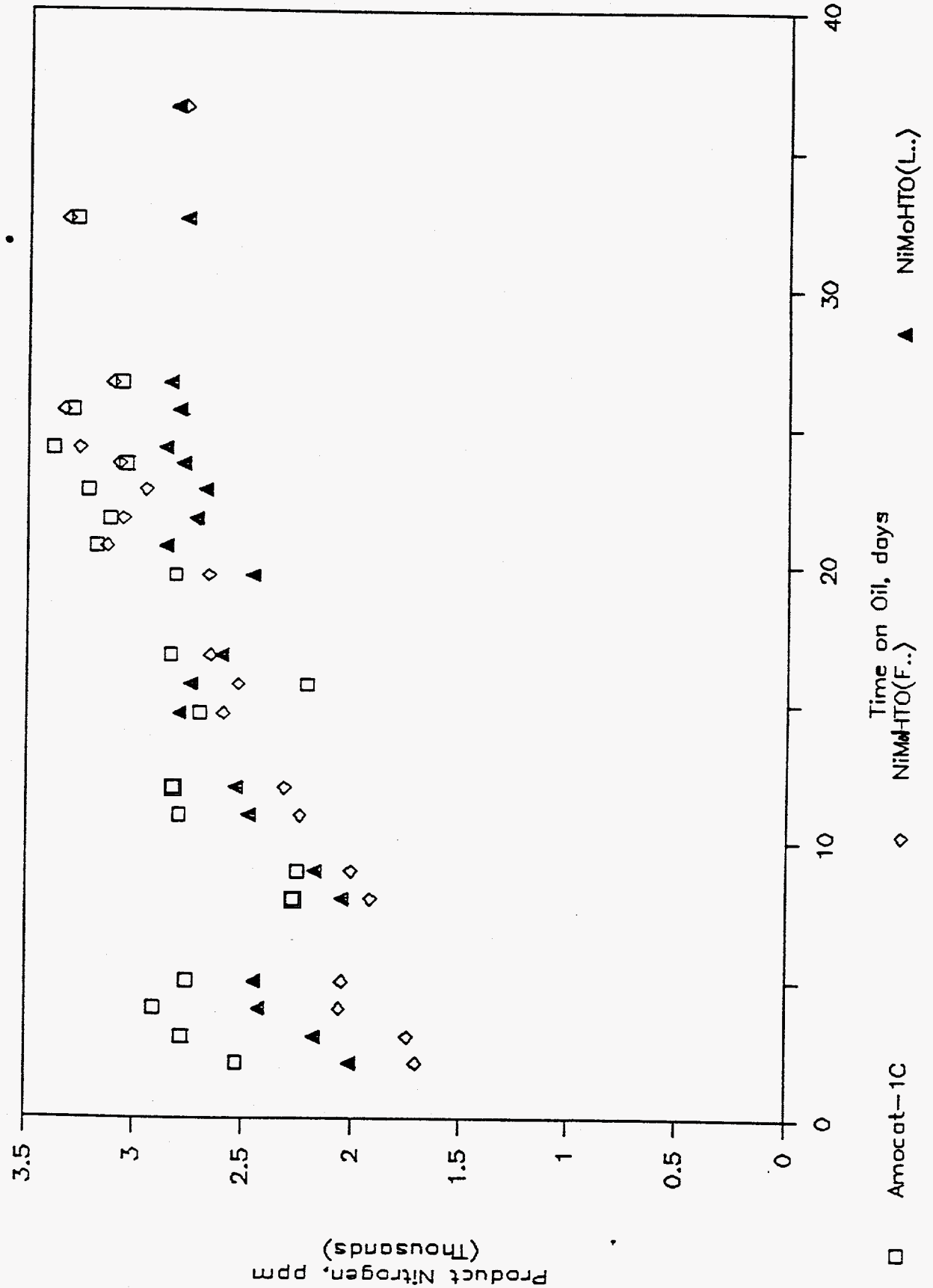

Product Nitrogen vs. Time on Oil
Product Nitrogen, ppm
(Thousands)
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
Time on Oil, days
Amocat-1C
NiMoHTO(F..)
NiMoHTO(L..)

FIGURE 44

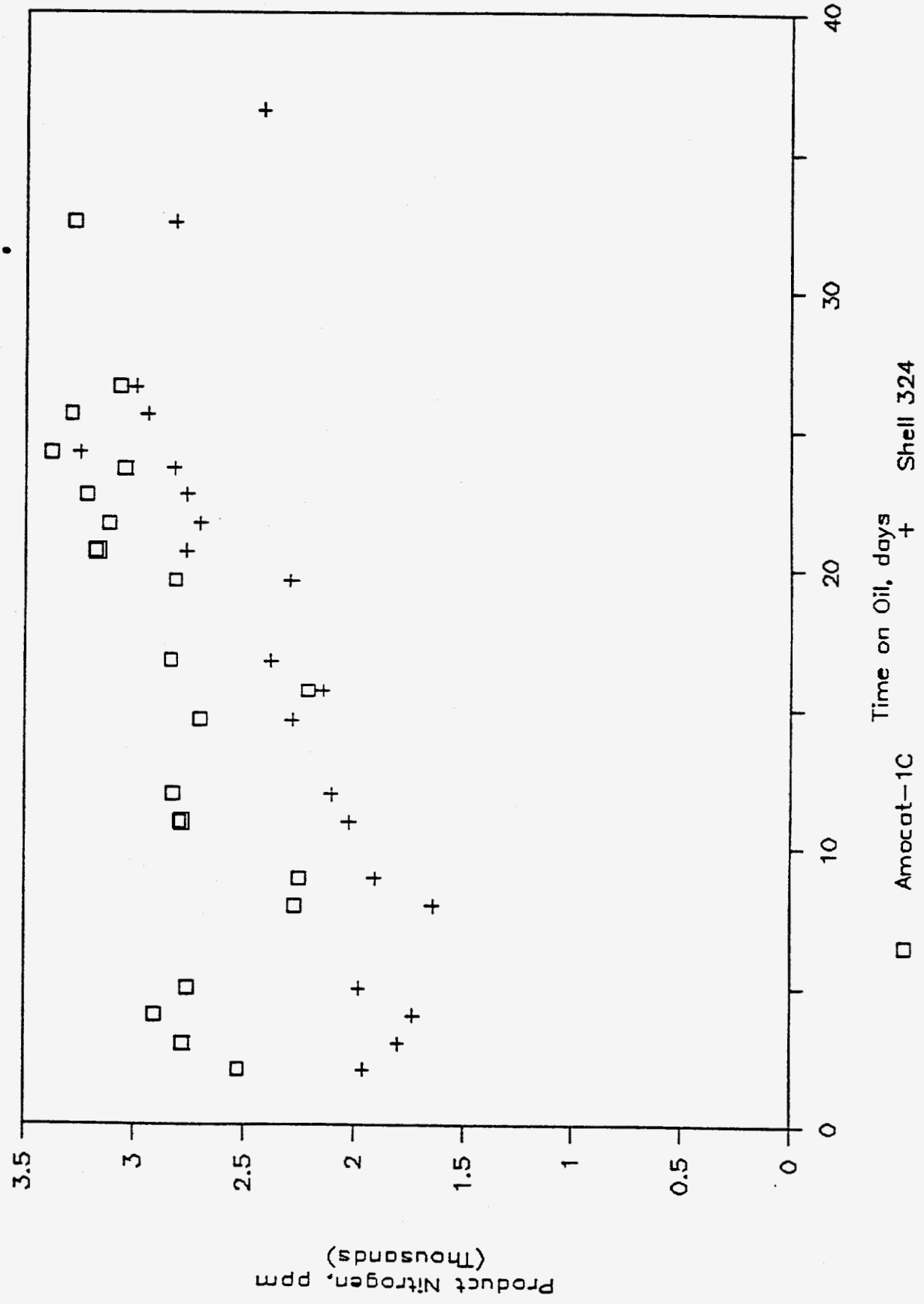
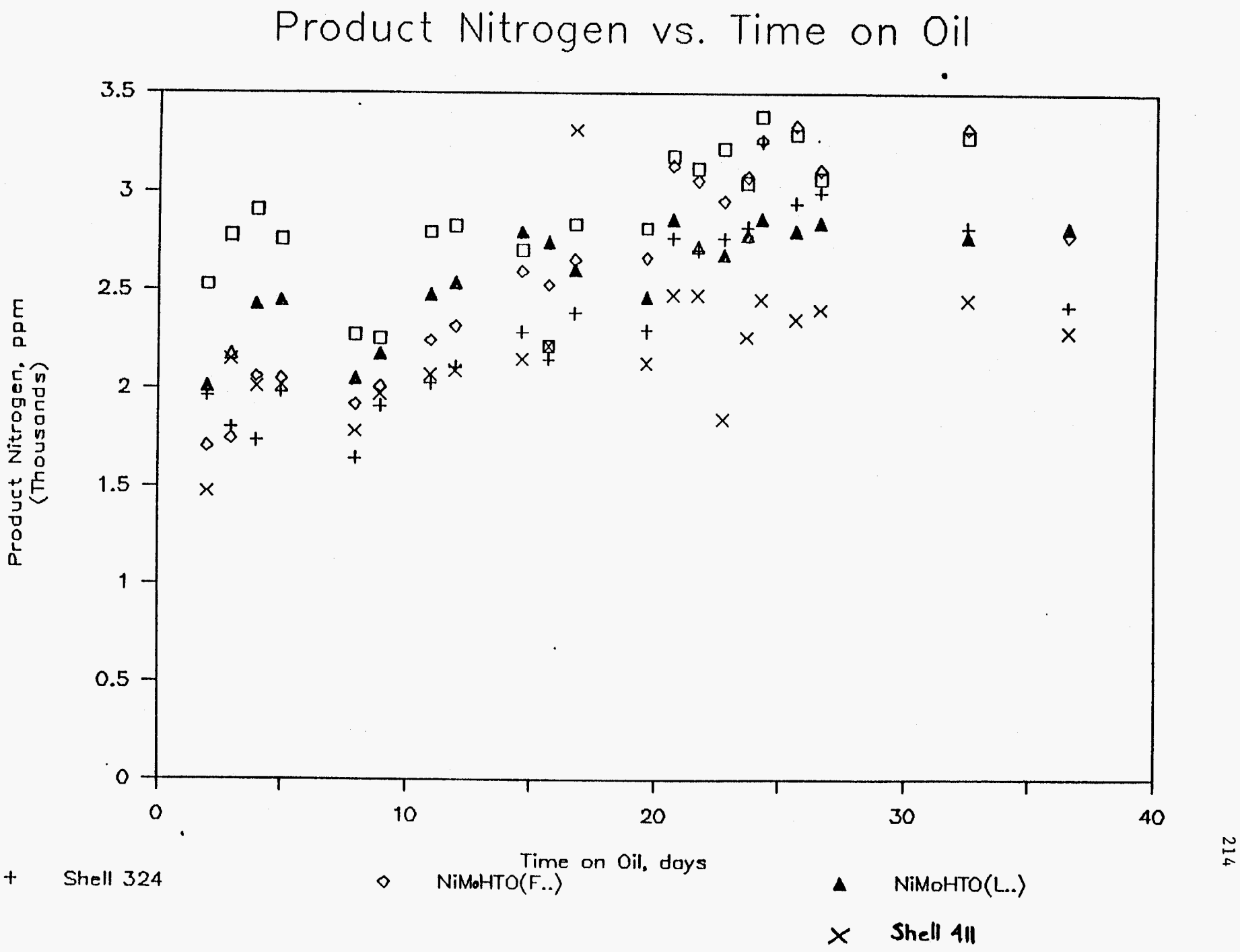
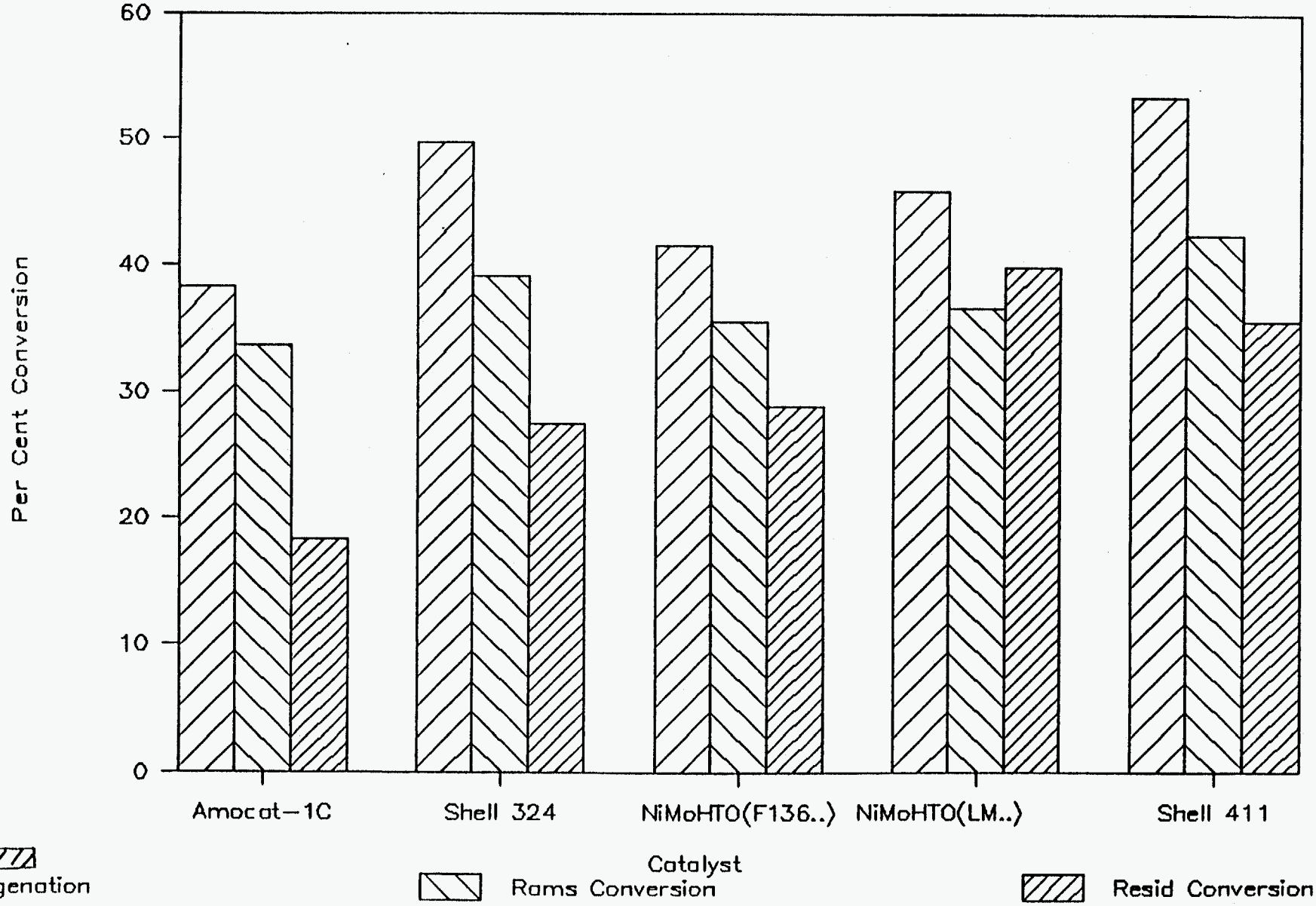

Product Nitrogen vs. Time on Oil
Product Nitrogen, ppm
(Thousands)
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
Time on Oil, days
Amocat-1C
Shell 324

FIGURE 45


Product Nitrogen vs. Time on Oil
Product Nitrogen, ppm (Thousands)
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
Time on Oil, days
+ Shell 324
◇ NiMoHTO(F..)
▲ NiMoHTO(L..)
× Shell 411

Conversions at Twenty Days on Oil



F. RE 47

Conversions at Thirty Two Days on Oil

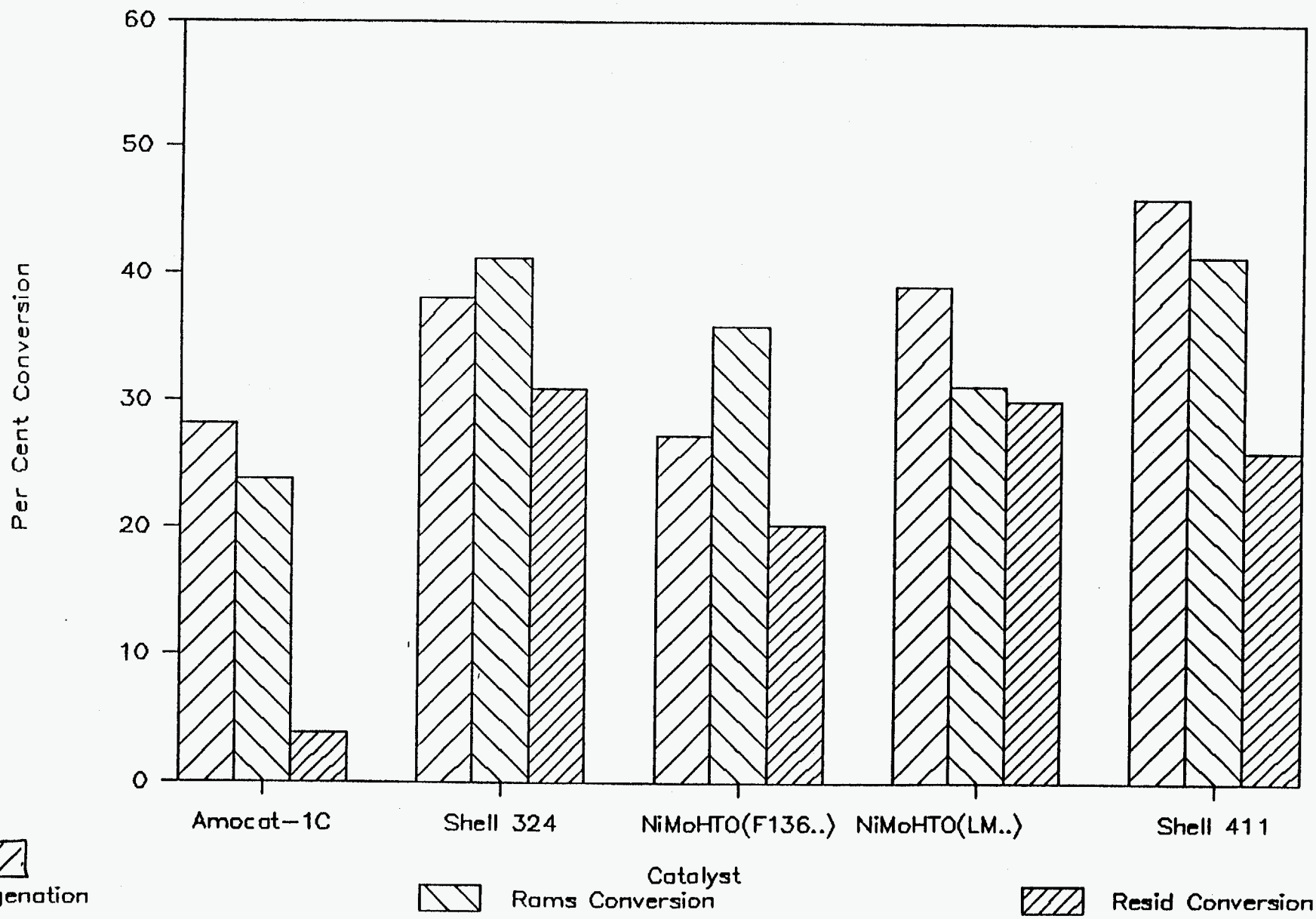
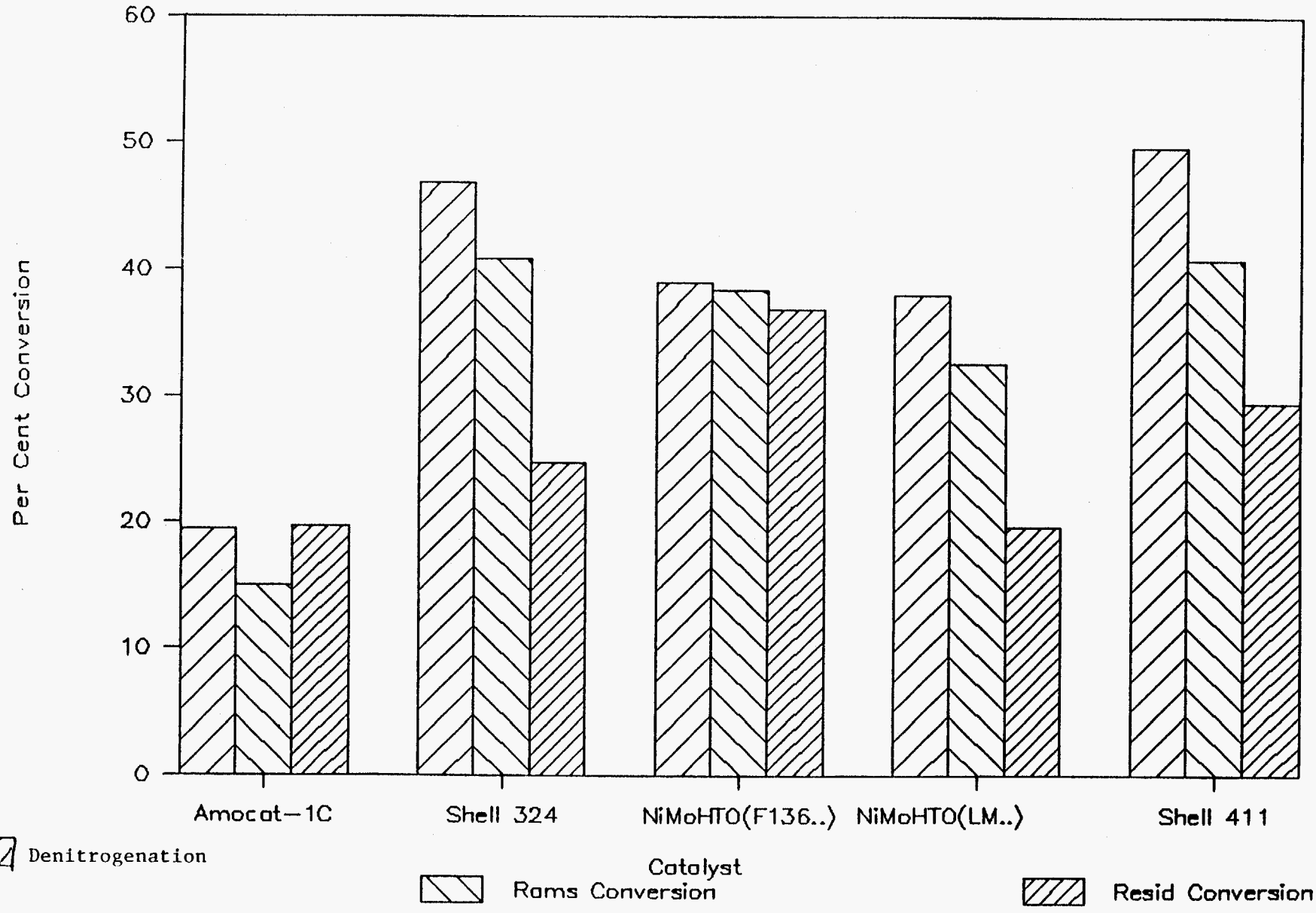


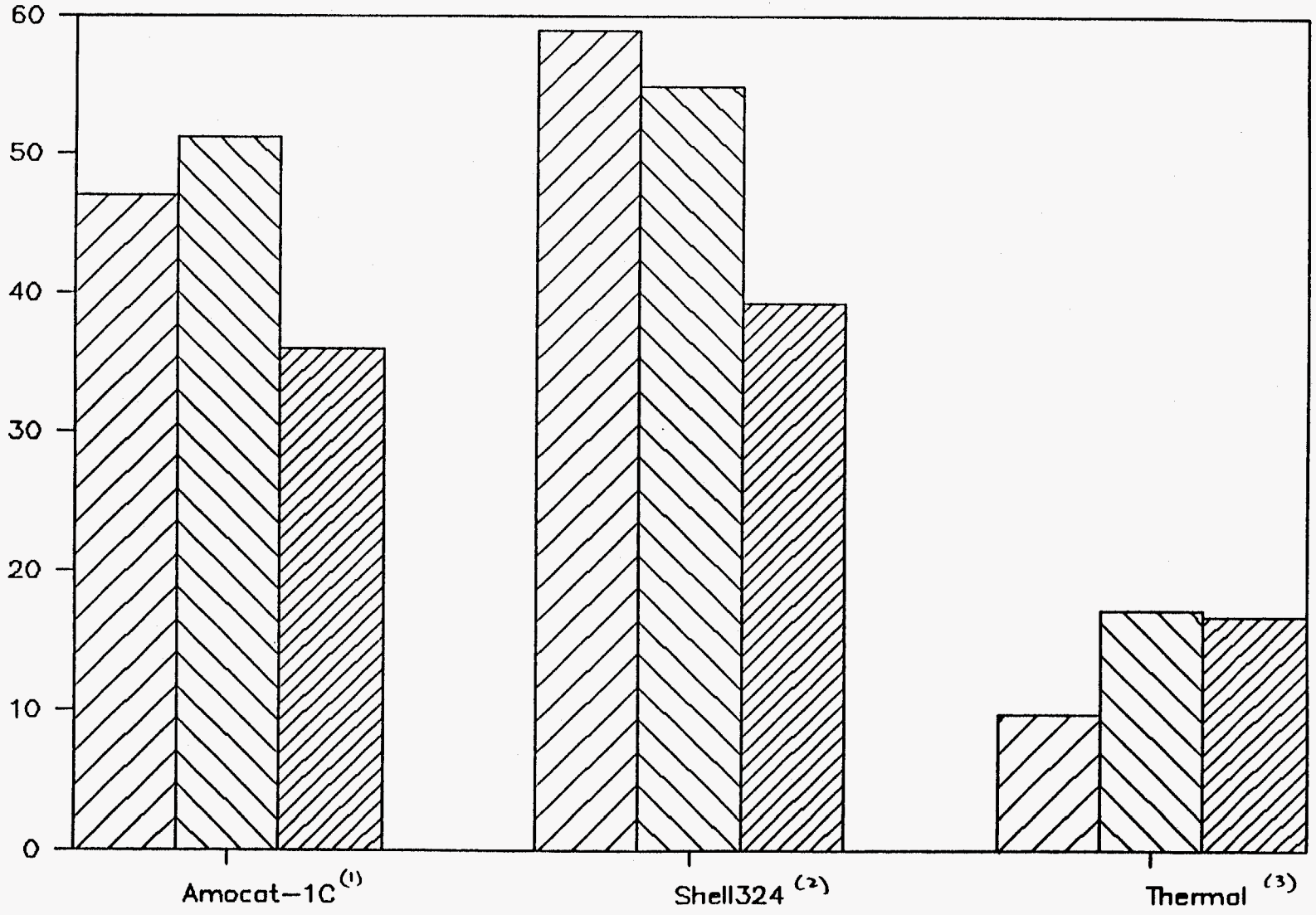
FIGURE 48

Conversions at Thirty Seven Days on Oil



F. RE 49

Conversions from Previous Runs



(1) Average of results from the first 5 runs. ~Day 14 on oil.

(2) Run 3A ~ Day 14 on oil.

(3) ~

TABLE 1

RESULTS OF EXPLORATORY MICROAUTOCLAVE RUNS
WITH INDIANA NO. 5 REFERENCE COAL

Run No.	119	125	121	123
Reaction Conditions:				
Time, Min	10	10	30	30
Temp, F	750	751	751	751
Charge:				
Coal(1)	2.0087	2.0382	5.0047	2.0068
V-1072(2)	16.0225	16.0285	10.4607	10.0427
Yields, Wt% MAF:				
Oil+Gas(3)	12.9	17.2	22.4	28.7
Asph	42.6	33.6	39.9	33.0
Preasph	27.6	33.1	23.3	20.7
THF Ins	16.8	16.1	14.4	17.7
TOL Sol	55.6	50.8	62.3	61.7
THF Sol	83.2	83.9	85.6	82.3

(1) The coal is Indiana No. 5, Old Ben Mine, obtained from Wilsonville by way of Conoco Coal Company.

(2) V-1072 is vacuum bottoms from Wilsonville Run 255A, Sample 84415.

(3) Hexane solubles.

TABLE 2

RESULTS OF 300 CC AUTOCLAVE RUNS WITH BURNING STAR IL NO. 6 COAL

Run No. (14052)	105	111	109	113	116
Coal	Hazen Research "Coarse"			Resource Engineering	
Charge:					
Coal	25.5016	25.1186	25.1208	25.0944	25.1966
Tetralin	49.7400	50.7400	50.7800	51.1600	50.1400
Reaction:					
Time, Min	0	10	60	60	60
Temp, F	750	754	755	753	826
Yields, % MAF:					
Oil+Gas	16.3	22.2	34.9	19.5	45.0
Asphaltenes	19.5	20.6	31.7	34.5	27.1
Preasphaltenes	37.9	31.3	20.4	11.6	5.1
THF Insoluble	26.3	25.9	12.9	34.4	22.8
TOL Soluble	35.8	42.8	66.7	54.0	72.1
THF Soluble	73.7	74.1	87.1	65.6	77.2

TABLE 3

RESULTS OF MICROAUTOCLAVE RUNS WITH MARTIN LAKE LIGNITE BENEFICIATED COALS[1]

Run No. (14176-)	62	99	21	64	66	101	103	39	105	107
Coal[2]	Fines	Fines	Coarse	SO2 Coarse	Over Flow	Over Flow	Over Flow	Under Flow	Under Flow	Under Flow
Yields										
Oil+Gas	62.1	58.7	48.0	43.0	46.8	45.4	42.3	44.5	48.9	46.7
Asph	18.0	23.9	24.3	22.5	23.8	31.1	23.7	20.5	25.8	22.5
Preasph	6.0	5.4	3.3	17.4	10.7	3.5	14.7	11.9	11.3	11.0
THF Ins	13.9	12.0	24.5	17.1	18.7	20.1	19.3	23.1	14.1	19.8
TOL Sol	80.1	82.6	72.3	65.5	70.6	76.5	66.0	65.0	74.7	69.2
THF Sol	86.1	88.0	75.5	82.9	81.3	79.9	80.7	76.9	85.9	80.2
Ash Balance Out/In	0.87	0.81	1.04	1.02	0.96	1.07	---	1.05	0.86	0.89

Notes: 1) Reaction Conditions: 750°F, 60 minutes, S/C=2/1.

2) Coals: Fines: -60 mesh
Coarse: 6x60 mesh
SO_2-Coarse: Coarse coal that was tested with sulfurous acid.
Overflow: SO_2-Coarse coal with a gravity below 1.35.
Underflow: SO_2-Coarse coal with a gravity above 1.35.

TABLE 4

RESULTS OF 300 CC AUTOCLAVE REFERENCE RUNS
MADE WITH BLACK THUNDER COAL

Run No.	64	67	25	199	82
NB No.	14252	14252	14252	14052	10250
Coal	Raw	Raw	Raw	Raw	Raw
Moisture, Wt%	27.20	27.20	27.98	27.98	27.66
Ash (MF), Wt%	7.16	7.16	7.15	7.15	6.37
Conditions of Liquefaction:					
Time, Min	10	10	10	10	10
Temp, F	751	752	812	825	828
Solvent/Coal	2/1	2/1	2/1	2/1	2/1
Yields, Wt%	31.5	11.8	47.5	49.9	44.5
MAF:	14.7	20.5	22.3	26.9	31.9
Oil+Gas	12.3	12.1	10.1	11.1	9.6
Asphaltenes	41.5	55.6	20.1	12.0	14.0
Preasphaltenes	46.2	32.2	69.8	76.8	76.4
THF Insoluble	58.5	44.4	79.9	88.0	86.0
TOL Soluble				-	
THF Soluble					

TABLE 5

RESULTS OF 300 CC AUTOCLAVE RUNS
WITH BLACK THUNDER COAL

Run No.	82	199	11	39	60	62	98
Conditions of Pretreatment:							
Method	None	None	Oven Dried[1]	Oven Dried	Air Blow	Air Blow	Age
Temp, F	--	--	210	210	Room	Room	Room
Time	--	--	16 Hr	16 Hr	7 Days	7 Days	16 Hr
Coal, Wt%:							
Moisture	28.0	28.0	7.1	7.1	5.9	5.9	19.8
Ash (MF)	6.4	7.1	7.1	7.1	6.5	6.5	7.1
Conditions of Liquefaction:							
Time, Min	10	10	10	10	10	10	10
Temp, F	828	825	832	828	825	832	827
Solvent/Coal	2/1	2/1	2/1	2/1	2/1	2/1	2/1
Yields, Wt% MAF:							
Oil+Gas	44.5	49.9	46.3	41.9	52.8	53.9	46.4
Asphaltenes	31.9	26.9	24.5	26.5	20.5	18.1	30.1
Preasphaltenes	9.6	11.1	11.6	10.5	11.3	12.3	9.3
THF Insoluble	14.0	12.0	17.6	21.1	15.4	15.8	14.1
TOL Soluble	76.4	76.8	70.8	68.4	73.2	71.9	76.5
THF Soluble	86.0	88.0	82.4	78.9	84.6	84.2	85.9

(1) Vacuum oven with a nitrogen sweep.

TABLE 6

LIQUEFACTION OF OXIDIZED BLACK THUNDER COAL
(ONCE-THROUGH YIELDS)

Coal Sample	Fresh, 385 Hr	Oxidized, 450 Hr
Conversion, Wt%	86.4	89.0
Yield, Wt% MAF Coal:		
C_1-C_3 Hydrocarbon	9.0	7.3
C_4-360F	7.9	9.3
360-650F	36.4	33.5
650-975F	22.3	16.0
975+F Resid	-3.5	10.6
Hydrogen Consumption, Wt% MAF	6.2	5.5

TABLE 7

Results of 300cc Autoclave Runs with Pretreated Martin Lake Lignite: Oven-Dried and Air-Blown

Run No.	Average[1]	186	184	14	145	149	191	89[2]	91[2]	101[2]
NB No.		14,052	14,052	14,252	14,052	14,052	14,052	14,252	14,252	14,252
Conditions of Pretreatment										
Method	Raw	Oven Dried	Oven Dried	Oven Dried	Air-Blow	Air-Blow	Air-Blow	Beaker	Beaker	Beaker
Temp, F		210	210	210	Room	Room	Room	Room	Room	Room
Time		16 hrs	16 hrs	16 hrs	7 days	7 days	7 days	16 hrs	16 hrs	16 hrs
Conditions of Liquefaction										
Time, Min.	10	10	10	10	10	10	10	10	10	10
Temp, F	825	815	818	825	822	827	827	829	829	827
Solvent/Coal	2/1	2/1	2/1	2/1	2/1	2/1	2/1	2/1	2/1	2/1
Yields										
Oil + Gas	57.0	43.9	45.4	46.9	43.4	46.6	54.5	56.6	54.6	46.9
Asphaltenes	15.7	17.5	17.3	15.5	16.1	15.2	13.0	15.3	13.4	21.7
Preasphaltenes	8.8	7.5	7.5	7.9	8.0	7.5	6.6	6.4	6.6	4.2
THF Ins.	18.5	31.1	29.8	29.6	32.4	30.7	25.9	21.7	25.5	27.2
TOL Sol.	72.7	61.4	62.8	62.5	59.6	61.8	67.5	71.9	68.0	68.6
THF Sol.	81.5	68.9	70.2	70.4	67.6	69.3	74.1	78.3	74.5	72.8
Coal, Wt%										
Moisture	--	0.0	0.0	0.0	6.9	6.9	5.6	18.5	19.5	24.7
Ash, (MF)	--	13.3	13.3	13.3	13.3	13.3	13.4	20.3	20.3	20.3

[1]Average of results of Runs 14,052-136 and -189 and 14,252-131.
[2]Compare these results to those of Run 14,252-82 of Table 4

TABLE 8

Results of 300 cc Autoclave Runs with Pretreated Martin Lake Lignite at Mild Liquefaction Conditions of 750°F and 10 Minutes

Run No.	42	38	48	53	40	57
12,417						
Conditions of Pretreatment [1]						
Method	Raw	Dried	Air-Blow	Warm-Air	Steamed	Azeo-trope
Temp, F	--	210	Room	140	220	405
Time	--	16 hrs	6 hrs	6 hrs	1.5 hrs	3.3 hrs
Coal						
Moisture, Wt%	32.1	0.0	12.5	6.7	16.3	0.0
Ash (MF) Wt%	11.3	10.9	11.1	11.1	11.4	11.2
Conditions of Liquefaction						
Time, Min.	10	10	10	10	10	10
Temp F	750	752	751	749	752	750
Solvent/Coal	2/1	2/1	2/1	2/1	2/1	3/1
Yields, Wt% MAF						
Oil + Gas	35.7	29.3	42.2	27.3	30.9	27.3
Asphaltenes	17.7	13.3	18.6	15.8	18.2	16.5
Preasphaltenes	16.0	11.0	10.2	6.5	13.5	5.6
THF Ins.	30.6	46.4	29.0	50.4	37.4	50.5
TOL Sol.	53.4	42.6	60.8	43.1	49.1	43.8
THF Sol.	69.4	53.6	71.0	49.6	62.6	49.5
Charge						
Coal	31.0593	30.7350	30.4063	30.3385	30.7756	21.0425
Dist	59.9200	61.2900	60.0300	60.1100	60.0900	60.2700

[1] Raw-as received
Dried-Lignite was dried in a vacuum oven with a nitrogen sweep.
Air-blown- lignite was fluidized in air.
Warm-air-air blown in a heated tube.
Steamed-steam blown for 1.5 hours, then nitrogen blown overnight at ambient temperature.
Azeotrope-heated in refluxing tetralin for about 3.3 hours, all of the water was recovered in an aqueous phase.

TABLE 9

RESULTS OF 300 CC AUTOCLAVE RUNS WITH VARIOUS MARTIN LAKE LIGNITE SAMPLES
AT LIQUEFACTION CONDITIONS OF 750F AND 60 MINUTES

Run No.	84	45	50	--	--	--	--	--	--
NB No.	12417	12417	12417						
Conditions of Pretreatment:									
Designation	Raw[1]	Dried[2]	Steamed[3]	FCL-127 (Raw)	Dried-127 Room, N_2[4]	Dried-127 Room, Air	Dried-127 Room, N_2 and Air	FCL-86, 1 Wilsonville	FCL-86,2 Wilsonville
Temp, F	--	210	220						
Time	--	16 Hr	1.5 Hr	--	5 Days	2 Days	2 Days Ea	Run 255 Feed	Run 255 Feed
Coal, Wt%:									
Moisture	30.9	0.0	16.3	20.6	7.3	17.4	9.6	16.1	10.8
Ash MF)	11.3	10.9	11.4	14.7	13.5	14.5	14.3	10.1	10.1
Conditions of Liquefaction:									
Time, Min	60	60	60	60	60	60	60	60	60
Temp, F	751	744	750	750	750	750	750	750	750
Solvent/Coal	2/1	2/1	2/1	6.7/1	6.7/1	6.7/1	6.7/1	6.7/1	6.7/1
Yields, Wt% MAF:									
Oil+Gas	46.8	37.1	50.8	59.6	54.9	57.7	49.7	58.3	54.8
Asphaltenes	22.2	17.8	15.0	10.1	14.2	9.1	16.1	3.8	5.4
Preasphaltenes	11.8	10.4	8.9	2.2	0.3	2.6	1.1	0.8	0.9
THF Insoluble	19.2	34.7	25.4	28.1	31.8	30.6	33.1	37.1	38.9
TOL Soluble	69.0	54.9	65.8	69.7	69.1	66.8	65.8	62.1	60.2
THF Soluble	80.8	65.3	74.6	71.9	68.2	69.4	66.9	62.9	61.1

(1) Raw--as received.
(2) Dried in a vacuum oven.
(3) Contacted with flowing steam.
(4) Placed in open container in a nitrogen glove box.

TABLE 10

LIQUEFACTION OF OXIDIZED MARTIN LAKE LIGNITE
(ONCE-THROUGH YIELDS)

Lignite Sample	Fresh, 500 Hr	Oxidized, 350 Hr
Conversion, Wt%	84.9	83.9
Yield, Wt% MAF Coal:		
$CO+CO_2$	3.5	6.0
C_1-C_3	11.3	12.3
Hydrocarbon:		
C_4-360F	12.6	14.4
360-650F	23.9	32.6
650-975F	8.9	-7.1
975+F Resid	10.4	15.4
Hydrogen Consumption, Wt% MAF	7.6	7.5

TABLE 11

COAL ANALYSIS

Coal	Illinois No. 6 Burning Star Bituminous	Black Thunder Subbituminous	Martin Lake Lignite
Proximate (As-Received Basis, Wt%):			
Moisture	3.7	27.7	29.9
Ash	9.1	4.8	9.4
Volatile	37.5	32.3	30.2
Fixed Carbon	49.7	35.2	30.5
Ultimate (Dry Basis, Wt%):			
Carbon	69.5	70.2	62.5
Hydrogen	4.6	4.9	4.4
Nitrogen	1.2	1.1	1.4
Sulfur	3.3	0.4	1.0
Ash	9.4	6.6	13.4
Oxygen (diff)	12.0	16.7	17.3

TABLE 12

Analyses of Beneficiated Il No. 6 Coal Samples

COAL	Combined Feed	Fines	Coarse	Overflow (Float)	Underflow (Sink)
PROXIMATE ANALYSES (As Received, wt%)					
Moisture	6.97	5.19	7.71	4.90	6.44
Ash	11.14	14.13	9.88	6.17	17.09
Volatile	35.02	33.50	35.66	37.84	32.47
Fixed C	46.87	47.18	46.75	51.09	44.00
	100.00	100.00	100.00	100.00	100.00
ULTIMATE ANALYSES (Dry Basis, wt%)					
Carbon	69.04	66.84	69.97	73.90	63.31
Hydrogen	4.65	4.40	4.76	5.15	4.34
Nitrogen	1.46	1.48	1.45	1.56	1.22
Sulfur	3.49	3.79	3.37	2.87	4.71
Ash	11.94	14.90	10.70	6.49	18.27
Oxygen (diff)	9.42	8.59	9.75	10.03	8.15
	100.00	100.00	100.00	100.00	100.00

TABLE 13

Analyses of Beneficiated Martin Lake Lignite Samples[1]

COAL	Combined Feed[2]	Fines	Coarse	SO_2 Treated Coarse	Overflow (Float)[3]	Underflow (Sink)[3]
PROXIMATE ANALYSES (Dry Basis), Wt%						
Ash	14.62	23.64	13.15	9.96	5.58	39.27
Volatile	42.52	37.72	43.30	43.17	45.83	35.93
Fixed C	42.86	38.64	43.55	46.87	48.59	24.80
	100.00	100.00	100.00	100.00	100.00	100.00
ULTIMATE ANALYSES (Dry Basis), Wt%						
Carbon	63.30	56.79	64.37	63.42	68.33	43.30
Hydrogen	4.53	3.96	4.62	4.34	4.94	3.20
Nitrogen	1.22	1.16	1.23	1.25	1.36	0.87
Sulfur	1.48	1.65	1.45	2.40	1.48	2.85
Ash	14.62	23.64	13.15	9.96	5.58	39.27
Oxygen (diff)	14.85	12.80	15.18	18.63	18.31	10.51
	100.00	100.00	100.00	100.00	100.00	100.00

Note: [1] Analyses by Commercial Testing and Engineering, Co.
[2] Combined coarse (10 x 60 mesh) and fines (-60 mesh).
[3] The overflow and underflow samples were recovered by heavy media separation of the SO_2 - treated coarse coal.

TABLE 14

ANALYSES OF SIZE BENEFICIATED SPRING CREEK COAL

Wt% Dry	Feed	Fines (-60 Mesh)	Coarse (8x60 Mesh)
C	71.76	71.10	71.92
H	5.27	4.89	5.36
N	1.09	0.87	1.15
S	0.36	0.41	0.35
O (diff.)	17.13	16.72	17.23
Ash	4.39	6.01	3.99
H/C Ratio	0.88	0.83	0.89
Ca/Al	--	1.43	1.65
Mg/Al	--	0.40	0.45
Na/Al	--	0.24	0.59
K/Al	--	0.04	0.01
Fe/Al	--	1.05	0.52
Ti/Al	--	0.07	0.09
Si/Al	--	1.28	0.75

TABLE 15

ANALYSES OF SO_2 AND DENSITY BENEFICIATED SPRING CREEK COAL

Wt% Dry	SO_2 Coarse Sink	SO_2 Coarse Float	SO_2 Coarse	Coarse (8x60 Mesh)
C	70.46	72.72	72.46	71.92
H	5.02	5.38	5.32	5.36
N	1.05	1.08	1.10	1.15
S	0.50	0.41	0.43	0.35
O (diff.)	17.13	17.13	16.90	17.23
Ash	5.84	3.28	3.79	3.99
H/C Ratio	0.85	0.89	0.88	0.89
Ca/Al	0.85	1.20	1.02	1.65
Mg/Al	0.25	0.25	0.21	0.45
Na/Al	0.03	--	0.07	0.59
K/Al	0.03	0.01	0.01	0.01
Fe/Al	1.07	0.81	0.77	0.52
Ti/Al	0.08	0.09	0.08	0.09
Si/Al	0.96	0.65	0.71	0.75

TABLE 16

SOLVENT ANALYSES

Wilsonville Run	257	258
Wilsonville Coal	Illinois No. 6 FSN-109	Black Thunder FSN-113
Elemental Analyses, Wt%		
C	89.26	89.54
H	8.83	8.28
N	0.57	0.80
S	0.08	0.05
O	1.26	1.33
Distillation, Wt%		
IBP-650°F	0.36	8.83
650-975°F	55.78	53.70
975+°F	43.83	37.46
650-935°F	52.94	50.34
935+°F	46.10	40.83
Solubility, Wt%		
THF Insolubles	0.12	0.09
Toluene Insolubles	1.07	1.31
Hexane Insolubles	7.96	15.33

TABLE 17

LIQUEFACTION OF DENSITY BENEFICIATED ILLINOIS NO. 6 COAL[m]

Coal Sample	Coarse	Float	Sink
Conversion, wt%[a]	93.3	94.6	92.6
Yield, wt% MAF coal			
C_1-C_3 Hydrocarbon	4.0	4.7	6.0
C_4-360°F	5.2	5.4	12.5
360-650°F	33.2	29.5	35.8
650-975°F	20.1	26.5	27.7
975+°F Resid	21.8	18.6	0.5
Hydrogen Consumption, %MAF	4.8	4.7	6.0

Notes: [m] Results from the following sample periods were used: 9 (coarse), 11-12 (sink), 14 (float), and 16 (float).
[a] Conversion, wt% MAF THF solubles.

TABLE 18

METALS IN UNCONVERTED COAL
(Weights Are Reported Relative To Aluminum)

Coal	Coarse	Float	Sink
Ca	0.33	0.14	0.39
Fe	2.07	1.58	2.73
Mg	0.08	0.08	0.08
Na	0.05	0.05	0.04
K	0.23	0.23	0.23
Ti	0.05	0.05	0.05
V	0.00	0.00	0.00
Zn	0.01	0.01	0.02
Mn	0.00	0.00	0.01
Cr	0.01	0.01	0.01
Ni	0.01	0.01	0.01

TABLE 19

LIQUEFACTION OF BENEFICIATED SAMPLES OF ILLINOIS NUMBER 6 COAL, ELEMENTAL ANALYSES

BENEFICIATED SAMPLE	COARSE					SINK		FLOAT			SOLVENT CORRECTION		COARSE	
SAMPLE PERIOD	2	3	4	5	9	11	12	14	15	16	18	19	21	22
DISTILLATE (360-650 F, WT%)														
C			87.5		87.5		87			86.9		86.8	87.7	
H			11.2		11.1		11.2			11		11.4	10.9	
S			0.02		0.04		0.06			0.09		0.01	0.08	
O			0.82		1.45		1.22			1.58		1.70	1.41	
N			0.22		0.22		0.18			0.28		0.14	0.28	
TOTAL			99.8		100		99.6			99.8		100	100	
VACUUM DISTILLATE (650-975 F, WT%)												[c]		
C			89.8		89.6		89.4			89.6		89.9	89.1	
H			9.65		9.67		9.70			9.49		8.71	9.68	
S			0.01		0.02		0.03			0.05		0.03	0.04	
O			0.41		0.53		0.53			0.63		0.90	0.55	
N			0.66		0.36		0.33			0.41		0.44	0.35	
TOTAL			101		100		100			100		100	99.7	
RESID + UNCONVERTED COAL (975+ F, WT%)												[c]		
C			77.9		80.2		71.3			83.3		89.9	84.1	
H			6.37		6.60		5.57			6.27		8.71	6.96	
S			0.87		1.07		2.19			0.75		0.03	0.66	
O (DIFFERENCE)			1.14		1.30		1.36			0.77		0.87	-.12	
N			0.58		0.91		0.82			1.08		0.44	0.94	
TOTAL			98.9		98.7		98.6			99.2		99.1	100	
THF INSOLUBLES	15.5	15.5	20.4	16.8	16.4	30.5	27.7	16.7	14.4	14.4	0.04	0.04	12	12
RESID THF INSOLUBLES (WT%)														
ASH	69.7	69.7	64.4	64.9	60.4	69	67.8	52.3	54.4	54.4	50	50	62.2	62.2
K			10E3		10E3		10E3			9700			10E3	
MG			3620		3470		3460			3360			3480	
AL			45E3		43E3		44E3			43E3			43E3	
CA			15E3		14E3		17E3			5900			12E3	
FE			97E3		89E3		12E4			68E3			80E3	
MO			92		84		86			84			77	
NA			2120		2010		1580			2250			2010	
NI			232		207		231			207			184	
TI			2020		1950		1900			2330			1790	
V			155		146		161			171			146	

a) Results are for analyses of product from coal plus recycle solvent.
b) The naphtha (IBP-360 F) fraction was not analyzed because the it contained tetrahydrofuran.
c) Analyses are for combined 650-975+F fraction (unable to distill this material).

TABLE 20

Analyses of Spent Catalyst Samples
from the Illinois No. 6 Run

Catalyst	Stage 1	Stage 2	Fresh
Elemental Analyses, wt%			
Primary Metals:			
Mo	6.60	8.00	9.10
Ni	1.35	1.63	2.22
Al	26.90	32.40	35.40
Si	1.07	1.13	1.39
Deposits:			
C	23.36	15.46	--
H	1.51	1.02	--
S	5.05	5.94	.20
Ti	2.72	.85	.00
Fe	.42	.24	.02
Na	.14	.21	.08
Mg	.13	.03	.00
V	.10	.01	.00
Ca	.07	.02	.00
Pore Properties:			
Volume <1200 A dia. cc/g	.12	.31	.59
Volume >1200 A dia. cc/g	.07	.07	.00
BET Surface Area m2/g	62	132	200

TABLE 21

METALS IN MARTIN LAKE LIGNITE SAMPLES
(WEIGHTS ARE REPORTED RELATIVE TO ALUMINUM)

	Feed	Fines	Coarse	SO_2 Treated		
				Coarse	Float	Sink
Ca	1.903	0.659	2.105	0.113	0.258	0.163
Mg	0.385	0.270	0.404	0.021	0.054	0.114
Na	0.094	0.089	0.095	0.037	0.042	0.035
K	0.057	0.191	0.035	0.032	0.021	0.047
Fe	1.644	1.505	1.667	1.025	1.058	7.120*
Ti	0.091	0.078	0.093	0.096	0.102	0.320
Si	1.782	3.352	1.526	1.747	1.808	5.760

*Contaminated with magnetite

TABLE 22

SO_2-TREATED MARTIN LAKE LIGNITE

Lignite Sample	Coarse	SO_2-Treated Feed
Conversion, Wt%	84.7	91.3
Yield, Wt% MAF Lignite:		
C_1-C_3 Hydrocarbon	7.3	6.2
C_4-360F	13.2	14.1
360-650F	33.5	33.1
650-975F	24.7	9.6
975+F	-6.3	12.0
Hydrogen Consumption, Wt% MAF	7.4	7.4

Notes

(1) Results from the following sample periods were used: 4-6 (coarse), 8-10 (SO_2-treated), and 15 (solvent).

(2) Results from the fines fraction are not reported because the feed rate was low due to mechanical difficulties.

TABLE 23

COMBINED SO_2 TREATMENT AND DENSITY BENEFICIATION

Lignite Sample	SO_2-Treated		
	Feed	Float	Sink
Conversion, Wt%	90.4	88.3	82.1
Yield, Wt% MAF Lignite:			
C_1-C_3 Hydrocarbon	7.2	8.8	5.9
C_4-360F	10.8	9.1	11.1
360-650F	33.7	42.7	45.9
650-975F	17.7	23.8	24.8
975+F Resid	7.5	-8.5	-30.5
Hydrogen Consumption, Wt% MAF	7.2	7.2	9.2

Note: Results from the following sample periods were used: 7-8 (SO_2-treated feed), 10-12 (SO_2-treated float), 4-5 (SO_2-treated sink), and 15 (solvent).

TABLE 24

Liquefaction of Size Beneficiated and SO2/Water Washed Lignite: Elemental analyses

BENEFICIATED SAMPLE	COARSE					SO2 WASH			FINES		SOLVENT CORRECTION[a]
SAMPLE PERIOD	2	3	4	5	6	8	9	10	12	13	15
DISTILLED PRODUCT ANALYSES (WT%)											
DISTILLATE (360-650 F, WT%)											
C	.	.	.	88.3	.	.	87.5	.	.	88.6	88
H	.	.	.	11.3	.	.	11.3	.	.	11	11
S	.	.	.	0.01	.	.	0.01	.	.	0.00	0.00
O	.	.	.	0.51	.	.	1.05	.	.	0.32	0.52
N	.	.	.	0.23	.	.	0.31	.	.	0.20	0.27
TOTAL	.	.	.	100	.	.	100	.	.	100	99.8
VACUUM DISTILLATE (650-975 F, WT%)											
C	.	.	.	89.6	.	.	89.2	.	.	89.4	89.3
H	.	.	.	9.75	.	.	9.77	.	.	9.89	9.63
S	.	.	.	0.01	.	.	0.02	.	.	0.03	0.01
O	.	.	.	0.30	.	.	0.40	.	.	0.22	0.36
N	.	.	.	0.35	.	.	0.47	.	.	0.45	0.57
TOTAL	.	.	.	100	.	.	99.9	.	.	100	99.9
RESID + UNCONV COAL (975+ F, WT%)											
C	.	.	.	79.1	.	.	83.7	.	.	70.4	90.5
H	.	.	.	6.13	.	.	6.55	.	.	5.36	6.99
S	.	.	.	0.75	.	.	0.52	.	.	0.81	0.07
O (DIFFERENCE)	.	.	.	3.44	.	.	1.35	.	.	4.22	.
N	.	.	.	0.92	.	.	0.88	.	.	0.82	0.91
TOTAL	.	.	.	96.6	.	.	98.6	.	.	95.8	.
THF INSOLUBLES	.	22.6	24	23	24.3	12.8	14.2	15	25.3	30.6	0.93
THF INSOLUBLES (WT%)											
ASH	.	39.7	40.2	41.9	41.4	49.7	49.6	48.3	57.5	60	.
K	.	.	.	720	.	.	1030	.	.	3350	.
MG	.	.	.	7800	.	.	1690	.	.	6400	.
AL	.	.	.	9300	.	.	49E3	.	.	33E3	.
CA	.	.	.	48E3	.	.	9500	.	.	38E3	.
FE	.	.	.	43E3	.	.	56E3	.	.	42E3	.
MO	.	.	.	127	.	.	44	.	.	6.20	.
NA	.	.	.	1930	.	.	1130	.	.	1540	.
NI	.	.	.	134	.	.	185	.	.	127	.
TI	.	.	.	2380	.	.	2870	.	.	2480	.
V	.	.	.	89	.	.	111	.	.	89	.
SI	.	.	.	10E4	.	.	73E3	.	.	12E4	.

a) Results are from analyses of product from coal plus recycle solvent.
b) The naphtha (IBP-360 F) fraction was not analyzed because it contained large amounts of tetrahydrofuran.

TABLE 25

Liquefaction of SO2-Water Washed, Density Beneficiated Lignite: Elemental Analyses

BENEFICIATED SAMPLE	SO2 SINK				SO2 COARSE		SO2 FLOAT			SOLVENT CORRECTION[a]
SAMPLE PERIOD	2	3	4	5	7	8	10	11	12	19
DISTILLATE (360-650 F, WT%)										
C	.	.	.	88.1	87.5	.	.	.	87.7	88.3
H	.	.	.	11.1	11.1	.	.	.	11	10.8
S	.	.	.	0.00	0.01	.	.	.	0.02	0.01
O	.	.	.	0.82	1.42	.	.	.	1.37	0.86
N	.	.	.	0.31	0.35	.	.	.	0.34	0.34
TOTAL	.	.	.	100	100	.	.	.	100	100
VACUUM DISTILLATE (650-975 F, WT%)										
C	.	.	.	90	89.5	.	.	.	89.9	89.9
H	.	.	.	9.92	9.71	.	.	.	9.55	9.67
S	.	.	.	0.01	0.01	.	.	.	0.01	0.02
O	.	.	.	0.49	0.58	.	.	.	0.56	0.55
N	.	.	.	0.35	0.38	.	.	.	0.38	0.38
TOTAL	.	.	.	101	100	.	.	.	100	100
RESID + UNCONV COAL (975+ F, WT%)										
C	.	.	.	83.9	80.1	.	.	.	84.5	81.8
H	.	.	.	6.60	6.10	.	.	.	6.09	6.14
S	.	.	.	0.67	1.41	.	.	.	0.74	1.03
O (DIFFERENCE)	.	.	.	3.18	2.87	.	.	.	1.86	2.76
N	.	.	.	0.72	0.90	.	.	.	1.03	1.00
TOTAL	.	.	.	96.8	97.1	.	.	.	98.1	97.2
THF INSOLUBLES.....	.	.	22.4	22.4	14.8	16.3	12.9	.	12.9	12.7
THF INSOLUBLES (WT%)										
ASH	.	.	66	64.3	58	63.4	43.4	.	44.8	57.1
K	.	.	.	1990	1370	.	.	.	1220	1930
MG	.	.	.	3930	1550	.	.	.	1930	3120
AL	.	.	.	41E3	35E3	.	.	.	39E3	40E3
CA	.	.	.	9700	5700	.	.	.	11E3	10E3
FE	.	.	.	18E4	15E4	.	.	.	85E3	13E4
MO	.	.	.	70	57	.	.	.	86	83
NA	.	.	.	1190	890	.	.	.	1140	1340
NI	.	.	.	242	189	.	.	.	277	347
TI	.	.	.	8600	5800	.	.	.	5100	7100
V	.	.	.	700	640	.	.	.	430	600
SI	.	.	.	13E4	11E4	.	.	.	86E3	11E4

a) Results are from analyses of product from coal plus recycle solvent.
b) The naphtha (IBP-360 F) fraction was not analyzed because it contained large amounts of tetrahydrofuran. Yields of THF insolubles were estimated to improve ash balances when solids were retained in the distillation flask.

TABLE 26

HYDROGEN-TO-CARBON RATIOS FOR THE TWO LIGNITE RUNS

Run	51-216		51-217	
Feed	SO_2-Treated	Solvent	SO_2-Treated	Solvent
H/C Atomic Ratio				
360-650F	1.55	1.50	1.52	1.47
650-975F	1.31	1.29	1.30	1.29
975+F	0.94	0.93	0.91	0.90

TABLE 27

SPENT CATALYST ANALYSES: SO_2-TREATED
AND DENSITY BENEFICIATED MARTIN LAKE LIGNITE

Run	51-216		51-217		
Catalyst	Stage 1	Stage 2	Stage 1	Stage 2	Fresh
Elemental Analyses, Wt%					
Primary Metals:					
Mo	6.80	7.50	6.50	7.20	9.10
Ni	1.51	1.62	1.25	1.42	2.22
Al	28.1	29.0	22.8	25.3	35.40
Si	0.71	0.76	1.04	1.21	1.39
Deposits:					
C	15.18	14.14	31.03	23.91	--
Lt	1.14	1.16	1.86	1.64	--
S	5.83	5.76	5.35	7.68	0.20
Ti	0.67	0.18	0.43	0.33	0.00
Fe	0.89	0.15	0.87	0.73	0.02
Na	0.28	0.22	0.14	0.14	0.08
Mg	0.10	0.05	0.04	0.02	.00
Ca	0.01	0.01	0.00	0.00	.00
Cr	0.18	0.10	0.08	0.05	.00

Notes

(1) All samples are AMOCAT™ 1C catalyst, 1/2 inch diameter, manufactured by Ketjen.

(2) Run 51-216 used coarse, SO_2-treated feed, and fine fractions. Run 51-217 used SO_2-treated sink, SO_2-treated feed, and SO_2-treated float fractions.

TABLE 28

SPENT CATALYST PORE PROPERTIES: SO_2-TREATED
AND DENSITY BENEFICIATED MARTIN LAKE LIGNITE

Run	51-216		51-217		
Catalyst	Stage 1	Stage 2	Stage 1	Stage 2	Fresh
Volume <1200A dia., cc/g	0.29	0.30	0.07	0.12	0.59
Volume >1200A dia., cc/g	0.07	0.07	0.07	0.08	0.00
BET Surface Area, m^2/g	137	146	39	57	200

Notes

(1) All samples are AMOCAT™ 1C catalyst, 1/2 inch diameter, manufactured by Ketjen.

(2) Run 51-216 used coarse, SO_2-treated feed, and fine fractions. Run 51-217 used SO_2-treated sink, SO_2-treated feed, and SO_2-treated float fractions.

TABLE 29

The Results of the Pretreatment Runs with Martin Lake Lignite

Run No.	136	171 (14052)	178 (14052)	168 (14052)	16 (14252)
Coal	Raw	Pretreat	Pretreat	Pretreat	Pretreat
Time, Min.		30	30	30	30
Temp, F		505	552	604	607
Reaction Conditions					
Time, Min.	10	10	10	10	10
Temp, F	825	826	825	826	825
Yields					
Oil + Gas	53.9	54.8	61.5	47.8	59.7
Asphaltenes	16.7	17.3	16.4	28.9	18.2
Preasphaltenes	11.7	9.5	6.5	8.0	5.9
THF Insolubles	17.7	18.3	15.6	15.3	16.2
TOL Solubles	70.6	72.1	77.9	76.6	77.9
THF Solubles	82.3	81.7	84.4	84.7	83.8
Charge					
Coal	25.1103	20.4186	20.4102	20.3569	20.0651
Tetralin	49.96	41.11	41.52	40.70	40.04
Extraction Results					
Insolubles, g					
THF					
Tol	5.0574	4.1906	3.8520	3.8119	3.8607
Hex	6.8421	5.3726	4.6571	4.8012	4.5795
	2.5466	2.1482	2.0319	3.5677	2.2179

TABLE 30

Presoaking Run Results with Black Thunder Coal
(Liquefaction at 750°F/10 min)

Run No. (NB No.)	64 14,252	67 14,252	68 14,252
Conditions of pretreatment run: 50 psi nitrogen (cold)			
Time, Min. Temp. F	None	None	30 607
Reaction Conditions			
Time, Min Temp. F Gas Sample	10 751 No	10 752 No	10 753 No
Yields			
Oil + Gas	31.5	24.3	27.7
Asphaltenes	14.7	20.5	17.0
Preasphaltenes	12.3	12.1	12.2
THF Insolubles	41.5	43.1	43.1
TOL Solubles	46.2	44.7	44.6
THF Solubles	58.5	56.9	56.9
Charge, g Coal Tetralin	 25.1756 50.7687	 25.1566 52.2067	 25.2459 50.3750
Results			
Insolubles, g THF Tol Hex	 8.3783 10.4640 2.4982	 8.6418 10.7063 3.4770	 8.6756 10.7614 2.8985

TABLE 31

Presoaking Run Results with Black Thunder Coal
(Liquefaction at 810°F/10 min)

Run No. NB No.	25 14,252	22 14,252
Conditions of pretreatment run: 50 psi nitrogen (cold)		
Time, Min Temp, F	None	10 605
Conditions of liquefaction run: 500 psi hydrogen (cold)		
Time, Min Temp, F	10 812.2	10 807
Yields		
Oil + Gas	47.5	49.6
Asphaltenes	22.3	22.8
Preasphaltenes	10.1	12.2
THF Insolubles	20.1	15.4
TOL Solubles	69.8	72.4
THF Solubles	79.9	84.6
Charge, g Coal Tetralin	 20.0516 40.2500	 20.0570 40.5200
Extraction Results Insolubles, g THF Tol Hex	 3.7311 5.0838 2.9879	 3.1020 4.7378 3.0614

TABLE 32

Presoaking Run Results with Black Thunder Coal
(Liquefaction at 825°F/10 min)

Run No. NB no.	199 14,052	19 14,252	196 14,052	193 14,052
Conditions of pretreatment run: 50 psi nitrogen (cold)				
Time, Min Temp, F Gas Sample	none	30 404 Yes	30 503 Yes	30 604 Yes
Conditions of liquefaction run: 500 psi hydrogen (cold)				
Time, Min Temp, F Gas Sample	10 825.2 yes	10 828 yes	10 826.7 yes	10 825.4 yes
Yields				
Oil + Gas	49.9	53.1	56.3	50.2
Asphaltenes	26.9	23.1	21.5	25.0
Preasphaltenes	11.1	9.2	8.9	11.3
THF Insolubles	12.0	14.6	13.2	13.5
TOL Solubles	76.8	76.2	77.9	75.2
THF Solubles	88.0	85.4	86.8	86.5
Charge, g Coal Tetralin	 20.0974 40.2900	 20.0937 40.1700	 20.0948 40.1700	 20.1955 40.0100
Results				
Insolubles, g THF Tol Hex	 2.6508 4.1479 3.6181	 2.9903 4.2166 3.1018	 2.8079 4.0060 2.8952	 2.8645 4.3934 3.3716

TABLE 33

Results of GC Fixed Gases Analyses: Martin Lake Lignite Runs

Run No. 14052	170	177	164	167
Reactants, g				
Lignite	20.42	20.41	20.24	20.36
Tetralin	41.11	41.52	40.41	40.70
Time, Min.	30	30	30	30
Temp, F	505	552	604	604
Gas Volume, cc	3706.8	5253.8	6964.0	8113.9
at mm Hg	749.7	741.6	749.7	745.0
Conc. Mol%				
N_2	90.69	95.36	96.32	93.76
CO	0.22	0.00	0.00	0.44
CO_2	4.06	2.54	2.92	6.13
CH_4	0.00	0.00	0.05	0.18
H_2	5.03	ND	0.04	0.09
Grams CO_2	0.27	0.24	0.37	0.89
CO_2 as % MAF Coal	2.18	1.92	2.98	7.20

TABLE 34

Results of GC Fixed Gas Analyses: Black Thunder Coal Presoaking Runs

Run No. 14052	199	19	196	193
Reactants, g				
Coal Tetralin	20.10 40.29	20.04 40.17	20.09 40.17	20.20 40.01
Gas Analyses From Pretreatment Run				
Conditions of Pretreatment Run				
Time, Min Temp, F	none	30 404	30 503	30 604
Gas Volume, cc at mm Hg		2355.9 731.5	3368.3 746.5	3283.4 729.5
Conc. Mol% CO CO_2 CH_4 Grams CO_2 CO_2 as % MAF Coal		 0.10 2.44 ---- 0.10 0.75	 0.12 2.06 0.00 0.12 0.93	 0.32 3.07 0.15 0.18 1.31
Gas Analyses from Liquefaction Run				
Conditions of liquefaction run				
Time, Min Temp, F	10 825	10 828	10 827	10 825
Gas Volume, cc at mm Hg	8015.7 746.3	6338.4 726.6	9443.7 746.5	8284.0 746.3
Conc. Mol% CO CO_2 CH_4 H_2 Grams CO_2 CO_2 as % MAF Coal	 0.69 5.11 2.29 0.73 5.46	 0.74 4.02 2.47 79.60 0.44 3.32	 0.79 4.01 3.04 86.55 0.68 5.05	 0.60 2.82 2.12 86.95 0.42 3.10

TABLE 35

Aqueous Pretreatment Results with Martin Lake Lignite

Run No.	136 (14052)	180 (14052)
Conditions of pretreatment run: 50 psi nitrogen (Cold)		
Time, Min Temp, F	none	30 601
Conditions of liquefaction run: 500 psi hydrogen (cold)		
Time, Min Temp, F	10 825	10 826
Yields		
Oil + Gas	53.9	49.3
Asphaltenes	16.7	22.7
Preasphaltenes	11.7	8.2
THS Insolubles	17.7	19.8
TOL Solubles	70.6	72.0
THF Solubles	82.3	80.2
Charge, g Coal Tetralin Dist H_2O Panasol	 25.1103 49.9600	 20.2250 40.4439 5.0496
Added charge for the liquefaction run		
Tetralin		41.17
Results		
Insolubles g THF Tol Hex	 5.0574 6.8421 2.5466	 4.3351 5.3398 2.7817

TABLE 36

Aqueous Pretreatment Results with Black Thunder Coal

Run No. (NB No.)	199 14052	1 14252	8 14252
Conditions of pretreatment run: 50 psi nitrogen (cold)			
Time, Min Temp, F	none	30 601	30 602
Conditions of liquefaction run: 500 psi hydrogen (cold)			
Time, Min Temp, F	10 825.2	0 818	10 826
Yields			
Oil + Gas	49.9	43.4	45.7
Asphaltenes	26.9	21.7	22.4
Preasphaltenes	11.1	14.3	11.3
THF Insolubles	12.0	20.6	20.6
TOL Solubles	76.8	65.1	68.1
THF Solubles	88.0	79.4	79.4
Charge, g			
Coal	20.0974	20.0821	20.1510
Tetralin	40.2900		
Dist H_2O		40.4873	39.955
Panasol		5.0299	5.0168
Added charge for following liquefaction runs			
Coal		19.8769	
Tetralin		40.75	40.3291
Results			
Insolubles, g			
THF	2.6508	3.7596	3.8078
Tol	4.1479	5.6620	5.3310
Hex	3.6181	2.8865	3.0233

TABLE 37

Results of GC Fixed Gases Analyses:
Aqueous Pretreatment of Martin Lake Lignite

Run No.14,052	175	173	155	158	161	180
Reactants, G						
Lignite Water Panasol	20.15 ----- 40.09	20.39 40.40 -----	20.20 39.76 5.15	20.09 40.26 5.07	20.15 40.56 5.29	20.23 40.44 5.05
Time, Min. Temp. F	30 608	30 601	30 503	30 601	60 601	30 600
Gas Volume at mm Hg	8,225.8 746.5	3,513.1 759.3	3,698.0 745.7	4,834.0 741.9	4,384.0 751.1	2,901.9 749.8
Conc. Mol%						
N_2	-----	89.34	89.17	86.22	91.49	86.77
CO	0.52	0.22	0.00	0.15	0.00	0.45
CO_2	4.60	11.60	4.32	8.83	7.38	12.57
CH_4	0.22	0.24	0.00	0.14	0.12	0.21
H_2	-----	-----	-----	-----	0.19	-----
Grams CO_2	0.68	0.74	0.29	0.76	0.58	0.66
CO_2 as %MAF Coal	5.54	6.00	2.33	6.23	4.77	5.35

TABLE 38

Results of GC Fixed Gases Analyses: Aqueous Pretreatment of Black Thunder Coal

Run No. 14,052	199	1	8
Reactants, g			
Coal	20.10	20.08	20.15
Water	-----	40.49	39.96
Tetralin	40.29	-----	-----
Panasol	-----	5.03	5.02
Gas Analysis from Pretreatment Run Conditions of Pretreatment Run			
Time, Min.	none	30	30
Temp. F		601	602
Gas Volume, cc at mm Hg		3,165.1 740.7	None
Conc. Mol%			
N_2		90.56	
CO		0.16	
CO_2		6.71	
CH_4		0.21	
O_2		0.32	
H_2			
Grams CO_2*		0.38	
CO_2 as % MAF Coal		2.81	
Gas Analysis from Liquefaction Run Conditions of liquefaction run			
Time, Min.	10	0	10
Temp. F	825.2	818	826
Added charge for the liquefaction run			
Coal		19.8769	40.33
Tetralin		40.75	-----
Gas Volume, cc at mm Hg	8,015.7 746.25	none -----	6,078.4 743.5
Conc. Mol%			
N_2	11.49		6.45
CO	0.69		0.50
CO_2	5.11		2.66
CH_4	2.29		2.56
O_2	0.50		0.32
H_2			
Grams CO_2	0.73		0.29
CO_2 as % MAF Coal	5.46		2.14

TABLE 39

Presoaking Results with Black Thunder Coal and Molybdenum Octoate*

Run No. NB No.	199 14052	80 14252	71 14252	74 14252	77 14252
Conditions of pretreatment run: 50 psi nitrogen (cold)					
Time, Min Temp. F	none	none	30 607	30 601	30 602
Conditions of liquefaction run: 500 psi hydrogen (cold)					
Time, Min Temp. F	10 825.2	10 827	10 823	10 831	10 828
Yields					
Oil + Gas	49.9	55.8	52.0	44.2	48.5
Asphaltenes	26.9	21.5	25.3	21.3	24.0
Preasphaltenes	11.1	3.7	9.7	8.7	2.7
THF Insolubles	12.0	19.0	13.0	25.9	24.7
TOL Solubles	76.8	77.3	77.3	65.5	72.5
THF Solubles	88.0	81.0	87.0	74.1	75.3
Charge, g					
Coal	20.0974	25.0839	20.6211	20.8109	25.1153
Tetralin	40.2900	50.6004	40.4439	----	----
Dist H_2O	----	----	----	40.2223	50.3629
Catalyst	----	1.2644	1.0087	1.0850	1.2511
Added charge for following liquefaction funs					
Coal				12.1366	18.0434
Tetralin				35.4683	40.3362
Results					
Insolubles, g					
THF	2.6508	4.5283	2.8915	3.6259	5.3482
Tol	4.1479	5.1610	4.2375	4.5234	5.6639
Hex	3.6181	3.6441	3.5286	2.2005	2.7686

* Molybdenum Octoate (8 wt% Mo)

TABLE 40

Presoaking Results with Black Thunder Coal and $FeSO_4$

Run No. NB No.	199 14052	117 14252	125 14252	119 14252	127 14252
Conditions of pretreatment run: 50 psi nitrogen (cold)					
Time, Min Temp. F	none	none	none	30 205	30 204
Conditions of liquefaction run: 500 psi hydrogen (cold)					
Time, Min Temp. F	10 825.2	10 827.6	10 827	10 826.3	10 827
Yields					
Oil + Gas	49.9	----	53.5	----	47.2
Asphaltenes	26.9	----	24.8	----	27.3
Preasphaltenes	11.1	8.0	7.7	8.9	10.0
THF Insolubles	12.0	17.1	14.0	16.1	15.5
TOL Solubles	76.8	75.0	78.3	75.0	74.5
THF Solubles	88.0	82.9	86.0	83.9	84.5
Charge, g Coal Tetralin Catalyst	 20.0974 40.2900	 25.0206 50.7195 0.2532	 25.4080 50.5168 0.2542	 25.2451 50.2021 0.2561	 25.3911 50.0515 0.2751
Results					
Insolubles, g THF Tol Hex	 2.6508 4.1479 3.6181	 4.3368 5.7324 ----	 3.8600 5.2294 4.4007	 4.1961 5.7727 ----	 4.1158 5.8936 4.8517

TABLE 41

Results of the Caustic Pretreatment Runs

Run No.	103	104	107	108	51	56	112
Pretreatment Conditions							
Caustic, wt% Temp. F Time, Min	1 212 5	1 211 5	1 210 30	1 209 30	5 206 30	5 406 30	5 410 30
Charge, g							
Aqueous	49.816	50.060	50.082	50.170	50.712	50.010	50.914
Coal	24.988	25.112	25.308	25.343	25.090	25.165	25.350
Organic	16.983	17.068	17.201	17.225	17.053	17.104	17.229
Ash	1.208	1.214	1.223	1.225	1.213	1.216	1.225
Products, g							
Solids	21.300	21.910	20.400[1]	19.420	27.500	17.970	16.830
Total (wet) Organics	16.822	17.143	16.548	14.747	12.860	11.918	12.266
Ash	1.528	1.342	1.418	1.221	1.833	1.915	2.109
Filtrate, g							
Total	65.0	460.0	349.0	200.0	1200.0	755.0	625.0
Organics	0.309	0.633	0.393	0.550	6.000	4.813	4.922
Carbonate	0.048	0.170	0.259	0.148	0.889	0.559	0.694
Result Summary, as %							
Dissolved Coal	1.8	3.7	2.3	3.2	35.2	28.1	28.6
Organics Balance	101.2	105.1	100.0	89.7	115.8	101.1	103.8
Coal Ash Balance	126.5	110.6	115.9	99.7	151.1	157.4	172.1

Notes: 1. Estimated for 100% organic material balance.

TABLE 42

Analyses of Pretreated Black Thunder Coals

Pretreatment				
Agent	none	Water	1% NaOH	5% Acetic
Temp. F	----	500	200	400
Time, Min.	----	30	30	30
Proximate, wt%				
Moisture	23.60	2.14	13.26	24.13
Ash	5.13	6.06	6.78	3.14
Ultimate, wt% dry				
Carbon	69.60	69.57	70.34	71.83
Hydrogen	5.01	4.92	4.53	4.96
Nitrogen	1.07	0.97	0.84	0.79
Oxygen (diff)	17.14	17.93	16.00	17.56
Sulfur	0.46	0.42	0.47	0.45
Ash	6.72	6.19	7.82	4.41
	100.00	100.00	100.00	100.00
H/C Ratio	0.86	0.85	0.77	0.83

TABLE 43

Analyses of Metals in Pretreated/Liquefied coal[1]

Sample Designation	Raw Black Thunder	1 % NaOH, 200 °F Pretreated	5% Acetic Acid, 400°F Pretreated	5% Acetic Acid, 200 °F THF Insoluble [2]
Metal, Wt% Ash				
Fe	2.5	1.3	3.2	4.6
Na	0.6	13.1	0.3	0.3
K	0.5	0.4	0.1	0.1
Ca	17.1	14.7	7.2	11.1
Mg	2.2	1.2	0.5	0.8
Al	6.0	6.2	8.8	11.3
Ti	0.3	0.4	0.7	0.8
Si	6.4	---	---	---

Notes: 1. Inductively coupled plasma (ICP) analyses of the ash samples.

2. The THF insolubles from a liquefaction run made using coal that was pretreated with acetic acid.

TABLE 44

Results of Liquefaction Runs with Pretreated Coal

Run No.	25	199	103	107	50	111	55	122	46
(NB No.)	14252	14252	14252	14252	14252	14252	14252	14252	14252
Conditions of Pretreatment Run (Initial charge 50 psig nitrogen)									
Time, M	None	None	5	30	30	30	30	30	30
Temp, F			210.5	209.1	206	409.7	406.3	204.8	402
NAOH,%			1%	1%	5%	5%	5%		
ACETIC,%								5%	5%
P(max),psig			75	63	90	290	275	70	260
Conditions of Liquefaction Run (Initial charge 500 psig hydrogen)									
Time, M	10	10	10	10	10	10	10	10	10
Temp, F	812.2	825.2	827	827.8	816	828.4	820	819.7	823.5
YIELDS									
Oil+Gas	47.5	49.9	49.4	45.9	43.6	49.0	---	46.2	55.4
Asph	22.3	26.9	19.0	19.9	21.5	15.5	---	23.9	21.0
Preasph	10.1	11.1	7.4	5.9	4.3	11.7	---	16.3	10.2
THF Ins	20.1	12.0	24.3	28.3	30.6	23.8	---	13.6	13.3
TOL Sol	69.8	76.8	68.3	65.8	65.1	64.5	68.3	70.1	76.4
THF Sol	79.9	88.0	75.7	71.7	69.4	76.2	---	86.4	86.7
CHARGE									
Coal	20.0516	20.0974	25.1118	25.3434	25.0900	25.3499	25.1654	25.1320	25.0778
Tetralin	40.2500	40.2900							
H2O			50.0595	50.1696	50.7121	50.9141	50.0097	50.5698	50.1703
Effective charge to the liquifaction runs									
Coal			19.0994	18.0141	20.072	15.1268	16.1822	20.2585	20.2814
Tetralin			40.0604	40.4058	40.1334	40.2878	40.9826	40.3002	40.1623
Coal analysis: fraction moisture-free and moisture-ash-free									
MF Frn	0.7202	0.7202	0.8437	0.8222	0.5343	0.8541	0.7679	0.8275	0.7940
MAFFrn	0.6687	0.6687	0.7824	0.7593	0.4676	0.7288	0.6616	0.7885	0.7592
Extraction results									
Insolubles, g									
THF	3.7311	2.6508	4.8018	4.9977	4.2138	4.5214	---	2.9619	3.4119
Toluene	5.0838	4.1479	5.9038	5.8094	4.6144	5.8107	5.1126	5.5609	5.3570
Hexane	2.9879	3.6181	2.8350	2.7207	2.0137	1.7049	---	3.8256	4.0022

TABLE 45

RESULTS OF AU-44L PRETREATMENT RUNS AT 600°F

Background: Run 14436- Ext'n 15079-	94A 8	66C 9	65A 3	67A 14	67B 15
Conditions (1400 psig):					
Temperature, °F	Feed	Feed	600	600	600
Space Time, Min.	of	of	14	15	27
Hydrogen, SCFH	Run	Run	12	12	12
Run Time, Hr	65A	67A,B	19.3	12.5	8.1
Catalyst, ppm			--	1200	1200
Material Balance (g/hr):					
Feed Rate			1150.9	1076.5	495.3
Slurry Product			1083.7	998.8	482.1
Light Ends			3.00	3.60	2.40
C_1-C_3 Gases			0.04	0.02	0.02
C_4+ Gases			0.00	0.00	0.00
Carbon Monoxide			0.00	0.00	0.00
Carbon Dioxide			2.90	2.96	1.42
Water			60.3	84.0	32.7
% Recovery			99.9	101.2	104.7
Yields, Wt% Total Slurry (MAF Basis):					
Hexane Solubles	57.83	54.19	56.45	56.09	54.96
Asphaltenes	13.26	14.78	16.13	15.48	16.16
Preasphaltenes	1.86	3.16	3.10	4.06	3.22
Hexane Insolubles (Feed)	42.17	45.81	43.55	43.91	45.04
Toluene Insol (MAF Feed)	28.91	31.03	27.42	28.44	28.88
THF Insol (MAF Feed)	27.05	27.86	24.32	24.37	25.66
Yields, Wt% Feed Coal Only (MAF Basis):					
Asphaltenes	51.90	58.14	63.14	61.79	61.49
Preasphaltenes	7.28	12.45	12.14	16.21	12.24
Hexane Insol (MAF)	165.06	180.19	170.46	175.41	171.13
Toluene Insol (MAF)	113.16	122.05	107.32	113.62	109.63
THF Insol (MAF)	105.88	109.60	95.18	97.41	97.39
THF Sol (MAF)	-5.88	-9.60	4.82	2.59	2.61
Light Ends			0.00	0.00	0.00
C_1-C_3 Gases			0.02	0.01	0.01
C_4+ Gases			0.00	0.00	0.00
Carbon Monoxide			0.00	0.00	0.00
Carbon Dioxide			1.10	1.12	0.54

TABLE 46

RESULTS OF AU-44L TEMPERATURE STAGED PRETREATMENT RUNS

Background:										
Run 14436-	178D	65A	176A	176AX	177A	177AX	177K	177KX	178C	178CX
Ext'n 14436-	183		179	187	188	189	181	186	182	185
Conditions (1400 psig):										
Temperature, °F	Feed	600	625	625	650	650	675	675	700	700
Space Time, Min.		14	17	17	18	18	18	18	17	17
Hydrogen, SCFH		12	12	12	12	12	12	12	12	12
Run Time, Hr		19.3	7.75	7.75	14.5	14.5	7.25	7.25	2.1	2.1
(Lineout and Prod.)		0.0	0	0	0	0	0	0	0	0
Catalyst, % on Coal										
Material Balance (g/hr):										
Feed Rate (Prod. Period)		1150.9	927.6	927.6	1106.2	1106.2	924.5	924.5	892.5	892.5
Slurry Product		1083.7	890.5	890.5	1071.8	1071.8	868.8	868.8	836.2	836.2
Light Ends		3.00	7.75	7.75	5.12	5.12	7.3	7.3	7.3	7.3
C_1-C_3 Gases		0.04	0.10		0.18		0.42		0.66	
C_4+ Gases		0.00	0.01		0.02		0.06		0.17	
Carbon Monoxide		0.00	0.17		0.21		0.27		0.40	
Carbon Dioxide		2.8	3.01		3.89	0.00	4.49		5.66	
Water		60.3	45.7	45.7	37.8	37.8	44.4	44.4	44.4	44.4
% Recovery		99.91	102.12	101.76	101.16	100.77	100.13	99.57	100.26	99.48
Yields, Wt% Total Slurry (MAF Basis):										
Toluene Insol (MAF Feed)	31.05	27.42	27.31	26.90	28.78	28.58	27.49	27.28	25.13	24.61
THF Insol (MAF Feed)	28.14	27.32	23.11	23.70	24.42	23.90	21.47	21.60	19.33	19.78
Yields, Wt% Feed Coal Only (MAF Basis):										
Toluene Insol (MAF)	120.39	107.32	105.91	104.29	111.60	110.80	106.61	105.78	97.43	95.44
THF Insol (MAF)	109.11	95.18	89.60	91.91	94.70	92.68	83.24	83.76	74.96	76.70
THF Sol (MAF)	-9.11	4.82	10.40	8.09	5.30	7.32	16.76	16.24	25.04	23.30
Light Ends		0.00	0.01		0.00		0.01		0.01	
C_1-C_3 Gases		0.02	0.05		0.07		0.20		0.32	
C_4+ Gases		0.00	0.00		0.01		0.03		0.08	
Carbon Monoxide		0.00	0.08		0.08		0.13		0.20	
Carbon Dioxide		1.10	1.40		1.52		2.10		2.73	

TABLE 47

RESULTS OF AU-44 RUNS WITH MOLYVAN-L CATALYST

Background:								
Run No.	15D	131	34B	33C	23C	15C	14A	13A
Extraction No.	31	131	36	35	30	29	28	27
Conditions: (2000 psig)								
Temperature, °F	feed	feed	650	700	725	750	775	800
Space Time, min			27	26.9	27	25.3	26.5	26.4
Hydrogen, Scfh			15	15	15	15	15	15
Catalyst, ppm (Molyvan-L)	1000	0	1000	1000	1000	1000	1000	1000
Run Time, hr (after lineout)			2.75	4.00	4.00	4.00	4.00	4.05
Material Balance: (g/hr)								
Feed Rate (Operating Period)	100.0	100	637.4	608.4	626.5	635.6	635.6	645.7
Slurry Product	100.0	100	611.3	593.6	577.7	574.3	586.2	598.0
Light Ends			11.1	9.9	13.9	9.8	16.4	7.6
C_1-C_3 Gases			0.0	0.1	0.9	1.8	2.8	5.4
C_4^+ Gases			0.0	0.0	0.2	0.5	1.1	2.0
Carbon Monoxide			0.0	0.0	0.4	0.5	0.7	0.9
Carbon Dioxide			0.4	0.5	4.7	5.6	6.0	7.0
Water			11.3	9.3	39.0	43.5	37.0	34.9
% Recovery			99.5	100.8	101.4	99.6	102.3	101.6
Yields, Wt% Total Feed On An MAF Basis:								
TOL Insol (MAF Feed)	27.25	27.48	23.50	19.36	16.36	14.01	10.96	9.34
THF Insol (MAF Feed)	26.30	26.89	21.26	16.50	13.09	11.08	8.85	7.53
Yields, Wt% MAF Feed Coal Basis:								
Tol Insol (MAF)	106.14	106.80	91.84	75.67	63.93	54.57	42.70	36.37
THF Insol (MAF)	102.44	104.51	83.10	64.50	51.16	43.17	34.46	29.33
Light Ends			0.02	0.02	0.02	0.02	0.03	0.01
C_1-C_3 Gases			0.02	0.08	0.62	1.19	1.89	3.65
C_4^+ Gases			0.00	0.00	0.13	0.34	0.77	1.33
Carbon Monoxide			0.02	0.03	0.27	0.36	0.46	0.59
Carbon Dioxide			0.24	0.35	3.27	3.83	4.12	4.72

TABLE 48

FTIR ANALYSES OF SELECTED SAMPLES OF UNCONVERTED COAL (THF INSOLUBLES)

Sample:	36-C	116-A	196-A	10-A	39-A	38-A	32-C	32-A	38-D
Conditions:									
Temp, °F	---	600	600	600	650	700	750	800	840
Time, min	---	30	17	27	30	30	30	30	30
Catalyst	---	STEAM	None	Moly Octoate	Moly-L	Moly-L	Moly-L	Moly-L	Moly-L
Conv., MAF:	None	None	2.6	2.6	16.9	35.5	56.8	70.7	79.9
Intensity:									
Frequency:									
3050	0.58	0.71	0.49	0.51	0.81	0.73	0.60	0.94	0.61
2900	22.70	21.50	15.80	18.70	28.05	27.30	17.50	19.70	16.10
1735	0.094	0.110	0.140	0.119	0.150	0.160	0.030	---	0.050
1703	3.32	3.34	2.78	2.94	2.58	3.12	1.57	1.37	0.29
1655	2.06	1.58	1.95	1.94	1.71	1.07	2.04	1.91	1.25
1600	11.50	17.70	12.20	13.05	16.10	18.90	15.60	20.00	18.20
1555	0.97	0.99	0.74	0.71	0.79	1.35	1.22	1.61	0.87
1100	0.76	0.81	0.56	0.47	0.50	0.75	1.07	1.00	1.66
1040	3.12	0.39	0.97	1.13	2.02	1.60	1.34	1.80	2.02
1010	0.35	0.11	0.25	0.17	0.21	0.54	0.55	1.00	5.64

TABLE 49

ASSIGNMENTS OF OBSERVED FTIR SPECTRA

Wavenumber (cm^{-1})	Functional Group Interpretations
3050	Aryl C-H
2900	Aliphatic C-H
1735	Saturated Ketones/Aldehydes, Esters
1703	Saturated, Unsaturated, and Aryl Carboxylic Acids, Aryl and Unsaturated Ketones/Aldehydes
1648	Unsaturated and Aryl Carboxylic Acids, Aryl and Unsaturated Ketones/Aldehydes, Quinones
1655	Unsaturated Ketones, Quinones, Olefins (C=C Stretch)
1614	Aromatic Ring Stretch, Highly Conjugated H-bonded Carbonyl
1585	Carboxylic Acid Salt, Aromatic Ring Stretch
1555	Carboxylic Acid Salt?
1100	Phenoxy Structures, Ethers
1040	Ethers, Alcohols
1010	Ethers, Alcohols

TABLE 50

COAL ANALYSES

Coal	Black Thunder Subbituminous	
Batch Number	FCL-126	FCL-135
As Received, Wt% H_2O	23.60	23.31
Dry, Wt%		
C	69.60	69.05
H	5.01	5.23
N	1.07	.90
S	.46	.50
O (Difference)	17.14	17.64
Ash	6.72	6.68
Wet, Wt%		
Fe	.13	.18
Na	.03	.05
K	.03	.02
Ca	.88	.88
Mg	.11	.15
Al	.31	.42
Ti	.02	.03
Si	.33	.57

TABLE 51

SOLVENT ANALYSES

Wilsonville Run		258
Wilsonville Coal		Black Thunder Subbituminous
Batch Number		FSN-136
Elemental Analyses, Wt%		
C		89.25
H		8.26
N		.75
S		.05
O		1.69
Distillation, Wt%		
IBP-650°F		8.55
650-935°F		49.92
935+°F		41.52
Solubility, Wt%		
THF Insolubles		.22
Toluene Insolubles		.99
Hexane Insolubles		4.31

TABLE 52

ANALYSES OF SULFATED IRON OXIDE CATALYST

	Sulfated Iron Oxide
Elemental Analyses	
Fe	39.7
S	--
O (calc. for Fe_2O_3)	17.1
Moisture	37.4
Pore Properties	
BET Surface Area, m^2/g	189
Pore Volume, cc/g	.15
Average Pore Radius, Å	16

TABLE 53

DECARBOXYLATION OF BLACK THUNDER COAL IN A PRETREATMENT STAGE: NET YIELDS FROM COAL

Stage 1, °F	--	650	700	700	750
Stage 2, °F	800	800	800	800	800
Stage 1 H_2, SCFB	--	1000	500	0	0
Yields, Wt% of MAF Coal					
CO_2+CO	4.8	5.0	5.2	5.2	5.0
C1-C3	8.4	6.8	8.7	6.5	7.1
C4-360°F	6		4	2	4
360-650°F	29		33	24	19
650-935°F	14		8	9	7
935°F+	12		20	33	34
C_4-935°F	48		45	35	30
Conversion	85.6		89.0	89.7	87.4
Hydrogen	-5.4			-3.5	

TABLE 54

DECARBOXYLATION OF BLACK THUNDER COAL IN A PRETREATMENT STAGE: ANALYSES OF DISTILLED FRACTIONS

Stage 1, °F	--	700
Stage 2, °F	800	800
Stage 1 H_2, SCFB	--	0
Wt% Analysis		
360-650°F Aromatic C	41	41
H/C	1.44	1.47
N	.40	.43
O	2.6	4.0
650-935°F Aromatic C	54	54
H/C	1.22	1.22
S	.04	.04
N	.57	.49
O	1.2	1.4
935°F+, Solids		
H/C	.84	.80
S	.41	.49
N	1.19	1.15
O	1.6	1.9

TABLE 55

SIEVE FRACTIONS OF PULVERIZED BLACK THUNDER SUBBITUMINOUS COAL

Mesh Size	Wt% Retained
60	0.00
100	1.65
140	11.38
230	27.52
325	40.52
400	12.94
Pan	5.76

TABLE 56

SIEVE FRACTIONS OF PULVERIZED MARTIN LAKE LIGNITE

Mesh Size	Wt% Retained
60	0.00
100	0.18
140	1.79
230	18.71
325	39.31
400	25.04
Pan	14.52

TABLE 57

COAL ANALYSES

Coal	Black Thunder Subbituminous	Martin Lake Lignite	Illinois No. 6 Bituminous
As Received, Wt%			
H_2O	23.60	31.52	6.05
Dry, Wt%			
C	69.60	62.16	69.54
H	5.01	4.40	4.56
N	1.07	1.44	1.17
S	0.46	1.63	3.26
O (Difference)	17.14	15.28	12.03
Ash	6.72	15.09	9.44
Fe	0.17	1.68	1.19
Na	0.04	0.06	0.05
K	0.03	0.06	0.18
Ca	1.15	1.01	0.37
Mg	0.15	0.27	0.06
Al	0.40	1.14	0.99
Ti	0.02	0.07	0.05
Si	0.43	2.16	2.15

TABLE 58

BATCH LIQUEFACTION OF ILLINOIS NO. 6 COAL

Sample	Conversion 100-MAF Insol	Preasphaltenes	Asphaltenes	Oil and Gas Difference
Argonne Premium	87.6	2.4	37.7	47.4
DOE-1	79.9	1.9	63.1	15.0
DOE-2	90.4	1.9	35.8	52.7
DOE-3	89.2	1.4	33.1	54.7
Oxidized	89.6	1.0	45.5	43.1

TABLE 59

ANALYSES OF ILLINOIS NO. 6 COAL SAMPLES

Sample	DOE-1 Chunks	DOE-2 Ground	DOE-3	Argonne Premium
Wt% (Dry):				
C	74.50	74.21	69.54	65.65
H	4.47	4.52	4.56	4.23
N	1.48	1.50	1.17	1.16
S	2.67	2.68	3.26	4.83
O (difference)	6.65	6.99	12.03	8.65
Ash	10.23	10.10	9.44	15.48
H/C	0.72	0.73	0.79	0.77

TABLE 60

LIQUEFACTION OF BLACK THUNDER SUBBITUMINOUS COAL[1]

Coal Sample	Fresh, 190 Hrs.	Fresh, 385 Hrs.	Oxidized, 450 Hrs.
Conversion, Wt%[2]	86.0	86.4	89.0
Yield,[3] Wt% MAF Coal			
$CO+CO_2$	2.5	2.4	2.2
C_1-C_3 Hydrocarbon	8.3	9.0	7.3
C_4-360°F	4.6	7.9	9.3
360-650°F	33.6	36.4	33.5
650-975°F	32.8	22.3	16.0
975+°F Resid	-8.0	-3.5	10.6
Hydrogen Consumption, Wt% MAF	6.3	6.2	5.5

Notes

[1]Results from the following sample periods were used: 8 (fresh, 190 hrs.); 16-17 (fresh, 385 hrs.); and 19-20 (oxidized, 450 hrs.).

[2]Conversion is reported as wt% MAF THF insolubles.

[3] Once-through yields are calculated by subtracting solvent corrections from mass balance yields in Table B-1 in the Appendix. Yields with solvent recycle are between once-through and uncorrected yields.

TABLE 61

C/C Liquefaction of Black Thunder Subbituminous Coal: Elemental Analyses

	REFERENCE BLACK THUNDER SUBBITUMINOUS											AIR OXIDIZED		SOLVENT CORRECTION	
SAMPLE PERIOD	4	5	6	7	8	10	13	14	15	16	17	19	20	25	26
DISTILLED PRODUCT ANALYSES (WT%)															
DISTILLATE (360-650 F, WT%)															
C					87.5			88					88.1		87.7
H					11			11.1					10.9		11.1
S					0.01			0.01					0.01		0.00
O					1.44			0.93					0.94		0.79
N					0.29			0.33					0.33		0.32
TOTAL					100			100					100		99.9
VACUUM DISTILLATE (650-975 F, WT%)															
C					89.7			89.6					89.6		89.6
H					9.65			9.84					9.74		9.80
S					0.01			0.01					0.01		0.01
O					0.52			0.44					0.44		0.48
N					0.42			0.36					0.43		0.40
TOTAL					100			100					100		100
RESID + UNCONVERTED COAL (975+ + UNCONV. COAL, WT%)															
C					83.5			85.2					82.2		90.3
H					6.34			6.49					6.13		7.28
S					0.14			0.11					0.14		0.08
O (DIFFERENCE)					3.07			2.17					4.88		1.39
N					0.96			1.01					0.95		0.95
TOTAL					96.9			97.8					95.1		98.6
THF INSOLUBLES.....	19.8	24.4	15.3		22.7	19.6	13.5	18.3	21.4	17.6	24.6	15.9	22.7	2.48	2.28
RESID THF INSOLUBLES (WT%)															
ASH	30.3	28.8	31.7		26.2	29	40.6	27.5	27.5	26	23.8	26	25.2		
K					630			630					620		
SI					37E3			30E3					33E3		
AL					17E3			21E3					20E3		
CA					34E3			42E3					42E3		
FE					13E3			12E3					10E3		
MG					8500			7900					7500		
MO					21			21					20		
NA					2730			2550					2310		
NI					82			75					65		
TI					1810			1390					1510		
V					86			67					60		

Notes: Analyses are for product from coal plus recycle solvent.
The naphtha (IBP-360F) fraction was not analyzed because it contained large amounts of tetrahydrofuran.

TABLE 62

ANALYSES OF SPENT CATALYST SAMPLES
FROM THE BLACK THUNDER RUN

Catalyst	Stage 1	Stage 2	Fresh
Elemental Analyses, Wt%			
Primary Metals			
Mo	5.30	6.70	9.10
Ni	1.19	1.54	2.22
Al	21.80	25.50	35.40
Si	1.82	1.10	1.39
Deposits			
C	24.08	15.23	--
H	1.65	1.28	--
S	9.62	6.19	0.20
Ti	0.28	0.04	0.00
Fe	6.00	0.58	0.02
Na	0.41	0.60	0.08
Mg	0.17	0.05	0.00
V	0.04	0.02	0.00
Ca	0.34	0.09	0.00
Pore Properties			
Volume <1200 Å Diam., cc/g	0.14	0.34	0.59
Volume >1200 Å Diam., cc/g	0.06	0.08	0.00
BET Surface Area, m^2/g	77	148	200

TABLE 63

LIQUEFACTION OF MARTIN LAKE LIGNITE[1]

Lignite Sample	Fresh, 210 Hr	Fresh, 290 Hr	Fresh, 500 Hr	Oxidized, 350 Hr
Conversion, Wt%[2]	86.9	81.7	84.9	83.9
Yield,[3] Wt% MAF Coal:				
$CO+CO_2$	3.0	2.8	3.5	6.0
C_1-C_3 Hydrocarbon	9.6	9.8	11.3	12.3
C_4-360°F	15.0	10.0	12.6	14.4
360-650°F	39.0	39.4	23.9	32.6
650-975°F	11.9	6.9	8.9	-7.1
975+°F Resid	-4.6	0.4	10.4	15.4
Hydrogen Consumption, Wt% MAF	8.6	--	7.6	7.5

[1]Results from the following sample periods were used: 9-10 (fresh, 210 hrs.); 13 (fresh, 290 hr); 22 (fresh, 500 hr); and 15-16 (oxidized, 350 hr).

[2]Conversion is reported as wt% MAF THF insolubles.

[3]Once-through yields are calculated by subtracting solvent corrections (sample periods 15-16) from mass balance yields in Table B-2 in the Appendix. Yields with solvent recycle are between once-through yields and uncorrected yields.

TABLE 64

C/C Liquefaction of Martin Lake, Texas Lignite: Elemental Analyses

	REFERENCE MARTIN LAKE LIGNITE									AIR OXIDIZED		SOLVENT CORRECTION		LIGNITE REFERENCE	
SAMPLE PERIOD	2	4	6	7	8	9	10	11	13	15	16	18	19	21	22
DISTILLED PRODUCT ANALYSES, WT%															
DISTILLATE (360-650 F)															
C		87.6					87.9				88.5		88.1		87.3
H		11.3					11.2				11.3		11.1		11.3
S		0.06					0.02				0.02		0.01		0.02
O		1.01					0.76				1.13		0.75		1.08
N		0.37					0.35				0.42		0.34		0.39
TOTAL		100					100				101		100		100
VACUUM DISTILLATE (650-975 F)															
C		89.1					89.8				89.9		89.8		89.9
H		10.1					9.84				9.68		9.49		9.83
S		0.01					0.01				0.02		0.01		0.01
O		0.45					0.33				0.53		0.45		0.46
N		0.41					0.43				0.55		0.50		0.49
TOTAL		100					100				101		100		101
RESID + UNCONV COAL (975+ F, SOLIDS)															
C		80.4					78.9				80.1		89.8		82.8
H		6.36					6.11				5.87		6.59		6.31
S		0.60					0.72				0.64		0.14		0.50
O (DIFFERENCE)		3.02					1.60				2.91				1.44
N		0.84					0.64				0.78		0.82		0.71
TOTAL		97					98.4				97.1				98.6
THF INSOLUBLES	28.4	28.4	17	31.2	25.9	25.9	25	29.4	25.9	21.9	21.5	0.75	2.31	17.3	19.4
RESID THF INSOLUBLES															
ASH	31	31	39.6	46.7	50.9	50.9	47.9	47.6	45	46.6	45.2			43.8	42.2
K															
SI		38E3					5900				61E3				6800
AL		25E3					27E3				25E3				23E3
CA		27E3					7200				4400				15E3
FE		33E3					54E3				49E3				43E3
MG		5300					6200				6700				4500
MO		22					25				25				19
NA		1370					2030				2240				2020
NI		85					134				174				114
TI		1580					2340				2440				2410
V		65					90				105				89

Notes: Analyses are for product from coal plus recycle solvent. The naphtha (IBP-360F) fraction was not analyzed because it contained large amounts of tetrahydrofuran.

TABLE 65

ANALYSES OF SPENT CATALYST SAMPLES
FROM THE MARTIN LAKE LIGNITE RUN

Catalyst	Stage 1	Stage 2	Fresh
Elemental Analyses, Wt%			
Primary Metals			
Mo	4.70	6.20	9.10
Ni	1.00	1.48	2.22
Al	18.50	22.80	35.40
Si	2.34	1.12	1.39
Deposits			
C	31.25	21.36	--
H	1.52	1.25	--
S	5.22	5.15	0.20
Ti	0.13	0.04	0.00
Fe	2.83	0.26	0.02
Na	0.20	0.26	0.08
Mg	0.21	0.09	0.00
V	0.02	0.02	0.00
Ca	2.18	0.32	0.00
Pore Properties			
Volume <1200 Å Diam., cc/g	0.08	- 0.25	0.59
Volume >1200 Å Diam., cc/g	0.08	0.08	0.00
BET Surface Area, m^2/g	17	123	200

TABLE 66

LIQUEFACTION OF ILLINOIS NO. 6 COAL

Sample	61 Hr	155 Hr[1]	408 Hr
Conversion, Wt%[2]	90.3	93.2	86.4[3]
Yield,[4] Wt% MAF Coal:			
$CO+CO_2$	.9	1.2	
C_1-C_3 Hydrocarbon	5.2	7.7	--
C_4-360°F	8.9	8.6	4.7
360-650°F	27.9	27.6	20.5
650-935°F	15.9	9.3	-.5
935+°F Resid	26.9	38.9	40.0
Hydrogen Consumption, Wt% MAF	6.5	4.5	4.8

[1]Results from 90-178 hrs were averaged.

[2]Conversion is reported as 100-wt% MAF THF insolubles.

[3]Results from 273-408 hours were averaged. A partially blocked valve may have caused low apparent conversions at the end of the run.

[4]Once-through yields are calculated by subtracting solvent corrections (448-471 hrs) from yields in Table B-3 of the Appendix. Yields with recycle are between once-through and uncorrected yields.

TABLE 67

C/C Liquefaction of Illinois No. 6 Coal: Elemental Analyses

	REFERENCE ILLINOIS NO. 6 COAL										SOLVENT CORRECTION	
SAMPLE PERIOD	2	3	4	6	8	10	12	14	16	18	20	21
DISTILLATE (360-650 F), WT%												
C		87.5			86.3					86.1	85.8	
H		11.6			11.6					11.3	11.9	
S		0.01			0.01					0.01	0.01	
O		0.91			1.52					2.06	1.66	
N		0.26			0.25					0.29	0.18	
TOTAL		100			99.6					99.8	99.6	
VACUUM DISTILLATE (650-RESID), WT%												
C		89.2			89.6					89.5	89.9	
H		10.4			9.52					9.58	9.92	
S		0.05			0.06					0.07	0.02	
O		0.36			0.53					0.63	0.33	
N		0.21			0.30					0.32	0.25	
TOTAL		100			100					100	100	
RESID + UNCONV COAL, WT%												
C		82			80.5					81.6	88.6	
H		6.83			6.46					6.69	7.61	
S		0.74			0.96					0.93	0.27	
O (DIFFERENCE)		2.73			1.65					1.91	1.50	
N		0.90			1.07					1.07	0.82	
TOTAL		97.3			98.4					98.1	98.5	
THF INSOLUBLES												
RESID THF INSOLUBLES, WT%												
ASH												
K		14E3			15E3					17E3		
SI		19E4			20E4					21E4		
AL		87E3			91E3					96E3		
CA		35E3			31E3					28E3		
FE		10E4			11E4					11E4		
MG		5000			4500					4800		
MO		124			92					87		
NA		3420			3790					3940		
NI		257			279					166		
TI		2640			2720					2720		
V		279			240					215		

Notes: Analyses are for product from coal plus recycle solvent. The naphtha (IBP-360F) fraction was not analyzed because it contained large amounts of tetrahydrofuran.

TABLE 68

ANALYSES OF SPENT CATALYST SAMPLES
FROM THE ILLINOIS NUMBER 6 RUN

Catalyst	Stage 1	Stage 2	Fresh
Elemental Analyses, Wt%			
Primary Metals			
Mo	5.90	8.10	9.10
Ni	1.25	1.63	1.39
Al	23.50	31.60	35.40
Si	.98	1.22	1.39
Deposits			
C	25.35	7.86	--
H	1.59	1.50	--
S	4.78	5.86	.20
Ti	1.54	.14	.00
Fe	.44	.14	.02
Na	.12	.11	.08
Mg	.05	.01	.00
V	.18	.00	.00
Ca	.00	.00	.00
Pore Properties			
Volume <1200 Å Diam., cc/g	.16	.38	.59
BET Surface Area, m^2/g	65	151	200

TABLE 69

COMPARISON OF COAL FEEDSTOCKS: UNCORRECTED YIELDS

Feedstock	Black Thunder	Martin Lake Lignite	Illinois No. 6
Wt% of MAF Coal			
Conversion	84.8	86.9	93.2
C_1-C_3 Hydrocarbon	12.3	13.9	10.7
$CO+CO_2$	2.8	4.0	1.4
C_4-360°F	9.8	20.6	9.2
360-650°F	47.5	55.0	35.8
650-975°F	19.3	.0	5.3
975+°F	-18	-19	27.9
Hydrogen Consumption	9.0	11.0	5.6
Elemental Analyses, Wt%			
360-650°F, H/C	1.51	1.53	1.61
S	.01	.02	--
N	.29	.35	.25
O	1.4	.8	1.5
650-975°F, H/C	1.29	1.31	1.28
S	.01	.01	.06
N	.42	.43	.30
O	.5	.3	.5
975+°F and Solids			
H/C	.91	.93	.96
S	.14	.72	.96
N	.96	.64	1.07
O	3.1	1.6	1.7
Hours	190	197-220	90-178

TABLE 70

COMPARISON OF FEEDSTOCKS: ONCE-THROUGH YIELDS FROM COAL

Feedstock	Black Thunder	Martin Lake Lignite	Illinois No. 6
Wt% of MAF Coal			
Conversion	84.8	86.9	93.2
C_1-C_3 Hydrocarbon	8.3	9.6	7.2
$CO+CO_2$	2.5	3.0	1.2
C_4-360°F	4.6	15.0	8.6
360-650°F	33.6	39.0	26.1
650-975°F	32.8	11.9	8.8
975+°F	-8.0	-4.6	37.4
Hydrogen Consumption	6.3	8.6	4.5
Hours	190	197-220	90-178

Corrections for solvent reactions have been subtracted from yields in this Table.

TABLE 71

COMPARISON OF FEEDSTOCKS: SPENT CATALYST FROM THE FIRST STAGE

Feedstock	Black Thunder	Martin Lake Lignite	Illinois No.6	Fresh Catalyst
Wt% of Catalyst				
C	24.08	31.25	25.35	--
H	1.65	1.52	1.59	--
Ti	.28	.13	1.54	--
Na	.41	.20	.12	.08
Ca	.34	2.18	.00	.00
Fe	6.00	2.83	.44	.02
Pore Properties				
BET Surface Area, m^2/g	77	17	65	200
PV <1200 Å Dia., cc/g	.14	.08	.16	.59

TABLE 72

High Temperature Liquefaction of Illinois No. 6 Coal with AMOCAT™ 1C Catalyst: Product Yields

Stage 1 °F	790	790	800	800
Stage 2 °F	760	760	860	860
Catalyst Age, Hours	150	340	75	240
Yields, Wt% MAF Coal				
C_1-C_3	10.7		17.7	14.0
C_4-360 °F	9	5	18	6
360-650 °F	36	29	75	45
650 °F-Resid[1]	5	4	0	-8
Resid[1]	28	29	-35	26
Conversion	93.2	86.3[2]	92.4	95.0
Hydrogen Consumption	5.6	5.9	9.3	6.6
C_4+ Distillate	47	38	93	41

[1]Resid cut point was 935°F for the low-temperature run and 975°F for the high-temperature run.
[2]Coal conversion may appear low because solids accumulated before a valve that was malfunctioning.

TABLE 73

High-Temperature Liquefaction of Illinois No. 6 Coal with AMOCAT™ 1C
Catalyst: Product Analyses

Stage 1 °F	790	790	800	800
Stage 2 °F	760	760	860	860
Catalyst Age, Hours	150	340	75	240
Analyses, Wt%				
360-650°F				
Aromatic C	32	35	35	37
H/C	1.61	1.57	1.47	1.58
N	.25	.29	.23	.28
O	1.5	2.1	.6	2.0
650°F-Resid[1]				
Aromatic C	42	43	52	49
H/C	1.28	1.28	1.19	1.31
S	.06	.07	.02	.59
N	.30	.32	.30	.45
O	.5	.6	.3	1.0
Resid[1]+Solids				
H/C	.96	.98	.94	.91
S	.96	.93	.38	1.32
N	1.07	1.07	.79	.86

[1]Resid cut point was 935°F for the low-temperature run and 975°F for the high-temperature run.

TABLE 74

Analyses of Spent AMOCAT™ 1C Catalyst Samples:
High-Temperature Liquefaction of Illinois No. 6 Coal

Stage	Fresh	1	1	2	2
Temperature, °F		790	800	760	860
Run Length, Days	0	20	11	20	11
Elemental Analyses, Wt%					
Primary Metals					
Mo	9.10	5.9	4.20	8.10	5.50
Ni	2.22	1.25	.97	1.63	1.17
Al	35.40	23.50	16.40	31.60	20.60
Si	1.39	.98	2.68	1.22	1.46
Deposits					
C	--	25.35	39.76	7.86	44.61
H	--	1.59	2.01	1.50	2.01
S	.20	4.78	3.94	5.86	3.98
Ti	.00	1.54	.64	.14	.07
Fe	.02	.44	.79	.14	.11
Na	.08	.12	.12	.11	.16
Mg	.00	.05	.03	.01	.00
Ca	.00	.00	.23	.00	.00
Pore Properties					
Vol. <1200 Å Diam., cc/g	.59	.16	.08	.38	.03
BET Surface Area, m^2/g	200	65	29	151	10

TABLE 75

Liquefaction of Illinois No. 6 Coal: Distilled Product Yields

Process	C/C	T/C	T/C	Slurry	Slurry	Slurry	Slurry
Residence Time, Hours	3	3	3	3	3	1.5	3
Stage 1, °F	790	800	820	800	800	820	800
Stage 2, °F	760	760	760	800	800	820	800
Molyvan L, ppm MoOctoate, ppm	0 0	192 0	192 0	192 0	84 0	84 0	0 96
Catalyst Age, Hours	180	150	310				
Yields, Wt% of MAF Coal							
C_1-C_3	8.9	9.3	10.1	8.5	9.1	11.0	10.5
C_4-360°F	7	7	12	7	10	11	8
360-650°F	35	35	43	40	39	41	43
650-935°F	5	13	12	21	19	16	22
935°F+	28	15	7	8	8	5	3
C_4-935°F	47	56	67	68	66	68	72
Conversion	93.2	91.1	93.9	94.6	96.3	95.7	94.5
H_2 Consumption	5.6	5.4	6.1	5.1	5.7	4.9	4.8

C = With AMOCAT™ 1C catalyst T = Without AMOCAT™ 1C catalyst

TABLE 76

Liquefaction of Illinois No. 6 Coal: Product Analyses

Process	C/C	T/C	T/C	Slurry	Slurry	Slurry	Slurry
Residence Time, Hours	3	3	3	3	3	1.5	3
Stage 1 °F	790	800	820	800	800	820	800
Stage 2 °F	760	760	760	800	800	820	800
Molyvan L, ppm MoOctoate, ppm	0 0	192 0	192 0	192 0	84 0	84 0	0 96
Catalyst Age, Hours	150	150	310				
Analyses, Wt%							
360-650°F Aromatic C	32	40	40	43	43	43	43
H/C	1.61	1.49	1.49	1.47	1.48	1.46	1.45
N	.25	.41	.48	.65	.56	.54	.51
O	1.5	2.3	2.4	2.9	3.3	3.1	3.1
650-935°F Aromatic C	42	47	47	47	48	50	51
H/C	1.28	1.28	1.27	1.25	1.27	1.22	1.22
S	.06	.07	.07	.08	.09	.09	.09
N	.30	.36	.47	.60	.61	.52	.49
O	.5	.8	.9	1.1	1.2	1.1	1.0
935°F+, Solids							
H/C	.96	.95	.96	.98	.98	.92	.91
S	.96	1.00	.92	1.01	.88	.35	.95
N	1.07	1.14	1.18	.97	1.06	1.09	1.12

C = With AMOCAT™ 1C catalyst T = Without AMOCAT™ 1C catalyst

TABLE 77

Solvent-Only Periods from Illinois No. 6 Coal: Product Yields

Process	C/C	T/C	T/C	Slurry
Stage 1 Temp. °F	790	800	820	800
Stage 2 Temp. °F	760	760	760	800
Molyvan L, Mo/Solvent, ppm	0	64	64	48
Catalyst Age, Hrs.	460	460	380	--
Yields, Wt%				
C_1-C_3	1.7	3.0	3.2	1.7
C_4-360°F	0	4	4	-2
360-650°F	5	8	10	7
650-935°F	-2	-5	-5	0
935°F+	-5	-9	-12	-7
C_4-935°F	3	7	9	5
Hydrogen Consumption	.6	.9	.7	.5

TABLE 78

Solvent-Only Periods from Illinois No. 6 Coal: Product Analyses

Process	C/C	T/C	T/C	Slurry
Stage 1 Temp. °F	790	800	820	800
Stage 2 Temp. °F	760	760	760	800
Molyvan L, Mo/Solvent, ppm	0	64	64	48
Catalyst Age, Hours	460	380	460	--
Analyses, Wt%				
360-650°F				
Aromatic C	29	42	40	42
H/C	1.66	1.50	1.49	1.47
N	.18	.25	.29	.30
O	1.7	.6	.6	1.1
650-935°F				
Aromatic C	40	46	48	47
H/C	1.32	1.26	1.23	1.27
S	.02	.02	.02	.04
N	.25	.37	.34	.41
O	.3	.4	.5	.6
935+°F. Solids				
H/C	1.03	1.04	1.00	.99
S	.27	.14	.94[1]	.08
N	.82	.83	.91	.88

[1]Contaminated with coal from previous periods.
[2]The nominal residence time was 3 hours for these periods.

TABLE 79

Analyses of Spent AMOCAT™ 1C Catalyst Samples:
Illinois No. 6 Liquefaction

Stage	Fresh	1	2	2
Temperature, °F		790	760	760
Process		C/C	C/C	T/C
Oil-Soluble Mo, ppm				192
Run Length, Days	0	20	20	20
Elemental Analyses, Wt%				
Primary Metals				
Mo	9.10	5.9	8.10	6.50
Ni	2.22	1.25	1.63	1.37
Al	35.40	23.50	31.60	25.10
Si	1.39	.98	1.22	.99
Deposits				
C	--	25.35	7.86	24.98
H	--	1.59	1.50	1.42
S	.20	4.78	5.86	4.97
Ti	.00	1.54	.14	.58
Fe	.02	.44	.14	.17
Na	.08	.12	.11	.15
Mg	.00	.05	.01	.01
Ca	.00	.00	.00	.00
Pore Properties				
Vol. <1200 Å Diam., cc/g	.59	.16	.38	.21
BET Surface Area, m^2/g	200	65	151	84

TABLE 80

Illinois No. 6 Coal: Comparison of Wilsonville Results
Vs. Dispersed Mo in Stage 1 or Stages 1-2

Process	Wilsonville C/C 261-B	Amoco T/C	Amoco Slurry
Space Velocity[1] Coal WHSV[2], Stage 2	18.6 .51	7.1 .45	14.2 --
Stage 1, °F	790	820	820
Stage 2, °F	810	760	820
Catalyst, Stage 1	EXP-AO-60	Molyvan L, 192 ppm Mo	Molyvan L, 84 ppm Mo
Catalyst, Stage 2	EXP-AO-60	Amocat™ 1C	Molyvan L
Yields, Wt% of MAF Coal			
C_1-C_3	5.1	10.1	11.0
Resid[3]	4.5	7	5
C_4+ Distillate[3]	64	67	68
Conversion	91.7	93.9	95.7
H_2 Consumption	5.7	6.1	4.9

[1]Space velocity = lb. MAF coal/hr./ft^3 reactor volume
[2]Coal WHSV = lb. MAF coal/hr./lb. catalyst
[3]The Wilsonville distillate/resid cutpoint was about 950°F and the Amoco distillate/resid cutpoint was 935°F.

TABLE 81

LIQUEFACTION OF ILLINOIS NO. 6 COAL WITH
POWDERED Mo/SULFATED IRON OXIDE AND MOLYVAN L:PRODUCT YIELDS

Catalyst	Molyvan L	Mo/Wender[1]
Temperature, °F	820	820
Yields, Wt% of MAF Coal		
C1-C3[2]	--	--
C4-360°F	-6[3]	-8
360-650°F	14	17
650-935°F	7[4]	37
935°F+	51[4]	22
C_4-935°F	15[4]	46
Conversion	91.1	91.3
Hydrogen	-4.4	-4.3

1. Mo on sulfated iron oxide
2. Gas yields are not available for this run.
3. Less distillate was recovered from the product than in the liquefaction solvent.
4. The large amount of 935+°F resid and product solubilities from this run suggest that coal reactivity was lower than previous tests, but relative ranking of catalyst activities should be correct.

TABLE 82

LIQUEFACTION OF ILLINOIS NO. 6 COAL WITH
POWDERED Mo/SULFATED IRON OXIDE AND MOLYVAN L:PRODUCT ANALYSES

Catalyst	Molyvan L	Mo/Wender
Temperature, °F	820	820
Wt% Analysis		
360-650°F Aromatic C	42	39
H/C	1.45	1.50
N	.43	.38
O[1]	.2	1.0
650-935°F Aromatic C	45	46
H/C	1.28	1.26
S	.10	.09
N	.36	.39
O	.7	.7
935°F+, Solids		
H/C	.96	.95
S	.75	.72
N	1.16	1.25

The oxygen analysis is corrected for the presence of dioxane, and is not very accurate.

TABLE 83

LIQUEFACTION OF ILLINOIS NO. 6 COAL WITH
MoC, MoN_2, OR MoS_2 POWDER:PRODUCT YIELDS

Catalyst	Molyvan L	MoC	MoN_2	MoS_2
Mo ppm/coal	84	400	300	500
Yields, Wt% of MAF Coal				
Oils[1]	70	43	52	42
Asphaltenes[2]	0	-2[3]	4	-1[3]
Preasphaltenes[4]	3	29	32	33
C4-360°F	11	0	--	2
360-650°F	41	32	--	6
650-935°F	16	6	--	-1
935°F+	5	25	--	58
C_4-935°F	68	38	--	7
Conversion	95.7	81.1	84.6	89.0

All tests were at 820°F and 1.5 hours nominal residence time.

1. Hexane solubles (does not include gases)
2. Hexane insolubles - toluene insolubles
3. Product contained less asphaltenes than the liquefaction solvent.
4. Toluene insolubles - THF insolubles

TABLE 84

C/T LIQUEFACTION OF BLACK THUNDER SUBBITUMINOUS COAL:
DISTILLED PRODUCT YIELDS

Process	C/C AMOCAT™ 1C	C/T AMOCAT™ 1C	Slurry
Residence Time, Hours	3	3	3
Stage 1 °F	790	780	800
Stage 2 °F	740	800	800
Catalyst Age, Hours	190	110	
Molyvan L, ppm Mo Mo Octoate, ppm Mo Iron Oxide, Wt% TPS-20, Wt%	0 0 0 0	0 0 1.0 2.0	96 0 1.0 2.0
Yields, Wt% of MAF Coal			
C1-C3	12.3	(16)	15.1
C4-360°F	10	31	26
360-650°F	48	53	47
650-935°F	19	11	-8
935°F+	-18	-32	-4
C_4-935°F	77	94	65
Conversion	84.8	93.7	90.2
Hydrogen	-9.0	-8.3	-6.5

TABLE 85

C/T LIQUEFACTION OF BLACK THUNDER SUBBITUMINOUS COAL:
YIELDS WITH AMOCAT™ 1C CATALYST IN STAGE 1

Process	C/T	C/T
Stage 1 Catalyst	AMOCAT™ 1C	AMOCAT™ 1C
Stage 1 °F	780	780
Stage 2 °F	800	800
Catalyst Age, Hours	110	280
Fe_2O_3, Wt% TPS-20, Wt%	1.0 2.0	1.0 2.0
Yields, Wt% of MAF Coal		
C1-C3	(16)	17.8
C4-360°F	31	21
360-650°F	53	23
650-935°F	11	12
935°F+	-32	0
C_4-935°F	94	57
Conversion	93.7	87.4
Hydrogen	-8.3	-6.2

TABLE 86

C/T LIQUEFACTION OF BLACK THUNDER SUBBITUMINOUS COAL:
PRODUCT ANALYSES

Process	C/C AMOCAT™ 1C	C/T AMOCAT™ 1C	Slurry
Residence Time, Hrs.	3	3	3
Reactor 1 Temp., °F	790	780	800
Reactor 2 Temp., °F	740	800	800
Catalyst Age, Hrs.	190	200	
Molyvan L, ppm Mo Mo Octoate, ppm Mo Iron Oxide, Wt% TPS-20, Wt%	0 0 0 0	0 0 1.0 2.0	96 0 1.0 2.0
Wt% Analyses			
360-650°F			
Aromatic Carbon		43	44
H/C	1.51	1.45	1.45
N	.29	.52	.52
O	1.4	1.7	3.1
650-935°F			
Aromatic Carbon		58	58
H/C	1.29	1.17	1.16
S	.01	.01	.28
N	.42	.56	.61
O	.5	.9	1.2
935°F+, Solids			
H/C	.91	.79	.80
S	.14	.56	.38
N	.96	1.05	1.26

C = With AMOCAT™ 1C catalyst T = Without AMOCAT™ 1C catalyst

TABLE 87

C/T LIQUEFACTION OF BLACK THUNDER SUBBITUMINOUS COAL:
YIELDS WITH AMOCAT™ 1C AND AMOCAT™ 1B IN THE FIRST STAGE

Process	C/T	C/T	C/T
Stage 1 Catalyst	AMOCAT™ 1C	AMOCAT™ 1B	AMOCAT™ 1B
Stage 1 °F	780	780	780
Stage 2 °F	800	800	800
Catalyst Age, Hours	110	110	120
Fe_2O_3, Wt% TPS-20, Wt% $FeSO_4/H_2O$, Wt%	1.0 2.0	1.0 2.0	 2.7
Yields, Wt% of MAF Coal			
C1-C3	(16) est.	14	17
C4-360°F	31	13	10
360-650°F	53	36	47
650-935°F	11	9	8
935°F+	-32	3	-6
C_4-935°F	94	58	65
Conversion	93.7	90.3	89.4
Hydrogen	-8.3	-5.4	-6.6

TABLE 88

C/T LIQUEFACTION OF BLACK THUNDER SUBBITUMINOUS COAL:
ANALYSES WITH AMOCAT™ 1C AND AMOCAT™ 1B IN THE FIRST STAGE

Process	C/T	C/T	C/T
Stage 1 Catalyst	AMOCAT™ 1C	AMOCAT™ 1B	AMOCAT™ 1B
Stage 1 °F	780	780	780
Stage 2 °F	800	800	800
Catalyst Age, Hours	110	110	120
Fe_2O_3, Wt% TPS-20, Wt% $FeSO_4/H_2O$, Wt%	1.0 2.0	1.0 2.0	 2.7
360-650°F, Wt%			
Aromatic C	42.5	43.5	44.0
H/C	1.45	1.44	1.45
N	.52	.45	.47
O	1.7	4.0[1]	4.0
650-935°F			
Aromatic C	57.5	54.5	56.6
H/C	1.17	1.18	1.17
S	.01	.04	.03
N	.56	.49	.54
O	.9	1.2	1.1
935+°F, Solids			
H/C	.79	.81	.85
S	.56	.37	.88
N	1.05	1.20	1.31

[1]This fraction contained some dioxane that was used in the product workup.

TABLE 89

C/T LIQUEFACTION OF BLACK THUNDER SUBBITUMINOUS COAL:
PRODUCT YIELDS SHOWING CATALYST DEACTIVATION

Process	C/T	C/T	C/T	C/T
Stage 1 Catalyst	Am. 1B	Am. 1B	Am. 1B	Am. 1B
Stage 1 °F	780	780	780	780
Stage 2 °F	800	780	780	780
Catalyst Age, Hours	120	190	260	320
$FeSO_4/H_2O$, Wt% $FeSO_4/CH_3OH$, Wt% $FeSO_4/H_2O/CH_3OH$, Wt%	2.7	2.7	1.1	2.7
Yields, Wt% of MAF Coal				
C1-C3	17.3	11.9	(11)	10.3
C4-360°F	10	8	6	4
360-650°F	47	29	31	26
650-935°F	8	15	7	3
935°F+	-6	12	17	27
C_4-935°F	65	52	44	33
Conversion	89.4	90.8	86.9	88.4
Hydrogen	-6.6	-5.6	-5.6	-4.8

TABLE 90

C/T LIQUEFACTION OF BLACK THUNDER SUBBITUMINOUS COAL:
PRODUCT ANALYSES SHOWING CATALYST DEACTIVATION

Process	C/T	C/T	C/T	C/T
Stage 1 Catalyst	Am. 1B	Am. 1B	Am. 1B	Am. 1B
Stage 1 °F	780	780	780	780
Stage 2 °F	800	780	780	780
Catalyst Age, Hours	120	190	260	320
$FeSO_4/H_2O$, Wt% $FeSO_4/CH_3OH$, Wt% $FeSO_4/H_2O/CH_3OH$, Wt%	2.7	2.7	1.1	2.7
360-650°F, Wt%				
Aromatic C	44.0	44.0	42.5	43.6
H/C	1.45	1.45	1.44	1.45
N	.47	.46	.45	.45
O	4.0[1]	4.5	4.0	4.5
650-935°F				
Aromatic C	56.5	55.0	54.4	55.4
H/C	1.17	1.21	1.19	1.19
S	.03	.04	.04	.03
N	.54	.55	.50	.55
O	1.1	1.4	1.3	1.4
935+°F, Solids				
H/C	.85	.83	.84	.82
S	.88	.80	.27	.72
N	1.31	1.35	1.24	1.32

[1]This fraction contains some dioxane that was used in the product workup.

TABLE 91

SPENT FIRST STAGE CATALYSTS: BLACK THUNDER SUBBITUMINOUS COAL

Catalyst	AMOC.™ 1C	AMOC™ 1C	AMOC.™ 1B	AMOC.™ 1C	AMOC.™ 1B
Temperature, °F	790	780	780	Fresh	Fresh
Run	51-218	135-23	135-25		
Run Length, Days	24	17	17		
Elemental Analyses, Wt%					
Primary Metals					
Mo	5.30	7.50		9.10	10.30
Ni	1.19	1.63		2.22	.24
Al	21.80	34.60		35.40	--
Si	1.82	1.64		1.39	1.10
Deposits					
C	24.08	28.71	29.24		
H	1.65	1.58	1.61		
S	9.62?	4.88	4.00	.20	.23
Ti	.28	.03		.00	--
Fe	6.00	.79		.02	.02
Na	.41	.74		.08	.09
Mg	.17	.11		.00	.00
Ca	.34	.44		.00	.00
Pore Properties					
Vol. <1200 Å Diam., cc/g	.14	.17	.17	.59	.63
BET Surface Area, m^2/g	77	76	67	200	194

TABLE 92

Dispersed Molybdenum Catalysts for Liquefaction of Black Thunder Subbituminous Coal; Distilled Product Yields

Process	C/C	Slurry	Slurry	Slurry	Slurry	Slurry
Residence Time, Hours	3	3	3	3	3	1.5
Stage 1 °F	790	800	800	800	820	820
Stage 2 °F	740	800	800	800	820	820
Catalyst Age, Hours	190					
Molyvan L, ppm MoOctoate, ppm Fe_2O_3, Wt% TPS-20, Wt%	0 0 0 0	96 0 0 0	96 0 1.0 2.0	0 96 1.0 2.0	96 0 0 0	96 0 0 0
Yields, Wt% of MAF Coal						
C1-C3	12.3	13.3	15.1	12.4	24.8	18.9
C4-360°F	10	22	26	29	31	24
360-650°F	48	40	47	43	50	41
650-935°F	19	1	-8	-5	-26	-28
935°F+	-18	5	-4	-2	-4	17
C_4-935°F	77	58	65	67	55	37
Conversion	84.8	89.9	90.2	91.6	88.1	88.2
Hydrogen	-9.0	-5.7	-6.5	-6.8	-7.4	-4.8

TABLE 93

Dispersed Catalysts for Liquefaction of Black Thunder Subbituminous Coal: Product Analyses

Process	C/C	Slurry	Slurry	Slurry	Slurry	Slurry
Residence Time, Hrs.	3	3	3	3	3	1.5
Reactor 1 Temp., °F	790	800	800	800	820	820
Reactor 2 Temp., °F	740	800	800	800	820	820
Catalyst Age, Hrs.	190					
Molyvan L, ppm Mo Mo Octoate, ppm Mo Iron Oxide, Wt% TPS-20, Wt%	0 0 0 0	96 0 0 0	96 0 1.0 2.0	0 96 1.0 2.0	96 0 0 0	96 0 0 0
Wt% Analyses						
360-650°F						
Aromatic C		44	44	43	46	46
H/C	1.51	1.45	1.45	1.45	1.40	1.43
N	.29	.47	.52	.53	.53	.48
O	1.4	3.0	3.1	3.0	2.8	3.2
650-935°F						
Aromatic C		57	58	57	62	63
H/C	1.29	1.16	1.16	1.17	1.11	1.11
S	.01	.04	.28	.28	.03	.04
N	.42	.57	.61	.61	.64	.63
O	.5	1.2	1.2	1.2	1.2	1.4
935°F+, Solids						
H/C	.91	.80	.80	.81	.73	.74
S	.14	.36	.38	.51	.18	.31
N	.96	1.22	1.26	1.28	1.25	1.28

TABLE 94

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

Residence Time, Hours	1.5	1.5
Temperature, °F	800	820
Yields, Wt% MAF Coal		
C1-C3	10.4	19.2
C4-360°F	4	7
360-650°F	25	31
650-935°F	6	2
935°F+	21	9
C_4-935°F	35	40
Conversion	84.5	87.0
Hydrogen	-4.2	-5.1

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

TABLE 95

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

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

TABLE 96

ANALYSES OF SULFATED IRON OXIDE CATALYST

	Sulfated Iron Oxide	Red Mud
Elemental Analyses		
Fe	39.7	58.9
S	--	0.0
O (calc. for Fe_2O_3)	17.1	25.3
Moisture	37.4	--
Pore Properties		
BET Surface Area, m^2/g	189	<1
Pore Volume, cc/g	.15	.04
Average Pore Radius, Å	16	96

TABLE 97

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

Nominal Residence Time, Hours	1.5	1.5	1.5	1.5
Temperature, °F	800	800	800	800
Molyvan L, ppm Mo:Coal	100	100	100	0
Wender's, ppm Mo:Coal	0	0	0	100
Wt% Fe:Coal	0	0.7	0.7	0.7
$FeSO_4/H_2O$, Wt% Fe:Coal	0.7	0	0	0
TPS-20, Wt%	0	0	5.0	5.0
Yields, Wt% of MAF Coal				
C1-C3	10.4	10.6	8.9	8.4
C4-360°F	4	6	4	6
360-650°F	25	29	29	29
650-935°F	6	5	14	14
935°F+	21	18	13	12
C_4-935°F	35	39	47	48
Conversion	84.5	84.9	86.0	85.6
Hydrogen	-4.2	-4.2	-5.4	-5.4

TABLE 98

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

Nominal Residence Time, Hours	1.5	1.5	1.5	1.5
Temperature, °F	800	800	800	800
Molyvan L, ppm Mo:Coal	100	100	100	0
Wender's, ppm Mo:Coal	0	0	0	100
Wt% Fe:Coal	0	0.7	0.7	0.7
$FeSO_4/H_2O$, Wt% Fe:Coal	0.7	0	0	0
TPS-20, Wt%	0	0	5.0	5.0
Wt% Analysis				
360-650°F				
Aromatic C	43	43	42	41
H/C	1.42	1.40	1.43	1.44
N	.41	.42	.46	.40
O	2.9	2.7	2.8	2.6
650-935°F				
Aromatic C	55	56	53	54
H/C	1.20	1.19	1.22	1.22
S	.04	.04	.04	.04
N	.54	.56	.55	.57
O	1.4	1.4	1.3	1.2
935°F+, Solids				
H/C	.80	.80	.84	.84
S	.57	.54	.52	.41
N	1.25	1.19	1.20	1.19

TABLE 99

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

Residence Time, Hours	1.5	1.5
Solvent	Black Thunder	Illinois No. 6
Temperature, °F	800	800
Yields, Wt% MAF Coal		
C1-C3	10.4	9.6
C4-360°F	4	4
360-650°F	25	37
650-935°F	6	17
935°F+	21	3
C_4-935°F	35	58
Conversion	84.5	89.3
Hydrogen	-4.2	-4.6

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

TABLE 100

PROPERTIES OF THE REFERENCE FEEDSTOCK--
PANASOL/COAL RESID BLEND (FSN-106)

(Feedstock for Runs 3A and 4)

Composition:	
C, wt%	90.08
H, wt%	7.96
H/C Ratio	1.06
S, ppm	810
N, ppm	4620
O, wt%	1.86
O, wt% (by Difference)	1.42
Ramscarbon, wt%	17.4
Distillation:(1)	
IBP-650F, wt%	45
650-970F, wt%	7.6
970+F, wt%	47.4

(1) Temperatures are atmospheric pressure equivalents. IBP-650F cut obtained by distilling to an end point (vapor) of 460F at 45mm Hg. 650-970F cut obtained by distilling to an end point of 560F (vapor) at 1mm Hg.

TABLE 101

FEEDSTOCK PROPERTIES OF COAL GAS OIL USED IN RUN 6A[1]

C, wt%	88.54
H, wt%	10.73
H/C ratio	1.46
S, ppm	116
N, ppm	3580
O, wt%	0.35
O, wt% (by diff)	0.36
Aromatic Carbon, C^{13} NMR, %	33.5
Simulated Distillation, °F	
IBP	229
10%	580
20	610
30	633
40	652
50	671
60	691
70	715
80	742
90%	783
FBP	918

[1]From Run 257 at Wilsonville, C/C mode, Illinois No. 6 coal.

TABLE 102

PROPERTIES OF THE PANASOL/COAL RESID BLEND

	Ohio No. 6 Coal[2]	Il No. 6 Coal[3]
Composition:		
C, wt%	91.07	90.36
H, wt%	7.34	7.43
H/C Ratio	0.97	0.99
S, ppm	587	2349
N, ppm	5650	6420
O, wt%	1.36	1.39
O, wt% (by Difference)	0.97	1.33
Ramscarbon, wt%	21.2	23.3
Distillation:[1]		
IBP-650F, wt%	52.4	49.1
650-970F, wt%	5.9	2.4
970+F, wt%	41.7	48.5

(1) Temperatures are atmospheric pressure equivalents. IBP-650F cut obtained by distilling to an end point (vapor) of 460F at 45mm Hg. 650-970F cut obtained by distilling to an end point of 560F (vapor) at 1mm Hg.

(2) Feedstock for Run 3B, Reactor A.

(3) Feedstock for Run 3B, Reactors B and C.

TABLE 103

PROPERTIES OF THE PANASOL/COAL RESID BLEND--
MARTIN LAKE LIGNITE COAL

(Feedstock for Run 3B, Reactors D and E)

Composition:	
C, wt%	90.52
H, wt%	7.72
H/C Ratio	1.02
S, ppm	580
N, ppm	6800
O, wt%	3.32
O, wt% (by Difference)	1.02
Ramscarbon, wt%	15.2
Distillation:(1)	
IBP-650F, wt%	48.8
650-970F, wt%	8.1
970+F, wt%	43.1

(1) Temperatures are atmospheric pressure equivalents. IBP-650F cut obtained by distilling to an end point (vapor) of 460F at 45mm Hg. 650-970F cut obtained by distilling to an end point of 560F (vapor) at 1mm Hg.

TABLE 104

CATALYT EVALUATED IN PILOT PLANT

Commercial Catalyst Bimodal: AMOCAT™ 1C AMOCAT™ 1B TK-771 (Topsoe) Unique: Idemitsu (CoMo with Y/Al_2O_3)	 Unimodal: Shell 411 Shell 324 HDN-60 (Cyanamid) RCM-4 (UOP) Resid HDS (10% Mo/Al_2O_3)
Modified Commercial Catalysts Active Promoter Added: Ru/AMOCAT™ 1A (SRI)	 Support Modifier Added: Ti/AMOCAT™ 1C Cr/AMOCAT™ 1C Ca/AMOCAT™ 1C
Experimental Catalysts In-House Preparations: Ru/AMOCAT™ Ir/AMOCAT™ NiMo/Cabot Aluminas Clarkson University: Mo_2C/Al_2O_3, WC Mo_2N Mo_2N or Mo_2C on AMOCAT™ Alumina	 Sandia: NiMo/HTO PdNiMo/HTO Pd/HTO CoMo/HTO

TABLE 105

TEST OF REPRODUCIBILITY COMPARISON OF PRODUCT QUALITIES FROM AMOCAT™ 1C, RUNS 1-4

	Feed	Run 1	Run 2	Run 3	Run 4	Average Runs 1-4	Std Dev Runs 1-4	% Deviation (100* Std Dev/Average)
C, Wt%	90.08	90.17	90.04	90.37	90.01	90.15	0.14	0.2
H, Wt%	7.96	9.32	9.44	9.52	9.44	9.43	0.07	0.8
H/C	1.06	1.24	1.26	1.26	1.26	1.26	0.01	0.7
S, ppm	810	117	59	55	60	73	26	35
N, ppm	4620	2290	2410	2380	2590	2418	108.9	5
O, wt%	1.86	1.48	1.82	1.04	--	1.45	0.32	22
Rams, Wt%	17.4	9.19	8.36	7.8	8.51	8.47	0.5	6
Distillation Cuts, wt%:								
IBP-650F	45	52.4	53.2	53.7	55.6	53.7	1.18	2
650-970F	7.4	16	18.2	15	14.2	15.9	1.50	9
970+F	47.5	31.6	28.6	31.3	30.2	30.4	1.18	4

TABLE 106

PROPERTIES OF CATALYSTS USED IN RUN 1

	Catalysts				
	AMOCAT™ 1C(1)	HDN-60(2)	Shell 411	Ru/AMOCAT™	Ir/AMOCAT™
Wt% Metals:					
Ni	2.4	2.6	2.4	--	--
Mo	10.7	14.3	14.7	--	--
Ru	--	--	--	3.1	--
Ir	--	--	--	--	3.1
N_2 Desorption:					
S_{BET}, m^2/g	195	155	165	193	194
PV, cm^3/g(3)	0.59	0.4	0.43	0.75	0.72
Hg Porosity:					
PV, cm^3/g(4)	0.17	--	--	0.21	0.22

(1) Used in Run 257 at Wilsonville.
(2) Criterion.
(3) <1000A diameter pores.
(4) >1000A diameter pores.

TABLE 107

COMPARISON OF PROPERTIES OF CATALYSTS USED IN RUN 3

	Idemitsu[1]	AMOCAT™ 1C	Shell 324	AMOCAT™ 1B	Resid HDS
Ni, wt%	NA	2.4	2.7	--	--
Mo, wt%	--	10.7	13.2	10.7	6.9
Co, wt%	--	--	--	--	--
S_{BET}, m^2/g	NA	195	150	193	200
PV_{N2} Desorp, cm^3/g	NA	0.59	0.48	0.66	0.65
Hg Porosimetry: PV 1000+ Angstrom Dia, cm^3/g	NA	0.17	--	0.17	--

(1) R-HYC4 (Idemitsu), CoMo/USY/Al_2O_3, cobalt, and molybdenum contents are unavailable.

TABLE 108

COMPARISON OF PHYSICAL PROPERTIES OF CATALYSTS USED IN RUN 4

	AMOCAT™ 1C	RCM-4	TK-771	Ru/AMOCAT™ 1A
Ni, wt%	2.4	1.67	2.7	--
Mo, wt%	10.7	8.7	9.3	~8.7
	--	--	--	~0.51
Co, wt%	--	--	--	~2.2
S_{BET}, m^2/g	195	179	200	~165
PV_{N2} Desorp, cm^3/g	0.59	0.79	0.47	~0.62
Hg Porosimetry:				
PV_{1000+} Angstrom Dia, cm^3/g	0.17	--	--	0.16

TABLE 109

PROCESS CONDITIONS FOR RUN 1A USING GAS OIL FEEDSTOCK[1]

	Catalysts				
Run Condition	AMOCAT™ 1C[1]	HDN-60[2]	Shell 411	Ir/AMOCAT™	Ru/AMOCAT™
LHSV,[1] h^{-1}	1	1	1	1	1
WHSV,[2] h^{-1}	1.9	1.1	1.1	1.8	1.8
Temp, F	700	700	700	700	700
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flow Rate, SCFB	5000	5000	5000	5000	5000

(1) Coal-derived gas oil from Run 257 at Wilsonville, V-1074.

(2) LHSV defined as the ratio of the volumetric flow rate (cm^3/h) of oil feed to the volume (cm^3) of catalyst measured by densely packing within a graduated cylinder.

(3) WHSV defined as the ratio of the weight flow rate (g/h) of oil feed to the weight of catalyst present within the reactor (g).

TABLE 110

PROCESS CONDITIONS FOR RUN 1B USING A COAL-RESID FEEDSTOCK[1]

Catalysts					
Run Condition	AMOCAT™ 1C[1]	HDN-60[2]	Shell 411	Ir/AMOCAT™	Ru/AMOCAT™
LHSV,[1] h^{-1}	0.5	0.5	0.5	0.5	0.5
WHSV,[2] h^{-1}	1.01	0.61	0.60	0.98	0.94
Temp, F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flow Rate, SCFB	10000	10000	10000	10000	10000

(1) 55.5 wt% resid (from CSD, Run 257, Wilsonville), 44.5 wt% Panasol.

(2) LHSV defined as the ratio of the volumetric flow rate (cm^3/h) of oil feed to the volume (cm^3) of catalyst measured by densely packing within a graduated cylinder.

(3) WHSV defined as the ratio of the weight flow rate (g/h) of oil feed to the weight of catalyst present within the reactor (g).

TABLE 111

CATALYSTS AND PROCESS CONDITIONS FOR RUNS 3A AND 3B

Reactor	A	B	C	D	E
Catalyst	Idemitsu	AMOCAT™ 1C	Shell 324	AMOCAT™ 1B	Resid HDS
LHSV,(1) h^{-1}	0.5	0.5	0.5	0.5	0.5
WHSV,(2) h^{-1}	0.79	1.01	0.61	0.99	0.72
Catalyst, g	6.8	5.3	8.8	5.4	7.5
Catalyst, cm^3	10	10	10	10	10
Temp, F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flow Rate, SCFB	10000	10000	10000	10000	10000

(1) LHSV defined as the ratio of the volumetric flow rate (cm^3/h) of oil feed to the volume (cm^3) of catalyst.

(2) WHSV defined as the ratio of the weight flow rate (g/h) of oil feed to the weight of catalyst present within the reactor (g).

TABLE 112

CATALYSTS AND PROCESS CONDITIONS FOR RUN 4[1]

Reactor	A	B	C	D	E
Catalyst	AMOCAT™ 1C	AMOCAT™ 1C	RCM-4	TK-771	Ru/AMOCAT™ 1A
LHSV,[2] h^{-1}	0.5	0.2	0.5	0.5	0.5
WHSV,[3] h^{-1}	1.01	0.41	0.88	0.67	0.88
Catalyst, g	5.3	13.25	6.1	8	6.1
Catalyst, cm^3	10	25	10	10	10
Temp, F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flow Rate, SCFB	10000	10000	10000	10000	10000

(1) 55.5 wt% resid (from CSD, Run 257, Wilsonville), 44.5 wt% Panasol.

(2) LHSV defined as the ratio of the volumetric flow rate (cm^3/h) of oil feed to the volume (cm^3) of catalyst.

(3) WHSV defined as the ratio of the weight flow rate (g/h) of oil feed to the weight of catalyst present within the reactor (g).

TABLE 113

PRODUCT ANALYSES FOR RUN 1B AFTER 9 DAYS ON COAL-RESID

	Catalyst					
	Feed	AMOCAT™ 1C	HDN-60	Shell 411	Ir/AMOCAT™	Ru/AMOCAT™
C, Wt%	90.08	89.72	89.83	89.64	90.76	90.64
H, Wt%	7.96	9.46	9.64	9.7	8.24	8.27
H/C	1.06	1.27	1.29	1.30	1.09	1.09
S, ppm	810	92	86	82	360	316
N, ppm	4620	2190	1600	1620	4610	4230
O by Diff	1.42	0.59	0.36	0.49	0.50	0.64
Ramscarbon	17.4	8.43	7.56	7.17	12.1	11.8
Distillation, wt%:						
IBP-650F	44.95	52.84	54.39	53.92	48.02	49.1
650-970F	7.55	17.09	19.05	20.88	13.88	15.3
970+F	47.49	30.06	26.55	25.19	38.08	35.6
H_2 Consumption, SCFB	--	890	990	890	95	--

TABLE 114

PRODUCT ANALYSES FOR RUN 1B AFTER 17 DAYS ON COAL-RESID

	Catalyst					
	Feed	AMOCAT™ 1C	HDN-60	Shell 411	Ir/AMOCAT™	Ru/AMOCAT™
C, Wt%	90.08	90.17	89.93	89.74	90.67	90.7
H, Wt%	7.96	9.32	9.62	9.59	8.22	8.22
H/C	1.06	1.24	1.28	1.28	1.09	1.09
S, ppm	810	117	54	54	49	41
N, ppm	4620	2290	1700	1700	4740	4610
O by Diff	1.42	0.27	0.49	0.49	0.63	0.61
Ramscarbon	17.4	9.19	7.93	7.93	12.8	12.6
Distillation, wt%:						
IBP-650F	44.95	52.33	54.6	55.51	48.2	48.9
650-970F	7.55	16.01	12.3	16.29	11.8	14.1
970+F	47.49	31.64	30.0	28.18	40.0	37.0
H_2 Consumption, SCFB	--	1000	1200	1100	330	250

TABLE 115

PRODUCT QUALITIES, RUN 3A, DAY 9 ON RESID

	Catalyst					
Reactor Catalyst	Feed	A Idemitsu	B AMOCAT™ 1C	C Shell 324	D AMOCAT™ 1B	E Resid HDS
C, Wt%	90.08	90.53	90.19	90.03	90.68	90.51
H, Wt%	7.96	8.84	9.47	9.53	8.83	8.88
H/C	1.06	1.17	1.26	1.27	1.17	1.18
S, ppm	810	113	56	55	135	170
N, ppm	4620	3250	2240	1840	2900	2810
O, wt%	1.86	1.77	1.31	1.17	1.79	1.23
O (by diff), wt%	1.42	0.29	0.11	0.25	0.19	0.31
Ramscarbon	17.4	10.1	7.72	7.39	9.11	9.6
Distillation Cuts, wt%:						
IBP-650F	44.9	51.7	54.2	54.4	53.6	53.6
650-970F	7.6	11.7	17.9	17.9	14	15
970+F	47.5	36.6	28	27.7	32.4	31.4

TABLE 116

PRODUCT QUALITIES, RUN 3A, DAY 14 RESID

	Catalyst					
Reactor Catalyst	Feed	A Idemitsu	B AMOCAT™ 1C	C Shell 324	D AMOCAT™ 1B	E Resid HDS
C, Wt%	90.08	90.71	90.37	90.05	91.28	90.44
H, Wt%	7.96	8.96	9.52	9.58	8.9	8.88
H/C	1.06	1.19	1.27	1.28	1.17	8.18
S, ppm	810	112	55	48	151	151
N, ppm	4620	3120	2380	1900	3040	3140
O, wt%	1.86	0.91	1.04	1.11	1.09	1.86
O by Diff	1.42	0.01	-0.13	0.18	-0.5	0.35
Ramscarbon, wt%	17.4	10.2	7.8	7.84	9.52	9.41
Distillation Cuts, wt%:						
IBP-650F	44.9	50.7	53.7	54.5	52.8	53
650-970F	7.6	10.4	15	16.7	12.8	14
970+F	47.5	38.9	31.4	28.8	34.4	33

TABLE 117

PSEUDO FIRST ORDER RATE CONSTANTS FOR CATALYSTS USED IN RUN 3A, DAY 9

	k_v[1]/k_{Mo}[2]				
	Idemitsu[3]	AMOCAT™ 1C	Shell 324	AMOCAT™ 1B	Resid HDS
Denitrogenation	0.18/NA	0.36/6.8	0.46/4.3	0.23/4.3	0.25/5.2
Ramsbottom Carbon	0.27/NA	0.41/7.7	0.43/4.0	0.32/5.9	0.32/6.7
Resid (970+F)	0.13/NA	0.26/4.9	0.27/2.5	0.19/3.5	0.21/4.4

(1) k_v = LHSV 0 (ln Co/C) where Co = feed concentration and C = product concentration of nitrogen, Ramsbottom carbon, or resid. LHSV was defined in Table 1.

(2) k_{Mo} = (WHSV/x_{Mo})O(ln Co/C) where x_{Mo} is the weight fraction molybdenum on the catalyst. WHSV was defined in Table 1, and Co and C were defined above.

(3) Molybdenum contents are unavailable.

TABLE 118

PSEUDO FIRST ORDER RATE CONSTANTS, RUN 3A, DAY 14

	$k_v^{(1)}/k_{Mo}^{(2)}$				
	Idemitsu[3]	AMOCAT™ 1C	Shell 324	AMOCAT™ 1B	Resid HDS
Denitrogenation	0.2/NA	0.33/6.2	0.44/4.1	0.21/3.9	0.19/4.0
Ramsbottom Carbon	0.27/NA	0.40/7.6	0.40/3.7	0.30/5.6	0.31/6.5
Resid (970+F)	0.10/NA	0.21/4.0	0.25/2.3	0.16/3.0	0.18/3.8

(1) k_v = LHSV O (ln Co/C) where Co = feed concentration and C = product concentration of nitrogen, Ramsbottom carbon, or resid. LHSV was defined in Table 1.

(2) k_{Mo} = (WHSV/x_{Mo})O(ln Co/C) where x_{Mo} is the weight fraction molybdenum on the catalyst. WHSV was defined in Table 1, and Co and C were defined above.

(3) Molybdenum contents are unavailable.

TABLE 119

PRODUCT QUALITIES, RUN 4, DAY 11 ON RESID

Reactor Catalyst	Feed	A AMOCAT™ 1C(1)	B AMOCAT™ 1C(2)	C RCM-4	D TK-771	E Ru/AMOCAT™ 1A
C wt%	90.08	90.00	89.56	89.99	89.97	89.95
H wt%	7.96	9.44	10	9.49	9.57	9.58
H/C	1.06	1.26	1.34	1.27	1.28	1.28
S, ppm	810	60	61	69	50	75
N, ppm	4620	2590	1520	2570	2170	2620
O, wt%	1.86					
O (by diff)	1.42	0.30	0.28	0.26	0.24	0.20
Ramscarbon	17.4	8.51	4.46	8.37	7.72	7.92
Distillation Cuts:						
wt%						
IBP-650°F	44.9	55.6	58.7	56.5	56	55.7
650-970°F	7.6	14.2	17.1	13.3	14.6	13.9
970+°F	47.5	30.2	24.2	30.2	29.4	30.4

(1) LHSV = 0.5

(2) LHSV = 0.2

TABLE 120

PSEUDO FIRST ORDER RATE CONSTANTS FOR CATALYSTS USED IN RUN 4, DAY 11

	$k_v^{(1)}/k_{Mo}^{(2)}$				
	AMOCAT™ 1C (0.5 LHSV)	AMOCAT™ 1C (0.2 LHSV)	RCM-4	TK-771	Ru/AMOCAT™ 1A
Denitrogenation	0.29/5.5	0.22/4.2	0.29/5.9	0.38/5.5	0.28/5.6
Ramsbottom Carbon	0.36/6.8	0.27/5.2	0.37/7.5	0.41/5.9	0.39/7.9
Resid (970+F)	0.23/4.3	0.13/2.5	0.23/4.7	0.24/3.5	0.22/4.5

(1) k_v = LHSV O (ln Co/C) where Co = feed concentration and C = product concentration of nitrogen, Ramsbottom carbon, or resid. LHSV was defined in Table 1.

(2) k_{Mo} = (WHSV/x_{Mo})O(ln Co/C) where x_{Mo} is the weight fraction molybdenum on the catalyst. WHSV was defined in Table 1, and Co and C were defined above.

TABLE 121

PRODUCT ANALYSES FOR RUN 1A AFTER 10 DAYS ON OIL

	Catalyst					
	Feed	AMOCAT™-1C	HDN-60	Shell 411	Ir/AMOCAT™	Ru/AMOCAT™
C, Wt%	89.41	89.25	89.27	89.29	89.52	89.5
H, Wt%	9.71	10.31	10.37	10.37	9.81	9.81
H/C	1.30	1.39	1.39	1.39	1.32	1.32
S, ppm	232	69	52	49	392	201
N, ppm	3580	2530	1870	1760	3290	3490
O by Diff	0.50	0.18	0.17	0.16	0.30	0.32
H_2 Consumption, SCFB	--	156	165	165	--	--

TABLE 122

PRODUCT QUALITIES, RUN 3B, OHIO NO. 6 RESID FEED

Reactor Catalyst	Feed	A Idemitsu
C, wt%	91.07	90.34
H, wt%	7.34	9.29
H/C	0.97	1.24
S, ppm	587	132
N, ppm	5650	3160
O, wt%	1.36	--
O (by diff)	0.97	0.05
Ramscarbon	21.2	14.1
Distillation Cuts, wt%:		
IBP-650F	52.4	57
650-970F	5.9	7.3
970+F	41.7	35.7

TABLE 123

PRODUCT QUALITIES, RUN 3B, MARTIN LAKE LIGNITE RESID

Reactor Catalyst	Feed	D AMOCAT™ 1B	E Resid HDS
C, wt%	90.52	90.5	91.17
H, wt%	7.72	9.19	8.28
H/C	1.02	1.22	1.09
S, ppm	580	128	139
N, ppm	6800	3160	2510
O, wt%	3.32	--	--
O (by diff)	1.02	-0.03	0.21
Ramscarbon	15.2	14.1	9.64
Distillation Cuts, wt%:			
IBP-650F	48.8	57.5	55.4
650-970F	8.1	16.5	12.5
970+F	43.1	26	32.1

TABLE 124

PRODUCT QUALITIES, RUN 3B, ILLINOIS NO. 6 RESID-T/C MODE

Reactor Catalyst	Feed	B AMOCAT™ 1C	C Shell 324
C, wt%	90.36	91.15	90.83
H, wt%	7.43	8.26	9.19
H/C	0.99	1.09	1.22
S, ppm	2349	125	112
N, ppm	6420	3080	2510
O, wt%	1.39	NA	NA
O (by diff)	1.33	0.35	-0.22
Ramscarbon	23.2	9.62	9.63
Distillation Cuts, wt%:			
IBP-650F	49.1	59	59.6
650-970F	2.41	2.8	12
970+F	48.5	28.2	28.4

TABLE 125

COMPARISON OF PROPERTIES OF CATALYSTS USED IN RUN 5

	LoTi/AMOCAT™1C	HiTi/AMOCAT™1C	AMOCAT™1C	LoCr/AMOCAT™1C	HiCr/AMOCAT™1C
Ni, wt%	1.8	1.66	2.67	1.93	2.33
Mo, wt%	9.2	8.4	9.34	8.5	8.4
Ti, wt%	2.91	5.8	--	--	--
Cr, wt%	--	--	--	2.4	5.5
S_{BET}, m^2/g	168	161	200	172	160
PV_{N2} Desorp, cm^3/g	0.62	0.58	0.47	0.53	0.52
Hg Porosimetry					
$P_{1000 angstrom\ Dia}$, cm^3/g	0.18	0.17	0.17	0.15	0.13

TABLE 126

CATALYSTS AND PROCESS CONDITIONS FOR RUN 5

Reactor	A	B	C	D	E
Catalyst	LoTi/AMOCAT™1C	HiTi/AMOCAT™1C	AMOCAT™1C	LoCr/AMOCAT™1C	HiCr/AMOCAT™1C
LHSV(2),h-1	0.5	0.5	0.5	0.5	0.5
WHSV(3),h-1	0.83	0.81	1.01	0.81	0.79
g Catalyst	6.5	6.65	5.3	6.65	6.8
cm^3 Catalyst	10	10	10	10	10
Temp., F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flowrate, SCFB	10000	10000	10000	10000	10000

(1) 55.5 wt% resid (from CSD, Run 257, Wilsonville), 44.5 wt% Panasol.

(2) LHSV defined as the ratio of the volumetric flowrate (cm^3/h) of oil feed per volume of catalyst (cm^3).

(3) WHSV defined as the ratio of the weight flowrate (g/h) of oil feed to the weight of catalyst present within the reactor (g).

TABLE 127

PRODUCT QUALITIES, RUN 5, DAY 11, ON RESID

Reactor		A	B	C	D	E
Catalyst	Feed	LoTi/ AMOCAT™ 1C	HiTi/ AMOCAT™ 1C	AMOCAT™ 1C	LoCr/ AMOCAT™ 1C	HiCr/ AMOCAT™ 1C
C, wt%	90.08	90.18	90.38	90.21	90.18	90.33
H, wt%	7.96	9.56	9.33	9.48	9.23	9.18
H/C	1.06	1.27	1.24	1.26	1.23	1.22
S, ppm	810	58	56	46	73	100
N, ppm	4620	2410	2360	2390	3000	3010
O, wt%	1.86	0.26	0.17	0.21	0.15	0.17
O (by diff)	1.42	0.01	0.05	0.07	0.28	0.18
Ramscarbon, wt%	17.4	7.94	8.04	7.64	8.29	9.19
Distillation Cuts, wt%:						
IBP-650F	44.9	54	54.3	54.5	53.5	54.6
650-970F	7.6	11	11.8	10.2	16.1	6.6
970+F	47.5	35	34.1	35.3	30.4	38.8

TABLE 128

PRODUCT QUALITIES, RUN 5, DAY 16, ON RESID

Reactor		A	B	C	D	E
Catalyst	Feed	LoTi/ AMOCAT™ 1C	HiTi/ AMOCAT™ 1C	AMOCAT™ 1C	LoCr/ AMOCAT™ 1C	HiCr/ AMOCAT™ 1C
C, wt%	90.08	90.08	89.2	90.3	90.25	90.2
H, wt%	7.96	9.34	9.24	9.38	9.24	9.15
H/C	1.06	1.25	1.24	1.25	1.23	1.22
S, ppm	810	58	66	39	65	89
N, ppm	4620	2420	2460	2560	2890	2980
O, wt%	1.86	0.18	0.12	0.17	0.18	0.16
O (by diff)	1.42	0.33	1.31	0.06	0.21	0.34
Ramscarbon, wt%	17.4	7.76	9.05	8.56	8.79	9.28
Distillation Cuts, wt%:						
IBP-650F	44.9	56.4	53.2	54.3	54.3	54.6
650-970F	7.6	14.5	15.5	15.5	16.7	14.5
970+F	47.5	29.1	31.3	30.2	30	30.9

TABLE 129

HYDROGEN CONSUMPTION, SCFB

Total H_2 Consumption/H_2 Incorporated into Liquid Product(1)

Reactor	A	B	C	D	E
Catalyst	LoTi/ AMOCAT™ 1C	HiTi/ AMOCAT™ 1C	AMOCAT™ 1C	LoCr/ AMOCAT™ 1C	HiCr/ AMOCAT™ 1C
Day 11	920/700	780/560	830/640	730/520	670/470
Day 16	460/230	640/420	690/500	560/350	590/380

(1) H_2 incorporated into liquid product = total H_2 consumed - H_2 incorporated into off-gases (C_1-C_4).

TABLE 130

USED CATALYST PROPERTIES

	A LoTi/AMOCAT™1C	B HiTi/AMOCAT™1C	C AMOCAT™1C	D LoCr/AMOCAT™1C	E HiCr/AMOCAT™1C
Elemental Analysis					
C wt%	11.58	12.04	15.54	10.66	11.43
H wt%	1.16	1.12	1.43	1.14	1.17
H/C ratio	1.20	1.12	1.10	1.28	1.23
Surface Area					
Fresh S_{BET}, m^2/g	168	161	200	172	160
Used S_{BET}, m^2/g	137	129	122	166	132
Pore Volume, Digisorb Desorp.					
Fresh PV, cm^3/g	0.62	0.58	0.47	0.53	0.52
Used PV, cm^3/g	0.343	0.353	0.357	0.430	0.345

TABLE 131

PRODUCT QUALITIES AT FIRST MASS BALANCE, RUN 8[1]

Reactor	Feed	AMOCAT™ 1C	Ca/AMOCAT™ 1C
C, wt%	90.47	89.64	89.99
H, wt%	7.92	9.37	9.4
H/C Ratio	1.05	1.26	1.25
N, ppm	4570	2610	2420
S, ppm	980	150	113
O, wt%	1.86	--	--
Total	98.95	99.29	99.64
O (by diff), wt%	1.06	0.71	0.36
Ramscarbon, wt%	14.7	8.75	5.91
Distillation:			
IBP-650F	42.8	50.5	54.9
650-1000F	7.4	12.2	20.8
1000+F	49.8	37.3	24.3

(1) 168 hours on oil.

TABLE 132

PRODUCT QUALITIES AT SECOND MASS BALANCE, RUN 8[1]

Reactor	Feed	AMOCAT™ 1C	Ca/AMOCAT™ 1C
C, wt%	90.47	89.78	89.91
H, wt%	7.92	9.25	9.31
H/C Ratio	1.05	1.24	1.24
N, ppm	4570	3310	2780
S, ppm	980	304	202
O, wt%	1.86	0.69	0.68
Total	98.95	99.39	99.52
O (by diff), wt%	1.06	--	--
Ramscarbon, wt%	14.7	8.53	9.10
Distillation:			
IBP-650F	42.8	44.3	54.4
650-1000F	7.4	12.5	14.9
1000+F	49.8	43.2	30.7

(1) 336 hours on oil.

TABLE 133

COMPARISON OF PHYSICAL PROPERTIES
OF NiMo/CABOT ALUMINA CATALYSTS WITH AMOCAT™ 1C

	AMOCAT™ 1C	1.2 Cabot	1.4 Cabot	1 Cabot
Metals Analysis:				
Ni, wt%	2.4	2.63	2.69	2.8
Mo, wt%	10.7	10.4	10.7	10.8
N_2 Desorption:				
SA_{BET}, m^2/g	195	158	138	137
PV_{N2} Desorp, cm^3	0.59	0.42	0.43	0.41
Hg Porosimetry:				
PV_{1000+} Angstrom Dia, cm^3/g	0.17	0.4	0.65	1.1

TABLE 134

PROCESS CONDITIONS FOR AU-126 RUN 2

Reactor Catalyst	A AMOCAT™ 1C	B 1.2 Cabot	C 1.4 Cabot	D 1.7 Cabot	E 1.7 Cabot
LHSV,(1) h^{-1}	0.5	0.5	0.5	0.5	0.31
WHSV,(2) h^{-1}	1.01	1.22	1.38	1.73	1.01
Catalyst, g	5.3	4.4	3.9	3.1	5.3
Catalyst, cm^3	10	10	10	10	16
Temp, F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flow Rate, SCFB	10000	10000	10000	10000	10000

TABLE 135

PRODUCT QUALITIES AT DAY 7 ON RESID

Reactor Catalyst	Feed	A AMOCAT™ 1C	B 1.2 Cabot	C 1.4 Cabot	D 1.7 Cabot	E 1.7 Cabot
C, wt%	90.08	90.09	90.25	90.4	90.41	89.97
H, wt%	7.96	9.5	9.23	9.05	9.85	9.29
H/C Ratio	1.06	1.27	1.23	1.20	1.31	1.24
S, ppm	810	55	79	97	104	88
N, ppm	4620	2160	3030	3250	3470	2990
O, wt%	1.86	0.8	1.68	1.8	2.35	1.48
O (by diff), wt%	1.42	0.19	0.21	0.22	-0.62	0.43
Ramscarbon, wt%	17.4	8.05	9.74	9.72	10.1	9.2
Distillation:						
IBP-650F	44.9	54.67	52.9	51.5	51.2	53.5
650-970F	7.6	18.2	13.3	14.5	12.7	16.6
970+F	47.5	31.83	33.7	38.7	37.1	33.5

TABLE 136

PRODUCT QUALITIES AT DAY 15 ON RESID

Reactor Catalyst	Feed	A AMOCAT™ 1C	B 1.2 Cabot	C 1.4 Cabot	D 1.7 Cabot	E 1.7 Cabot
C, wt%	90.08	90.04	90.22	90.42	90.61	90.24
H, wt%	7.96	9.44	9.17	9.02	8.92	9.19
H/C Ratio	1.06	1.26	1.22	1.20	1.18	1.22
S, ppm	810	59	84	95	105	153
N, ppm	4620	2410	3250	3450	3540	3110
O, wt%	1.86	1.82	1.94	2.4	4.09	4.54
O (by diff), wt%	1.42	0.27	0.28	0.21	0.11	0.24
Ramscarbon, wt%	17.4	8.36	9.11	9.7	10.2	8.7
Distillation:						
IBP-650F	44.9	53.2	52.0	52.9	51.3	51.9
650-970F	7.6	18.2	13.3	14.5	12.7	16.6
970+F	47.5	28.6	34.8	32.7	35.7	31.6

TABLE 137

PSEUDO FIRST ORDER RATE CONSTANTS (hr^{-1})
ON A PER VOLUME CATALYST BASIS k_v AT DAY 7/DAY 15 ON RESID

	AMOCAT™ 1C	1.2 Cabot	1.4 Cabot	1.7 Cabot(1)	1.7 Cabot(2)
Denitrogenation	0.38/0.33	0.21/0.18	0.18/0.15	0.14/0.13	0.14/0.12
Ramscarbon Removal	0.39/0.37	0.29/0.32	0.29/0.29	0.27/0.27	0.20/0.22
Resid Conversion	0.20/0.25	0.17/0.16	0.10/0.19	0.12/0.14	0.11/0.13

(1) 10 cm^3 catalyst loaded in reactor.
(2) 16 cm^3 catalyst loaded in reactor.

TABLE 138

COMPARISON OF USED CATALYST PROPERTIES[1]

	AMOCAT™ 1C	1.2 Cabot	1.4 Cabot	1.7 Cabot	1.7 Cabot
C, wt%	10.07	5.45	7.28	8.27	6.98
H, wt%	1.57	1.25	1.03	1.11	1.09
Digisorb Desorption:					
Fresh S_{BET}, m^2/g	195	158	138	137	137
Used PV, cm^3/g	119	90	80	72	62
Fresh PV, cm^3/g	0.59	0.42	0.43	0.41	0.21
Used PV, cm^3/g	0.34	0.17	0.26	0.16	0.21
Hg Porosimetry:					
Fresh 1000 Å+, dia	0.17	0.4	0.65	1.1	1.1
Used 1000 Å+, dia	0.156	0.386	0.597	0.968	1.18

(1) Catalysts were Soxhlet extracted with THF prior to analyses.

TABLE 139

PROCESS CONDITIONS FOR HYDROTREATING, RUN 6A

Reactor	A	B	C	D	E
Catalyst	Mo_2N	Mo_2C/Al_2O_3	Shell 324	Thermal	AMOCAT™-1B
cm^3 catalyst[1]	8.4	3.4	1.2	0	1.6
g catalyst	14	2.44	0.73	0	0.69
cm^3 oil/h	4	4	4	4	4
LHSV[2]	0.48	1.2	3.3	--	2.5
WHSV[3]	0.28	1.6	5.3	--	5.6
Temperature, °F	680	680	680	680	680
Pressure, psig	2000	2000	2000	2000	2000

[1] 14/20 mesh particles densely packed in a graduated cylinder.

[2] Volume oil per hour divided by volume of catalyst.

[3] Weight of oil per hour divided by weight of catalyst.

TABLE 140

PROCESS CONDITIONS FOR RESID HYDROTREATING, RUN 6B

Reactor	A	B	C	D	E
Catalyst	Mo_2N	Mo_2C/Al_2O_3	Shell 324	Thermal	AMOCAT™-1B
cm^3 catalyst[1]	8.4	3.4	1.2	0	1.6
g catalyst	14	2.44	0.73	0	0.69
cm^3 oil/h	5	5	5	5	5
LHSV[2]	0.6	1.5	4.2	--	3.1
WHSV[3]	0.38	2.2	7.4	--	7.8
Temperature, °F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000

[1] 14/20 mesh particles densely packed in a graduated cylinder.

[2] Volume oil per hour divided by volume of catalyst.

[3] Weight of oil per hour divided by weight of catalyst.

TABLE 141

COMPARISON OF SURFACE AREAS AND CHEMISORPTION RESULTS

	Mo_2N	Mo_2C/Al_2O_3	Shell 324	AMOCAT™-1B
μmol O/g, static	--	--	984	1014[1]
μmol O/g, dynamic	--	--	167	99
μmol CO/g, static	51	110	--	--
μmol CO/g, dynamic	--	--	15	9.4
m^2/g, BET	21.5	238	155	193

[1] Estimated

TABLE 142

COMPARISON OF REACTOR PACKINGS ON VARIOUS BASES

Reactor	A	B	C	D	E
Catalyst	Mo_2N	Mo_2C/Al_2O_3	Shell 324	Thermal	AMOCAT-1B
cm^3	8.4	3.4	1.2	--	1.6
g	14	2.44	0.73	--	0.69
μmol O (static)	--	--	718	--	700[1]
μmol O (pulse)	--	--	122	--	68
μmol CO (static)	714	268	--	--	--
μmol CO (pulse)	--	--	11.3	--	6.5
m^2 (BET)	301	581	113	--	133
μmol N_2 (BET)[2]	3084	5953	1158	--	136

[1] Estimated

[2] Calculated by assuming one adsorbed N_2 molecule occupies 0.162 nm^2.

TABLE 143

PRODUCT QUALITIES AFTER 256h ON OIL FROM RUN 6A[1]

Reactor	A	B	C	D	E	Feed
Catalyst	Mo_2N	Mo_2C/Al_2O_3	Shell 324	Thermal	AMOCAT™-1B	
C, wt%	88.76	88.64	88.68	88.35	88.64	88.90
H, wt%	11.05	10.83	10.79	10.73	10.77	10.73
H/C ratio	1.50	1.47	1.46	1.46	1.46	1.46
S, ppm	28	49	38	84	55	116
N, ppm	1730	2410	2890	3480	2900	3588
O, wt%	0.15	0.20	0.22	0.33	0.27	0.30
O (by diff)	0.01	0.28	0.24	0.56	0.29	0.31
C_{13} NMR, Aromatics	29.6	32.1	32.3	33.4	33.0	33.0

[1] After 256h on oil.

TABLE 144

PRODUCT QUALITIES FROM RUN 6B WITH COAL RESID FEEDSTOCK

Reactor	A	B	C	D	E	Feed
Catalyst	Mo_2N	Mo_2C/Al_2O_3	Shell 324	Thermal	AMOCAT™-1B	
C, wt%	90.65	90.84	90.54	90.90	90.93	90.08
H, wt%	8.59	8.49	8.37	8.00	8.16	7.96
H/C ratio	1.14	1.12	1.11	1.06	1.08	1.06
S, ppm	229	344	223	540	306	810
N, ppm	3030	3340	3510	4170	3950	4620
O, wt%	0.43	0.42	0.54	0.76	0.52	1.86
O (by diff)	0.43	0.30	0.72	0.63	0.48	1.42
Rams, wt%	10.0	10.2	11.4	14.4	12.6	17.4
Distillation						
IBP-630°F	52.1	51.1	51.7	50.9	49.7	45
650-970°F	13.9	10.5	7.7	9.6	12.1	7.6
970°F+	34	38.4	40.6	39.5	38.2	47.4

TABLE 145

ESTIMATED RELATIVE FIRST ORDER
RATE CONSTANTS[a] PER "ACTIVE SITE"[b]

Catalyst	Desulfurization	Denitrogenation	Aromatic Saturation[c]
Mo_2N	1.3	3.4	3.4
Mo_2C/Al_2O_3[d]	2.1	5	3.1
MoS_2/Al_2O_3	0.67	0.98	0.41
$Ni\text{-}Mo\text{-}S/Al_2O_3$	1	1	1

[a] Calculated by $[\ln(c_o/c)_i]/[\ln(c_o/c)_{Ni\text{-}Mo}]$.

[b] As titrated by CO for the carbide and nitride and by O for the sulfides.

[c] By C^{13} NMR.

[d] Rate constant corrected by 718/268, the ratio of μmol O uptake by Ni-Mo to CO uptake by Mo_2C in the reactors.

TABLE 146

COMPARISON OF RATE CONSTANTS FOR DENITROGENATION

Reactor	A	B	C	D	E
Catalyst	Mo_2N	Mo_2C/Al_2O_3	Shell 324	Thermal	AMOCAT-1B
Feed N, ppm	3580	3580	3580	3580	3580
Product N, ppm	1730	2410	2890	3480	2990
ln (Feed N/Product N)	0.727	0.396	0.214	0.028	0.18
k_v[1]	0.485	0.653	1	--	0.631
k_w[2]	0.177	0.554	1	--	0.890
k_O, static[3]	--	--	2.98×10^{-4}	--	2.57×10^{-4}
k_O, pulse[4]	--	--	1.75×10^{-3}	--	2.65×10^{-3}
k_{CO}, static[5]	1.02×10^{-3}	1.48×10^{-3}	--	--	--
k_{CO}, pulse[6]	--	--	1.89×10^{-2}	--	2.77×10^{-2}
k_{N2}[7]	2.36×10^{-4}	1.65×10^{-5}	1.85×10^{-4}	--	1.32×10^{-4}

(1) Calculated by ln (Feed N/Product N)/(volume of catalyst) and then normalized to Shell 324.
(2) ln (Feed N/Product N)/(weight of catalyst) and then normalized to Shell 324.
(3) ln (Feed N/Product N)/(μmoles oxygen atoms adsorbed in static mode).
(4) ln (Feed N/Product N)/(μmoles oxygen atoms adsorbed in pulse mode).
(5) ln (Feed N/Product N)/(μmoles CO adsorbed in static mode).
(6) ln (Feed N/Product N)/(μmoles CO adsorbed in pulse mode).
(7) ln (Feed N/Product N)/(μmoles N_2 adsorbed in a monolayer during BET adsorption).

TABLE 147

SURFACE COMPOSITIONS MEASURED BY XPS

Mo_2N, atom %								
	C	O	Mo	S	N	Na	Al	Si
fresh	24.4	29.2	21.3	--	25.0	--	--	--
used	46.8	28.6	12.5	3.2	7.9	--	--	0.9
reduced[1]	12.8	42.9	26.2	--	18.1	--	--	--
Mo_2C/Al_2O_3, atom %								
	C	O	Mo	S	N	Na	Al	Si
fresh	4.8	37.8	1.9	--	--	--	55.5	--
used	33.4	40.0	2.0	1.4	0.8	0.2	22.2	--
reduced[1]	3.1	60.4	4.7	--	--	--	31.7	--

[1] Fresh catalyst reduced with flowing H_2 at atmospheric pressure and 790°F.

TABLE 148

BINDING ENERGIES MEASURED BY XPS OF THE FRESH, USED AND FRESH-REDUCED CATALYSTS

Catalyst	C_{1s}	O_{1s}	$Mo_{3d5/2}$		S_{2p}
Mo_2N Fresh	284.5 (80%) 280.9 (11%) 287.3 (9%)	531.1	Mo^{+4} 229.2 (53%)	Mo^{+6} 232.6 (47%)	--
Mo_2N used	284.7 (69%) 283.1 (21%) 280.3 (10%)	531.0	Mo^{+4} 228.9 (63%)	Mo^{+6} 232.4 (37%)	162.2 (91%) 169.0 (9%)
Mo_2N Reduced	284.5 (65%) 286.3 (18%) 288.6 (9%) 281.0 (8%)	530.6	Mo^{+4} 229.7 (53%)	Mo^{+6} 231.7 (34%) 233.5 (12%)	--
Catalyst	C_{1s}	O_{1s}	$Mo_{3d5/2}$		S_{2p}
Mo_2C/Al_2O_3 Fresh	284.5 (62%) 286.3 (26%) 288.9 (12%)	530.9	Mo^{+4} 229.6 (15%)	Mo^{+6} 232.4 (85%)	--
Mo_2C/Al_2O_3 Used	284.6	531.3	Mo^{+4} 229.6 (46%)	Mo^{+6} 232.6 (54%)	162.0 (68%) 168.9 (32%)
Mo_2C/Al_2O_3 Reduced	284.4 (61%) 285.8 (31%) 288.5 (8%)	531.4	Mo^{+4} 231.8 (20%)	Mo^{+6} 233.1 (80%)	--

(1) Numbers in parenthesis within the table are the atom percent of the element with the indicated binding energy.

TABLE 149

CATALYST LOADINGS IN REACTORS

Reactor	A	B	C	D	E
Catalyst	Shell 324	WC	Mo_2N	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
cm^3 Catalyst	10	6	10	10	10
g Catalyst	8.9	14.7	13.9	5.4	5.2
Process Conditions--Gas Oil					
Feed Rate, cc/h	5,10,20,10	5,10,20,10	5,10,20,10	5,10,20,10	5,10,20,10
LHSV, h^{-1}	0.5,1,2,1	0.5,1,2,1	0.5,1,2,1	0.5,1,2,1	0.5,1,2,1
Temperature, °F	700	700	700	700	700
Pressure, psig	2000	2000	2000	2000	2000
Process Conditions--Resid					
Feed Rate, cc/h	5	5	5	5	5
Temperature, °F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000

TABLE 150

FEEDSTOCK PROPERTIES

Designation	FSN-100	FSN-100 New	FSN-100+CS_2	
Description	Coal Gas Oil	Coal Gas Oil[1]	CS_2-Spiked Coal Gas Oil	Resid/Panasol Blend
Carbon, Wt%	89.51	88.94	89.54	90.9
Hydrogen, Wt%	9.74	9.63	9.78	7.93
H/C Ratio	1.31	1.30	1.31	1.05
Nitrogen, ppm	3820	3600	3950	4920
Sulfur, ppm	268	218	2070	800
Oxygen, Wt%	0.89	0.44	0.47	0.73
% Aromatic Carbon, C^{13} NMR	42.3	41.5	41.5	69.6
Distillation, Wt%:[2]				
IBP-650°F				48.9
650-1000°F				5.8
1000°F+				45.3

[1]Taken from a different drum than FSN-100 (column 2 above) and designated FSN-100 NEW.

[2]Temperatures are atmospheric pressure equivalents; IBP-650°F obtained by distilling to an EP (vapor) of 460°F at 45 mm Hg; 650-970°F obtained by distilling to an EP (vapor) of 560°F at 1 mm Hg.

TABLE 151

CHARACTERIZATION OF CATALYSTS BY CO CHEMISORPTION

	WC	Mo_2N	Mo_2C	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
μmol CO/g	45	--	37	41	63

TABLE 152

SURFACE COMPOSITION (ATOM%) MEASURED BY XPS
ON FRESH CATALYST REDUCED IN SITU
WITH HYDROGEN AT 790°F FOR 5 HOURS

Sample	Treatment	C	O	Al	Mo	W	Si	F	Na	N
Mo_2N	As Received	24.4	24.5	--	24.3	--	--	--	--	24.3
	790°F/H_2	16.9	27.2	--	33.6	--	--	--	--	22.4
WC	As Received	54.7	18.5	--	--	26.8	--	--	--	--
Mo_2C	As Received	59.7	10.5	--	29.7	--	--	--	--	--
	790°F/H_2	53.4	8.7	--	37.9	--	--	--	--	--
Mo_2N/AMOCAT™	As Received	16.2	47.9	30.2	2.0	--	2.2	0.2	0.4	1.0
	790°F/H_2	3.6	53.1	37.3	2.5	--	1.8	0.2	0.2	1.2
Mo_2C/AMOCAT™	As Received	18.7	45.6	31.2	2.1	--	2.3	--	--	--
	790°F/H_2	6.7	51.8	36.1	2.3	--	2.5	0.4	0.1	--

TABLE 153

XPS MEASURED BINDING ENERGIES (eV)
MEASURED ON FRESH CATALYSTS
REDUCED IN H_2 AT 790°F FOR 5 HOURS

Sample	Treatment	C1s	Mo3d5/2	W4f7/2	N1s
Mo_2N[b]	As received	284.6(73) 286.1(20)	228.7(59) 231.8(41)		397.3(85) 400.2(15)
	790°F/H_2	284.6(82) 286.3(18) 288.5(7)	228.8(68) 230.8(32)		397.6(83) 400.4(17)
Mo_2N/AMOCAT™	As received	285.0(87)[c] 287.6(13)	229.8(28) 232.1(72)		396.7 74.5
	790°F/H_2	284.4(82) 286.2(18)	229.8(25) 232.6(75)		397.2 74.5
Mo_2C[b]	As received	284.6(61) 283.2(27) 285.9(12)	228.2(84) 229.4(16)		
	790°F/H_2	284.6(58) 283.4(27) 285.9(15)	228.3(63) 229.4(27)		
Mo_2C/AMOCAT™[a]	As received	--	229.0(46) 231.8(54)		
	790°F/H_2	284.2(73) 286.0(20) 288.7(7)	229.2(58) 231.9(42)		
WC	As received	284.6(55) 282.9(30) 286.3(15)		31.8(74) 35.7(26)	

a. BE's were referenced to Al_2p at 74.5 eV.
b. BE's were referenced to C1s at 284.6 eV.
c. Numbers in parentheses are percent of component in the total peak envelope.

TABLE 154

SURFACE COMPOSITION (ATOM%)
MEASURED BY XPS ON USED CATALYSTS

													N/Mo or W Ratio	
Sample	C	O	Si	Mo	N	Al	Ni	S	P	Ca	W	S/Mo or W Ratio	Fresh	Used
Shell 324	33.4	35.2	--	1.5	1.1	23.9	0.1	3.0	1.7	--	--	2	--	0.73
WC	65.8	12.6	--	--	1.9	--	--	3.7	--	--	16.0	0.23	--	--
Mo_2N	58.6	13.8	--	13.0	6.7	--	--	6.9	--	0.8	--	0.53	0.66	0.51
Mo_2N/AMOCAT™	41.2	30.4	1.6	1.2	1.1	23.6	--	1.0	--	--	--	0.83	0.5	0.91
Mo_2C/AMOCAT™	43.5	30.6	--	1.5	--	23.2	--	1.0	--	0.1	--	0.67	--	--

TABLE 155

XPS MEASURED BINDING ENERGIES (eV)
MEASURED ON SPENT CATALYSTS

Sample	C1S	Mo3d5/2	W4f7/2	N1s	S2p
Shell 324[a]	284.5(81)[c] 285.7(19)	229.1		400.6	162.1
WC[b]	283.0(14) 284.6(67) 285.8(19)		31.9(80) 35.6(20)	400.6	162.3(80) 169.2(20)
Mo_2N[b]	284.6(87) 280.8(13)	228.6(83) 231.2(17)		397.4	161.8
Mo_2N/AMOCAT™[a]	284.6(76) 285.7(20) 289.3(4)	229.2(61) 232.1(39)		400.2	161.9
Mo_2C/AMOCAT™[a]	284.6(91) 286.3(6) 289.3(3)	228.9(73) 231.9(27)			162.2

a. BE's were referenced to Al_2p at 74.5 eV.
b. BE's were referenced to C1s at 284.6 eV.
c. Numbers in parentheses are percent of component in the total peak envelope.

TABLE 156

CHARACTERIZATION OF CATALYSTS BY
BY BET SURFACE AREA AND N_2 DESORPTION

	Shell 324	WC	Mo_2N	Mo_2C	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
N_2 Desorption						
Fresh Catalyst:						
Pore Volume, cm^3/g	0.416	0.068	0.075	0.537	--	--
Average Pore Diameter (4V/A), Å	104	91	31	716	--	--
Used Catalyst:						
Pore Volume, cm^3/g	0.253	--	--	--	--	--
Average Pore Diameter (4V/A), Å	78	--	--	--	--	--
BET Surface Area, m^2/g						
Fresh Catalyst:						
Clarkson	--	44	--	61	198	261
Micromeritics	160	30	96	30	--	--
Used Catalyst:						
Amoco	129	--	--	--	--	--

TABLE 157

PRODUCT QUALITIES AND CONVERSIONS
AFTER 72 HOURS ON COAL GAS OIL AT 5 CC/H FEED RATE

	Feed	Shell 324	WC	Mo_2N	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
Carbon, Wt%	89.51	89.39	89.64	89.28	89.62	89.47
Hydrogen, Wt%	9.74	10.41	10.2	10.17	10.07	10.15
H/C	1.31	1.40	1.37	1.37	1.35	1.36
Nitrogen, ppm	3820	2040	2130	2260	2900	2700
Sulfur, ppm	268	75	231	372	333	339
Oxygen, Wt%	0.89	0.14	0.22	0.25	0.21	0.2
C^{13} NMR, %	42.3	34.1	37.5	37.6	38.7	38.5
% Increase in H/C		7.0	4.6	4.7	3.3	4.3
N Conversion, %		47	44	41	24	29
S Conversion, %		72	14	0	0	0
O Conversion, %		84	75	72	76	78
Conversion of Aromatics (C^{13} NMR), %		19	11	11	9	9
Rate Constants:(1)						
kv, hdn		1.00	1.55	0.84	0.44	0.55
kv, hds		1.00	0.00	0.00	0.00	0.00
kv, hdo		1.00	1.26	0.69	0.78	0.81
kv, hyd(2)		1.00	0.93	0.55	0.41	0.44
kw, hdn		1.00	0.56	0.54	0.72	0.95
kw, hds		1.00	0.00	0.00	0.00	0.00
kw, hdo		1.00	0.46	0.44	1.29	1.38
kw, hyd(2)		1.00	0.34	0.35	0.68	0.75

(1) First-order kinetics for HDN, HDO, and HYD, second-order for HDS relative to Shell 324.
(2) Using conversion measured by C^{13}-NMR.

TABLE 158

PRODUCT QUALITIES AND CONVERSIONS
AFTER 120 HOURS ON COAL GAS OIL, 10 CC/H FEED RATE

	Feed	Shell 324	WC	Mo_2N	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
Carbon, Wt%	89.51	89.41	88.91	89.43	89.7	89.6
Hydrogen, Wt%	9.74	10.18	9.96	9.99	10.01	10.03
H/C	1.31	1.37	1.34	1.34	1.34	1.34
Nitrogen, ppm	3820	2270	2150	2190	2750	2790
Sulfur, ppm	268	131	266	274	284	368
Oxygen, Wt%	0.89	0.2	0.3	0.29	0.26	0.3
C^{13} NMR, %	42.3	37.2	38.9	39	39.4	39.7
% Increase in H/C		4.6	2.9	2.7	2.6	2.9
N Conversion, %		41	44	43	28	27
S Conversion, %		51	1	0	0	0
O Conversion, %		78	66	67	71	66
Conversion of Aromatics (C^{13} NMR), %		12	8	8	7	6
Rate Constants:(1)						
kv, hdn		1.00	1.84	1.07	0.63	0.60
kv, hds		1.00	0.01	0.00	0.00	0.00
kv, hdo		1.00	1.21	0.75	0.82	0.73
kv, hyd(2)		1.00	1.09	0.63	0.55	0.49
kw, hdn		1.00	0.67	0.68	1.04	1.03
kw, hds		1.00	0.00	0.00	0.00	0.00
kw, hdo		1.00	0.44	0.48	1.36	1.25
kw, hyd(2)		1.00	0.39	0.40	0.91	0.85

(1) First-order kinetics for HDN, HDO, and HYD, second-order for HDS relative to Shell 324.
(2) Using conversion measured by C^{13}-NMR.

TABLE 159

PRODUCT QUALITIES AND CONVERSIONS
AFTER 192 HOURS ON COAL GAS OIL FEEDSTOCK, 20 CC/H FEED RATE

	Feed	Shell 324	WC	Mo_2N	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
Carbon, Wt%	88.94	89.93	89.56	90.13	89.64	89.38
Hydrogen, Wt%	9.63	10.05	9.86	9.74	9.9	9.89
H/C	1.30	1.34	1.32	1.30	1.33	1.33
Nitrogen, ppm	3600	2550	2690	2530	2720	2830
Sulfur, ppm	218	174	269	243	256	256
Oxygen, Wt%	0.44	0.24	0.3	0.33	0.29	0.26
C^{13} NMR, %	41.5	38.3	39.5	39.5	40.2	39.7
% Increase in H/C		3.2	1.7	0	2.0	2.2
N Conversion, %		29	25	30	24	21
S Conversion, %		20	0	0	0	0
O Conversion, %		45	32	25	34	41
Conversion of Aromatics (C^{13} NMR), %		8	5	5	3	4
Rate Constants:(1)						
kv, hdn		1.00	1.41	1.02	0.81	0.70
kv, hds		1.00	0.00	0.00	0.00	0.00
kv, hdo		1.00	1.05	0.47	0.69	0.87
kv, hyd(2)		1.00	1.03	0.62	0.40	0.55
kw, hdn		1.00	0.51	0.65	1.34	1.19
kw, hds		1.00	0.00	0.00	0.00	0.00
kw, hdo		1.00	0.38	0.30	1.13	1.49
kw, hyd(2)		1.00	0.37	0.39	0.65	0.95

(1) First-order kinetics for HDN, HDO, and HYD, second-order for HDS relative to Shell 324.
(2) Using conversion measured by C^{13}-NMR.

TABLE 160

PRODUCT QUALITIES AND CONVERSIONS
AFTER 264 HOURS ON COAL GAS OIL FEEDSTOCK, 10 CC/H FEED RATE

	Feed	Shell 324	WC	Mo_2N	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
Carbon, Wt%	88.94	89.98	89.4	89.99	89.67	89.19
Hydrogen, Wt%	9.63	10.11	9.83	9.97	9.87	9.82
H/C	1.30	1.35	1.32	1.33	1.32	1.32
Nitrogen, ppm	3600	2640	2800	3130	3190	3190
Sulfur, ppm	218	135	245	187	208	176
Oxygen, Wt%	0.44	0.22	0.35	0.31	0.34	0.33
C^{13} NMR, %	41.5	36.8	38.6	38.9	39.4	39.4
% Increase in H/C		3.8	1.6	2.3	1.7	1.7
N Conversion, %		27	22	13	11	11
S Conversion, %		38	0	14	5	19
O Conversion, %		50	20	30	23	25
Conversion of Aromatics (C^{13} NMR), %		11	7	6	5	5
Rate Constants:(1)						
kv, hdn		1.00	1.35	0.45	0.39	0.39
kv, hds		1.00	0.00	0.27	0.08	0.39
kv, hdo		1.00	0.55	0.51	0.37	0.42
kv, hyd(2)		1.00	1.00	0.54	0.43	0.43
kw, hdn		1.00	0.49	0.29	0.64	0.67
kw, hds		1.00	0.00	0.17	0.13	0.66
kw, hdo		1.00	0.20	0.32	0.61	0.71
kw, hyd(2)		1.00	0.36	0.34	0.71	0.74

(1) First-order kinetics for HDN, HDO, and HYD, second-order for HDS relative to Shell 324.
(2) Using conversion measured by C^{13}-NMR.

TABLE 161

PRODUCT QUALITIES AND CONVERSIONS
AFTER 336 HOURS ON COAL GAS OIL, 72 H WITH CS2 SPIKED FEED, 10 CC/H

	Feed	Shell 324	WC	Mo_2N	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
Carbon, Wt%	88.94	89.43	89.69	89.32	89.75	89.48
Hydrogen, Wt%	9.78	10.11	9.89	9.87	9.96	9.91
H/C	1.31	1.36	1.32	1.33	1.33	1.33
Nitrogen, ppm	3950	2690	3250	2620	2820	2960
Sulfur, ppm	2070	130	207	168	232	181
Oxygen, Wt%	0.47	0.27	0.36	0.36	0.31	0.31
C^{13} NMR, %	41.5	36.7	38.6	38.8	39.3	39.1
% Increase in H/C		3.5	1.0	1.2	1.6	1.4
N Conversion, %		32	18	34	29	25
S Conversion, %		94	90	92	89	91
O Conversion, %		43	23	23	34	34
Conversion of Aromatics (C^{13} NMR), %		12	7	7	5	6
Rate Constants:(1)						
kv, hdn		1.00	0.85	1.07	0.88	0.75
kv, hds		1.00	1.01	0.76	0.53	0.70
kv, hdo		1.00	0.80	0.48	0.75	0.75
kv, hyd(2)		1.00	0.98	0.55	0.44	0.48
kw, hdn		1.00	0.31	0.68	1.45	1.29
kw, hds		1.00	0.37	0.49	0.87	1.20
kw, hdo		1.00	0.29	0.31	1.24	1.28
kw, hyd(2)		1.00	0.36	0.35	0.73	0.83

(1) First-order kinetics for HDN, HDO, and HYD, second-order for HDS relative to Shell 324.
(2) Using conversion measured by C^{13}-NMR.

TABLE 162

PRODUCT QUALITIES AND CONVERSIONS
AFTER 576 HOURS ON OIL, 240 H ON COAL RESID MIXTURE AT 5 CC/H

	Feed	Shell 324	WC	Mo_2N	Mo_2N/AMOCAT™	Mo_2C/AMOCAT™
Carbon, Wt%	90.9	90.35	90.57	90.62	90.73	90.5
Hydrogen, Wt%	7.93	9.38	8.65	8.78	8.91	9.12
H/C	1.05	1.25	1.15	1.16	1.18	1.21
Nitrogen, ppm	4920	2010	2810	3070	2610	2360
Sulfur, ppm	800	91	280	229	158	144
Oxygen, Wt%	0.73	0.17	0.39	0.39	0.26	0.27
C^{13} NMR, %	69.6	51.1	61.1	59.7	58.2	55.1
Distillation, Wt%:(1)						
IBP-650°F	48.9	53.0	50.9	51.1	53.2	53.7
650-1000°F	5.8	15.8	17.8	11.1	17.8	11.5
1000°F+	45.3	31.2	31.4	37.8	28.9	34.7
% Increase in H/C		19.0	9.5	11.1	12.6	15.5
N Conversion, %		59	43	38	47	52
S Conversion, %		89	65	71	80	82
O Conversion, %		77	47	47	64	63
Conversion of Aromatics (C^{13} NMR), %		27	12	14	16	21
Resid Conversion, %		31	31	17	36	23
Rate Constants:(2)						
kv, hdn		1.00	1.04	0.53	0.71	0.82
kv, hds		1.00	0.40	0.32	0.52	0.58
kv, hdo		1.00	1.72	0.43	0.71	0.68
kv, hyd(3)		1.00	1.70	0.50	0.58	0.76
kv, 1000+F		1.00	1.64	0.49	1.21	0.71
kw, hdn		1.00	0.38	0.34	1.17	1.40
kw, hds		1.00	0.14	0.20	0.86	1.00
kw, hdo		1.00	0.26	0.28	1.17	1.17
kw, hyd(2)		1.00	0.26	0.32	0.95	1.29
kw, 1000+F		1.00	0.60	0.31	1.99	1.22

(1) Temperatures are atmospheric pressure equivalents; IBP-650°F obtained by distilling to an EP (vapor) of 460°F at 45 mm Hg; 650-970°F obtained by distilling to an EP (vapor) of 560°F at 1 mm Hg.
(2) First-order kinetics for HDN, HDO, and HYD, second-order for HDS relative to Shell 324.
(3) Using conversion measured by C^{13}-NMR.

TABLE 163

RELATIVE REACTIVITIES OF SULFUR AND NITROGEN COMPONENTS IN COAL LIQUIDS

		k_{hds}/k_{hdn} (1)				
Feed	Hours on Stream	Shell 324	WC	Mo_2N	Mo_2N/ AMOCAT™	Mo_2C/ AMOCAT™
Coal Gas Oil	264	91	< 1	54	18	90
Coal Gas Oil + CS_2	336	188	223	133	27	175
Coal Resid	576	109	41	66	80	77

(1) k_{hds}, k_{hdn} refer to the rate constants for desulfurization (assume second-order) and denitrogenation (assume first-order), respectively.

Table 164

Catalysts for Run No. 7

Catalyst	AMOCAT™-1C	NiMo/HTO	Pd NiMo/HTO	Pd #1	Pd #2
Ni, wt%	2.4	NA	NA	--	--
Mo, wt%	10.7	NA	NA	--	--
Co, wt%	--	--	--	--	--
SA_{BET}, m^2/g	195	117	114	136	249
PV[1], cc/g	0.59	0.36	0.35	0.38	0.51
PV[2], cc/g	0.17	NA	NA	NA	NA

[1]Nitrogen desorption

[2]Hg Porosimetry, PV for >1000 Å Diam.

Table 165

Catalysts for Run No. 8

Catalyst	AMOCAT™-1C	Ca/AMOCAT™ -1C	Hi NiMo/Al_2O_3	CoMo/HTO	Pd #3
Ni, wt%	2.4	2.4	3.2	--	--
Mo, wt%	10.7	10.7	7.7	NA	--
Co, wt%	--	--	--	NA	--
SA_{BET}, m^2/g	195	NA	256	NA	211
PV[1], cc/g	0.59	NA	0.7	NA	0.50
PV[2], cc/g	0.17	NA	0.2	NA	NA

[1]Nitrogen desorption

[2]Hg Porosimetry, PV for >1000 Å Diam.

Table 166

Catalysts for Run No. 9

Catalyst	AMOCAT™-1C	Shell 324	NiMo/HTO (F)	NiMo/HTO (L)	Shell 411
Ni, wt%	2.4	2.7	2.1	1.9	2.4
Mo, wt%	10.7	13.2	10.1	5.7	14.7
Co, wt%	--	--	--	--	--
SA_{BET}, m^2/g	195	170	NA	NA	165
PV[1], cc/g	0.59	0.48	NA	NA	0.43
PV[2], cc/g	0.17	--	NA	NA	--

[1]Nitrogen desorption

[2]Hg Porosimetry, PV for >1000 Å Diam.

Table 167

Feedstock Properties of Coal Resid[1]

C, wt%	90.47
H, wt%	7.92
H/C ratio	1.05
S, ppm	980
N, ppm	4570
O, wt%	1.86
O, wt% (by diff)	1.06
Ramsbottom Carbon, wt%	14.7
Distillation[2]	
IBP-650°F, wt%	42.8
650-1000°F, wt%	7.4
970°F+, wt%	49.8

(1) Blend of nominally 50 wt% Panasol and 50 wt% coal-derived residuum (CSD, Wilsonville Run 257, C/C mode, Illinois No. 6 coal).

(2) Temperatures are atmospheric pressure equivalents
IBP-650°F obtained by distilling to an EP (vapor) of 460°F at 45 mm Hg
IBP-970°F obtained by distilling to an EP (vapor) of 560°F at 1 mm Hg

Table 168

Catalysts and Process Conditions for Run No. 7

Reactor	A	B	C	D	E
Catalyst	AMOCAT™-1C	NiMo/HTO	Pd NiMo/HTO	Pd #1	Pd #2
LHSV(1), h^{-1}	0.5	0.5	0.5	0.5	0.5
WHSV(2), h^{-1}					
g Catalyst	5.3	6.7	6.8	6.4	5.4
cm^3 Catalyst	10	10	10	10	10
Temp, °F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flow Rate, SCFB	10,000	10,000	10,000	10,000	10,000

(1) LHSV defined as the ratio of the volumetric flow rate (cm^3/h) of oil feed to the volume of the catalyst (cm^3).

(2) WHSV defined as the ratio of the weight flow rate (g/h) of oil feed to the weight of catalyst present within the reactor (g).

Table 169

Catalysts and Process Conditions for Run No. 8

Reactor	A	B	C	D	E
Catalyst	AMOCAT™-1C	Ca/ AMOCAT™-1C	Hi $NiMo/Al_2O_3$	CoMo/HTO	Pd #3
LHSV(1), h^{-1}	0.5	0.5	0.5	0.5	0.5
WHSV(2), h^{-1}					
g Catalyst	5.4	5.3	5.7	7.5	6.4
cm^3 Catalyst	10	10	10	10	10
Temp, °F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flow Rate, SCFB	10,000	10,000	10,000	10,000	10,000

(1) LHSV defined as the ratio of the volumetric flow rate (cm^3/h) of oil feed to the volume of the catalyst (cm^3).

(2) WHSV defined as the ratio of the weight flow rate (g/h) of oil feed to the weight of catalyst present within the reactor (g).

Table 170

Catalysts and Process Conditions for Run No. 9

Reactor	A	B	C	D	E
Catalyst	AMOCAT™-1C	Shell-324	NiMo/HTO (F)	NiMo/HTO (L)	Shell-411
LHSV(1), h^{-1}	0.5	0.5	0.5	0.5	0.5
WHSV(2), h^{-1}					
g Catalyst	5.5	9.2	7.5	7.6	9.5
cm^3 Catalyst	10	10	10	10	10
Temp, °F	760	760	760	760	760
Pressure, psig	2000	2000	2000	2000	2000
H_2 Flow Rate, SCFB	10,000	10,000	10,000	10,000	10,000

(1) LHSV defined as the ratio of the volumetric flow rate (cm^3/h) of oil feed to the volume of the catalyst (cm^3).

(2) WHSV defined as the ratio of the weight flow rate (g/h) of oil feed to the weight of catalyst present within the reactor (g).

Table 171

Product Qualities at First Mass Balance, Run 7[1]

Reactor	Feed	AMOCAT™ 1C	NiMo/ HTO	Pd NiMo/ HTO	Pd #1	Pd #2
Carbon, wt%	90.47	89.92	89.69	90.17	89.67	90.67
Hydrogen, wt%	7.92	9.33	9.27	9.19	8.37	8.50
H/C Ratio	1.05	1.25	1.24	1.22	1.12	1.13
Nitrogen, ppm	4570	2620	2390	2510	3730	3150
Sulfur, ppm	980	470	331	347	620	840
Oxygen, wt%	1.86	0.53	0.37	0.33	0.62	0.41
Total	98.95	100.09	99.60	99.98	99.10	99.98
Oxygen (by diff) wt%	1.06	0.44	0.77	0.35	1.52	0.43
Ramscarbon, wt%	14.7	8.44	8.62	8.75	11.8	10.5
Distillation						
IBP-650°F	42.8	53.9	54	52.6	50.8	52.1
650-1000°F	7.4	11.1	14.6	16.7	10.8	7.8
1000+°F	49.8	35	31.4	30.7	38.4	40.1

(1) 357 hrs on oil

Table 172

Product Qualities at Second Mass Balance, Run 7[1]

Reactor	Feed	AMOCAT™ 1C	NiMo/ HTO	Pd NiMo/ HTO	Pd #1	Pd #2
Carbon, wt%	90.47	89.98	90.26	90.23	90.71	90.54
Hydrogen, wt%	7.92	9.29	9.19	9.11	8.22	8.4
H/C Ratio	1.05	1.24	1.22	1.21	1.09	1.11
Nitrogen, ppm	4570	2740	2680	2810	4390	3860
Sulfur, ppm	980	241	233	315	480	480
Oxygen, wt%	1.86	0.25	0.2	0.15	0.42	0.27
Total	98.95	99.82	99.94	99.80	99.84	99.64
Oxygen (by diff) wt%	1.06	0.43	0.26	0.35	1.58	0.63
Ramscarbon, wt%	14.7	8.64	8.9	8.74	12.1	11.3
Distillation						
IBP-650°F	42.8	52.8	55.1	54.4	49.6	50.5
650-1000°F	7.4	10	13	9.7	12.1	12.8
1000+°F	49.8	37.2	31.9	35.9	38.2	36.8

(1) 574 hrs on oil

TABLE 173

PRODUCT QUALITIES AT FIRST MASS BALANCE, RUN 8[1]

Catalyst	Feed	AMOCAT™ 1C	Hi NiMo/Al_2O_3	CoMo/HTO	Pd #3
C, wt%	90.47	89.64	90.01	89.98	90.57
H, wt%	7.92	9.37	9.27	8.89	8.47
H/C Ratio	1.05	1.26	1.24	1.19	1.12
N ppm	4570	2610	2620	2740	3620
S, ppm	980	150	113	131	375
O, wt%	1.86	--	--	--	--
Total	98.95	99.29	99.55	99.16	99.44
O (by diff), wt%	1.06	0.71	0.45	0.84	0.56
Ramscarbon, wt%	14.7	8.75	8.17	9.53	10.4
Distillation:					
IBP-650F	42.8	50.5	55.3	51.8	52.3
650-1000F	7.4	12.2	14.7	13.4	13
1000+F	49.8	37.3	30	34.7	34.7

(1) 168 hours on oil.

TABLE 174

PRODUCT QUALITIES AT SECOND MASS BALANCE, RUN 8[1]

Catalyst	Feed	AMOCAT™ 1C	Hi NiMo/Al_2O_3	CoMo/HTO	Pd #3
C, wt%	90.47	89.78	90.11	90.18	90.61
H, wt%	7.92	9.25	9.23	8.90	8.40
H/C Ratio	1.05	1.24	1.23	1.19	1.11
N ppm	4570	3310	2780	3010	3870
S, ppm	980	304	171	184	354
O, wt%	1.86	0.69	0.38	0.40	0.54
Total	98.95	99.39	99.64	99.4	99.43
O (by diff), wt%	1.06	--	--	--	--
Ramscarbon, wt%	14.7	8.53	9.65	11.03	10.8
Distillation:					
IBP-650F	42.8	44.3	54.9	53.1	51.8
650-1000F	7.4	12.5	17	14.6	7.1
1000+F	49.8	43.2	28.1	32.3	41.1

(1) 336 hours on oil.

Table 175

Product Qualities After First Mass Balance, Run 9[1]

Reactor	Feed	AMOCAT™ 1C	Shell 324	NiMo/ HTO (F)	NiMo/ HTO (L)	Shell 411
Carbon, wt%	90.47	89.9	89.48	89.89	90.07	89.46
Hydrogen, wt%	7.92	9.29	9.39	9.23	9.02	9.45
H/C Ratio	1.05	1.24	1.26	1.23	1.20	1.27
Nitrogen, ppm	4570	2820	2300	2670	2470	2130
Sulfur, ppm	980	211	187	187	199	450
Oxygen, wt%	1.86	0.21	0.47	0.18	0.18	0.22
Total	98.95	99.70	99.59	99.59	99.54	99.39
Oxygen (by diff) wt%	1.06	0.80	1.12	0.87	0.90	1.08
Ramscarbon, wt%	14.7	9.74	8.95	9.47	9.3	8.45
Distillation						
IBP-650°F	42.8	48.9	51.3	50	54.1	54.6
650-1000°F	7.4	10.5	12.6	14.6	16	13.4
1000+°F	49.8	40.7	36.1	35.4	29.9	32

(1) 470 hrs on oil

Table 176

Product Qualities After Second Mass Balance, Run 9[1]

Reactor	Feed	AMOCAT™ 1C	Shell 324	NiMo/ HTO (F)	NiMo/ HTO (L)	Shell 411
Carbon, wt%	90.47	89.91	89.43	90.22	90.13	90.02
Hydrogen, wt%	7.92	9.09	9.37	9.22	8.98	9.47
H/C Ratio	1.05	1.21	1.26	1.23	1.20	1.26
Nitrogen, ppm	4570	3280	2830	3320	2780	2460
Sulfur, ppm	980	136	159	129	137	145
Oxygen, wt%	1.86	0.72	0.7	0.45	0.44	0.47
Total	98.95					
Oxygen (by diff) wt%	1.06	1.00	1.20	0.56	0.89	0.51
Ramscarbon, wt%	14.7	11.2	8.64	9.42	10.1	8.59
Distillation						
IBP-650°F	42.8	40.7	53.3	51	54.1	55.7
650-1000°F	7.4	11.3	12.4	9.3	11.1	7.5
1000+°F	49.8	47.9	34.4	39.7	34.8	36.8

(1) After 779 hrs on oil

Table 177

Product Qualities After Third Mass Balance, Run 9(1)

Reactor	Feed	AMOCAT™-1C	Shell 324	NiMo/ HTO (F)	NiMo/ HTO (L)	Shell 411
Carbon, wt%	90.47	89.92	90.07	90.01	90.41	89.87
Hydrogen, wt%	7.92	9.02	9.37	9.2	8.94	9.42
H/C Ratio	1.05	1.20	1.25	1.23	1.19	1.26
Nitrogen, ppm	4570	3680	2430	2790	2830	2300
Sulfur, ppm	980	173	114	129	147	159
Oxygen, wt%	1.86	0.78	0.72	0.53	0.68	0.57
Total	98.95					
Oxygen (by diff) wt%	1.06	1.06	0.56	0.79	0.65	0.71
Ramscarbon, wt%	14.7	12.5	8.7	9.04	9.9	8.7
Distillation						
IBP-650°F	42.8	36.1	53	53.1	52.7	54.6
650-1000°F	7.4	23.9	9.5	15.5	7.3	10.3
1000+°F	49.8	40	37.5	31.4	40	35.1

(1) After 876 hrs on oil

Table 178

NiMo ON SANDIA'S THIN-FILM HYDROUS TITANATE ON AMOCAT™ ALUMINA

Catalyst	Fresh HTO AMOCAT™ Alumina	Fresh AMOCAT™ 1C
Elemental Analyses, Wt%		
Primary Metals		
Mo	6.20	9.10
Ni	2.08	1.39
Al	33.80	35.40
Si	1.97	1.39
Deposits		
C	--	--
H	--	--
S	--	.20
Ti	6.70	.00
Fe	.02	.02
Na	.30	.08
Mg	.00	.00
V	.00	.00
Ca	.02	.00
Pore Properties		
Volume <1200 Å Diam., cc/g	.52	.59
BET Surface Area, m^2/g	175	200

TABLE 179

LIQUEFACTION OF ILLINOIS NO. 6 COAL WITH
POWDERED NiMo/HYDROUS TITANATE AND NiMo/ALUMINA: PRODUCT YIELDS

Catalyst	Molyvan L	.1% NiMo/Al_2O_3	.1% NiMo/TiO_2	.2% NiMo/TiO_2
Temp, °F	820	800	800	800
Yields, Wt% of MAF Coal				
C_1-C_3	11.0	10.7	8.5	9.5
C_4-360°F	11	6	4	6
360-650°F	41	29	28	26
650-935°F	16	25	20	20
935°F+	5	9	20	18
C_4-935°F	68	59	52	53
Conversion	95.7	91.2	91.8	91.3
Hydrogen	-4.9	-2.8	-2.7	-3.6

TABLE 180

LIQUEFACTION OF ILLINOIS NO. 6 COAL WITH POWDERED
NiMo/HYDROUS TITANATE AND NiMo/ALUMINA: PRODUCT ANALYSES

Catalyst	Molyvan L	.1% NiMo/Al_2O_3	.1% NiMo/TiO_2	.2% NiMo/TiO_2
Temp, °F	820	800	800	800
Wt% Analysis				
360-650°F Aromatic C	43	42	43	43
H/C	1.46	1.45	1.44	1.45
N	.54	.57	.58	.55
O	3.1	2.8	2.8	3.2
650-935°F Aromatic C	50	49	49	48
H/C	1.22	1.22	1.24	1.24
S	.09	.12	.15	.13
N	.52	.54	.54	.53
O	1.1	1.2	1.1	1.1
935°F+, Solids				
H/C	.92	.90	.91	.91
S	.35	1.01	1.10	1.14
N	1.09	1.27	1.25	1.25
O	2.0	1.8	1.6	2.4

Table 181

NiMo ON SANDIA'S THIN-FILM HYDROUS TITANATE ON AMOCAT™ ALUMINA

Catalyst	Fresh HTO AMOCAT™ Alumina	Fresh AMOCAT™ 1C
Elemental Analyses, Wt%		
Primary Metals		
Mo	6.20	9.10
Ni	2.08	1.39
Al	33.80	35.40
Si	1.97	1.39
Deposits		
C	--	--
H	--	--
S	--	.20
Ti	6.70	.00
Fe	.02	.02
Na	.30	.08
Mg	.00	.00
V	.00	.00
Ca	.02	.00
Pore Properties		
Volume <1200 Å Diam., cc/g	.52	.59
BET Surface Area, m^2/g	175	200

Table 182

COMPARISON OF CATALYSTS WITH ILLINOIS NO. 6 COAL FEED:
YIELDS AND ANALYSES

Catalyst	AMOCAT™ 1C	Sandia NiMo HTO/Al_2O_3
Conversion, Wt%	92.1	91.8
Oils	65	78
Asphaltenes	2	-11
Preasphaltenes	6	3
C_1-C_3 Hydrocarbon	8.2	11.4
CO+CO_2	1.2	1.1
C_4-360°F	9	12
360-650°F	36	41
650-935°F	12	31
935+°F	16	-15
Hydrogen Consumption	-6.7	-6.6
Elemental Analyses, Wt%		
360-650°F, H/C	1.59	1.53
Aromatic Carbon	28	37
S	--	--
N	.26	.29
O	0.9	2.20
650-935°F, H/C	1.40	1.31
Aromatic Carbon	38	46
S	.05	.02
N	.21	.33
O	.4	.6
935+°F and Solids, H/C	1.00	.97
S	.74	.79
N	.90	.98
O	2.7	4.4
Hours	61	72

TABLE 183

ANALYSES OF SPENT FIRST STAGE CATALYST SAMPLES
FROM ILLINOIS NO. 6 COAL LIQUEFACTION

Catalyst	Spent AMOCAT™-1C	Spent Sandia HTO AMOCAT™ Alumina
Elemental Analyses, Wt%	21 Days	7 Days
Primary Metals		
Mo	5.90	4.60
Ni	1.25	1.34
Al	23.50	25.80
Si	.98	1.18
Deposits		
C	25.35	24.72
H	1.59	1.81
S	4.78	--
Ti	1.54	5.40
Fe	.44	.21
Na	.12	.28
Mg	.05	.03
V	.18	.04
Ca	.00	.02
Pore Properties		
Volume <1200 Å Diam, cc/g	.16	.19
BET Surface Area, m^2/g	65	67

TABLE 184

ANALYSES OF SPENT SECOND STAGE CATALYST SAMPLES
FROM ILLINOIS NO. 6 COAL LIQUEFACTION

Catalyst	Spent AMOCAT™-1C	Spent Sandia HTO AMOCAT™ Alumina
Elemental Analyses, Wt%		
Primary Metals		
Mo	8.10	5.20
Ni	1.63	1.45
Al	31.60	27.50
Si	1.22	1.26
Deposits		
C	7.86	19.24
H	1.50	1.64
S	5.86	--
Ti	.14	5.40
Fe	.14	.09
Na	.11	.24
Mg	.01	.00
V	.00	.02
Ca	.00	.00
Pore Properties		
Volume <1200 Å Diam, cc/g	.38	.26
BET Surface Area, m^2/g	151	116

APPENDIX A

THE BENEFICIATION OF MARTIN LAKE TEXAS LIGNITE

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ABSTRACT

Martin Lake lignite from Wilcox County, Texas, contains a moderate level of ash (11.3%) and a high level of inertinite macerals (13.3%). These are both detrimental to liquefaction. A beneficiation process comprised of size selection, aqueous sulfur dioxide treatment, and sink/float separation using heavy media was evaluated and shown to be effective. In laboratory-scale equipment, the combined process reduced the lignite sample to one having 2.5% ash and 11.1% inertinite macerals. A lignite recovery of 82% was achieved, the remainder to be used as plant fuel.

Petrographic analyses of the various treated fractions were performed. The huminite macerals were concentrated in the low gravity fractions. The inertinites were concentrated in the high gravity fractions. Due to the association of the exinitic macerals with minerals, the distribution of these macerals was bimodal with relatively high levels in both the high and low gravity cuts.

INTRODUCTION

Coal contains organic components including plant remains such as woody species, waxes, spores, and seeds. This material decays and becomes compacted with individual components undergoing various degrees of alteration. Organic particles within coal have been microscopically identified and categorized as

macerals. The nomenclature used herein to categorize macerals corresponds approximately to that outlined by the ICCP for low-rank coal. Because these terms are not widely used for industrial applications, they have been simplified to a "maceral group" classification. This classification includes: "liptinites" that include resinite (fluorinite and bituminite), sporinite, cutinite and liptodetrinite; "huminites" that includes ulminite, humodetrinite, gelinite and corpohuminite; and "inertinites" which include fusinite (given herein as "inertinite"), macrinite, sclerotinite, semi-inertinite and inertodetrinite.

A number of papers (1-5) have related the liquefaction of coal to its maceral composition. In summary, vitrinite (huminite in low rank coal) liquefies well; exinites liquefy well, but more slowly that vitrinite; and inertinites liquefy poorly or not at all depending upon the specific maceral.

Coal beneficiation technologies strive to separate the more reactive macerals from the mineral matter and less reactive macerals. A relationship exists between the density of individual coal particles and their maceral composition (1-3). Maceral density increases in the order exinites <vitrinites <inertinites. Mineral matter has a high density, and it can often be removed with the high density coal particles.

Another aspect of beneficiation is particle size. Minerals are sometimes located at grain boundaries and can be liberated with sufficient pulverization. In addition, the unreactive maceral fusinite, which is charcoal-like, can break into small particles during crushing. Therefore, fusinite can be partially removed by screening.

EXPERIMENTAL

Coal Sample Preparation.--An as-received sample was riffled for a 1 kg split for an initial coal particle size distribution (Table I). The coal was then reduced in size by passing it through a roller mill, which was set to reduce the top size of the coal and minimize the generation of fines. After an intermediate screening, the sample was recombined and screened into four size fractions. The results of the sieve analyses are given in Table I.

Prior to gravity separation, the sized coal splits were dried with a nitrogen flow at about 45°C. Each split was then floated successively in Certigrav solutions with specific gravities of 1.25, 1.30, 1.35, and 1.40.

The two larger size fractions (+10 mesh and 10X20 mesh) were separated in a funnel-and-flask assembly. Small increments of coal were mixed with heavy liquid, stirred, and allowed to separate. The float fraction was recovered with a wire mesh spoon and another increment was introduced. After separation of the entire split, a stopper was inserted into the neck of the funnel-and-flask assembly and the residual float material recovered by filtration. After removing the stopper, the accumulated sink material was also recovered by filtration. The separated materials were rinsed with acetone and dried.

The two smaller size fractions (20X60 mesh and -60 mesh) were separated in 10 g increments, mixed with 400 ml Certigrav, and centrifuged at 1500 rpm for 20 minutes. The float fraction was recovered by suction, and the sink by filtration. Each of these fractions was filtered, rinsed with acetone and dried.

Two selected size fractions (10X20 and 20X60 mesh) were subjected to treatment with aqueous sulfur dioxide. Samples of these coals were gently mixed with 5 wt% SO2 solution overnight, filtered and flushed with water. They were then subjected to gravity separation and subsequent analysis. The coals were dried at 50C with a nitrogen flow. Three gravity fractions were obtained from each size fraction, namely: 1.3 float, 1.3X1.4 and 1.4 sink. All of the gravity separations were done using the flask-and-funnel method described above.

Petrographic Analyses.- Provided sufficient sample was available, polished coal pellets were made from each size/gravity fraction. Results of a combined white/blue-light petrographic analysis were based on 1000 point counts for each coal examined.

RESULTS AND DISCUSSION

Size Separation:

Because a roll crusher was used, the resulting lignite was primarily in the 10X20 and 20X60 mesh size ranges. About 14% was oversize (+10 mesh) and 8% was recovered as fines (-60 mesh). In a commercial facility, these fines would be rejected to serve as fuel, because 1) they are not effectively handled using sink/float techniques, and 2) they are often high in inertinites and are thus poor liquefaction feeds(1).

Sink/Float Separation:

Untreated Lignite Samples.--The sized lignite samples were separated into five specific gravity fractions: namely, 1.25 float, 1.25X1.30, 1.30X1.35, 1.35X1.40, and 1.40 sink. "1.25 Float" indicates that this fraction floats in a 1.25 specific gravity solvent, and "1.4 sink" indicates that the sample sinks in a 1.40 solvent. Due to limited amounts of some individual cuts, the 1.25 float fraction was combined with the 1.25X1.3 fraction, and the 1.3X1.35 and 1.35X1.4 fractions were combined. The yield distributions were recalculated to mirror these changes; see Table II in which a correction for moisture is included. Splits of the above combined fractions were analyzed for moisture, ash, and total sulfur.

Figure 1a is a block chart showing the yield distribution. The pattern is irregular, perhaps due to differences in sink/float techniques between the coarse (+10 and 10X20) and fine (20X60 and -60) samples. For the most part, the lignite yields are grouped in the 1.3 float and 1.4 sink fractions; the latter is 36% of the feed.

The ash distribution is given in Table III and Figure 2a. Even in the 1.3 float and 1.3X1.4 fractions, ash levels were in the range of about 6 to 9%. With the exception of an aberration at 20X60, the ash levels of the 1.4 sink samples were between 20 and 27%. Therefore, rejection of the 1.4 sink fractions as a feed for liquefaction would be obvious.

The sulfur contents of the sink/float fractions are given in Table IV. The weighted average of the 1.3 float fraction is 0.84 wt% sulfur while that of the 1.4 sink fraction is 0.92 wt%. Considering that the ash contents of these fractions are 6.6 and 18.4%, respectively, most of the sulfur is associated with the organic portion of the lignite. In addition, this sulfur appears to be dispersed among the various macerals.

SO2-Treated Lignite Samples.--Two selected size fractions (10X20 and 20X60) were subjected to aqueous SO2 treatment. Table V and Figure 1b show the distribution of coal that reported to each of the size/gravity fractions. In contrast to the results with untreated lignite, most of the lignite was recovered in the 1.3X1.4 gravity fraction. The 1.4 sink fraction made up only 10% of the lignite.

Table VI and Figure 2b show the ash distribution for the size/gravity fractions. The weighted ash content of the fractions having gravities less than 1.4 was about 2.5%. That of the 1.4 sink was 24.0%. The SO2-treatment not only reduced the ash content of the 1.3 float and 1.3x1.4 fractions, but it also increased the ash content of the sink fraction. Such treatment resulted in a sizeable increase in the efficiency of gravity separation. In summary, SO2-treatment in combination with sink/float separation results in a beneficiated coal stream containing about 3% ash with a recovery of about 90% of the coarse coal (+60 mesh).

The reduction of total ash is most likely due to removal of cations present as carboxylate salts in the coal. The persistence of mineral matter in the sink fractions as well as the selective removal of inorganics in the floats

supports this notion. Although discrete minerals appear not to have been removed by the treatment as determined by microscopic analysis, the higher ash contents of the sink fractions suggests that some liberation of mineral matter may have occurred as a consequence of the treatment.

Table IV shows the sulfur distribution for the size/gravity fractions of both the raw and SO2-treated lignite samples. The slightly higher sulfur content of the sink fractions is due to the presence of sulfide minerals. Examination of the data shows that the SO2-treatment increases the sulfur content by about 0.5% over all of the fractions.

Petrographic Analyses:

Maceral analyses of the raw whole lignite and the raw and SO2-treated lignite fractions were done. Table VII shows the maceral distribution of the raw whole lignite and Tables VIII and IX show those of the size/gravity fractions of the raw and treated lignites, respectively. Figures 4b, 5b and 6b illustrate the distribution of huminite (vitrinite), liptinite, and inertinite group macerals respectively.

The distribution of the macerals was improved as a result of the SO2-treatment; namely, the amount of total inertinite macerals was reduced in the low gravity fractions and increased in the high gravity ones. As calculated from Table 9, the inertinite levels in the 1.3 float of the raw combined 10X20 and 20X60 fractions was 7.8%, while that of the equivalent SO2-treated sample was 3.7%. The weighted total inertinites level of the 1.4 float sample was 11.1% with an inertinite (fusinite) level of 1.7%. Similarly, the levels of liptinites in the 1.3 float samples increased due to the SO2-treatment, namely

7.2% vs. 10.8%, respectively. The +10 mesh fraction was not treated, but it is assumed that the effect would be similar. The -60 mesh fines fraction would be rejected, so the effect of SO2-treatment on it is not considered.

Humitite Distribution.--The float fractions accumulated large amounts of huminite macerals. This was due to the abundance of the huminite maceral, ulminite, which is characterized by the presence of a cellular structure, often manifested by open pores. Ulminite tends to occur as relatively large grains of humic material, and so can have less associated detrital mineral than the finer grained humodetrinite macerals.

Plates A + B show some of the typical huminite group macerals. Note that ulminite often displays cellular structure. Most of the ulminite in the float fractions is the "texto-ulminite" type, whereas that found in the sink fractions is the eu-ulminite type. It seems probable that the relative enrichment of huminite in the float fractions is due to buoyancy imparted by air entrapped in texo-ulminite.

Nearly all of the gelinite is of the levigelinite type except in the 20x60 float fraction where the porigelinite type was more common.

Humodetrinite is actually a maceral subgroup composed of the macerals attrinite and densinite. Most of the humodetrinite was densinite.

Corpohuminite was rare.

Inertinite Distribution.--For the most part, the inertinite group macerals have accumulated in the sink fractions, which is due in large part to the genetic association between inertodetrinite with discrete detrital mineral matter particles.

Plate C shows some typical inertinite group macerals. Figure 6 shows the distribution of inertinite group macerals which are shown to be enriched in the sink fractions. Much of the variation shown in Figure 6 is due to the presence of inertodetrinite. This maceral is often found in dull lithotypes and is associated with large amounts of mineral matter. This may account for its relative enrichment in the sink fractions.

Liptinite Distribution.--The distribution of liptinite group macerals in these fractions was bimodal. These macerals were small in size and they were not liberated by the comminution to which the lignite had been subjected. Consequently, their distribution was controlled by the nature of the macerals and minerals with which they were associated, rather than by the known low densities of these substances.

Plate D illustrates how fluorescence microscopy allows the petrographer to more easily recognize liptinite group macerals. Indeed, the recognition of liptinite group macerals in sink fractions of low rank coals is quite difficult in normal white reflected light. (All of the petrographic analyses reported herein were accomplished in both white and blue light).

Ash Distribution.--In low-rank coals, ash is derived from both discrete minerals and organically associated cations which have replaced the hydrogen in carboxyl groups. The higher ash contents in the sink fractions result from contributions from mineral species. Discrete mineral matter is likely to have been deposited in paleo-topographic lows in the coal-forming paleoswamp. This suggested cause for the enrichment of mineral species is supported by the higher inertodetrinite content of the sink fractions; inertodetrinite is commonly thought to have had a detrital origin.

The distribution of organically associated inorganic matter is likely to be related to the distribution of huminite macerals. These macerals are clearly enriched in the float fractions, so that relatively high proportions of carboxylates are likely to be found in these fractions.

In the case of raw lignite separation, comparisons of the +10 mesh fraction with the 10X20 mesh fraction, and of the 20X60 mesh fraction with the -60 fraction, reveal that the larger sized material contained slightly more ash than the finer material at the same gravity (Table IV). The only exception is the -60 mesh 1.4 sink which yielded 21% ash compared to only 13% for the 20X60 mesh 1.4 sink material. The -60 mesh sink fraction also contained abundant -5 micron material which was conspicuously missing from the -60 mesh float fraction. These observations suggest that removal of very fine particles significantly reduce ash content, but that the larger particles may have higher proportions of carboxylate salts. These observations support our suggestion to reject the fines fraction and carry out an SO2-treatment of the coarser fractions prior to sink/float beneficiation.

CONCLUSIONS

The following conclusions are drawn from a study of beneficiating Martin Lake, Texas lignite using a process combining crushing, sizing, aqueous sulfur dioxide treatment, and sink/float techniques:

1) Martin Lake lignite can be significantly beneficiated as a coal liquefaction feedstock by the above combined process.

2) After lignite, containing 11.3% ash, was mildly crushed and sieved at 60 mesh, the fines fraction contained 18.1% ash and it made up only 8% of the feed. (Considering poor conversion of fines in the past, this fraction would be rejected to serve as plant fuel.)

3) Sink/float separation of coarse, raw lignite was somewhat effective with only 62% recovery of a 1.4 gravity float fraction containing 6.8% ash and 7.8% inertinites. The 1.4 gravity sink contained an ash level of 18.4% and an inertinite level of 24.2%. (The feed lignite contained 13.3% inertinites with 2.5% fusinite.)

4) Treatment of the coarse lignite with aqueous SO2 resulted in a reduction of ash content of about 50%.

5) Sink/float technology was effective in beneficiating SO2-treated coarse lignite. This gave a 1.40 specific gravity cut with a recovery of about 90% containing about 2.5% ash with a weighted total inertinites level of 11.1% and a fusinite level of 1.7%.

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TABLE I. PARTICLE SIZE DISTRIBUTION OF SAMPLES

	Mesh Size	Weight % Coal
INITIAL SIZE DISTRIBUTION (as received coal)	+10	42%
	10 X 40	45%
	40 X 100	9%
SECOND SIZE DISTRIBUTION (after milling)	+10	14%
	10 X 20	50%
	40 X 80	10%
	80 X 100	4%
	-100	3%
FINAL SIZE DISTRIBUTION (used for gravity separation)	+10	14%
	10 X 20	51%
	20 X 60	27%
	-60	8%

TABLE II. LIGNITE WEIGHT DISTRIBUTION IN THE VARIOUS SIZE/GRAVITY FRACTIONS
(calculated on a dry basis)

MESH SIZE	GRAVITY FRACTION 1.3 F	1.3 X 1.4	1.4 S	Total
+10	10.76	0.38	2.42	13.58
10 X 20	33.68	6.41	9.79	49.88
20 X 60	7.75	1.01	19.13	27.89
-60	1.26	0.28	7.12	8.65
Total	53.46	8.07	38.47	100

TABLE III. ASH DISTRIBUTION IN THE SIZE/GRAVITY FRACTIONS
(calculated on a dry basis)

SIZE FRACTION	GRAVITY FRACTION 1.3 F	1.3 X 1.4	1.4 S	Total
+10	7.21	9.58	26.8	10.76
10 X 20	6.54	7.92	24.6	10.26
20 X 60	6.29	6.18	13.4	11.16
-60	6.07	5.77	20.9	18.09
Total	6.63	7.72	18.4	11.26

TABLE IV. SULFUR CONCENTRATIONS IN THE SIZE/GRAVITY FRACTIONS
(calculated on a dry basis)

SIZE FRACTION	GRAVITY FRACTION 1.3 F	1.3 X 1.4	1.4 S	Total
+10	0.89	0.93	1.11	0.93
10 X 20	0.82	0.80	1.17	0.89
20 X 60	0.90	0.92	0.77	0.81
-60	0.77	0.77	0.89	0.87
Total	0.84	0.82	0.92	0.87

TABLE IVa. SULFUR CONCENTRATIONS IN THE SO_2-TREATED SAMPLES
(calculated on a dry basis)

SIZE FRACTION	GRAVITY FRACTION 1.3 F	1.3 X 1.4	1.4 S	Total
10 X 20	1.46	1.36	2.32	1.45
20 X 60	1.29	1.22	2.08	1.41

TABLE V. YIELD DISTRIBUTION OF THE SIZE/GRAVITY FRACTIONS OF THE SO_2-TREATED LIGNITE SAMPLES
(calculated on a dry basis)

SIZE FRACTION	GRAVITY FRACTION 1.3 F	1.3 X 1.4	1.4 S	Total
10 X 20				
% Fraction	13.4	78.5	8.2	100.0
% Whole coal	6.7	39.2	4.1	49.9
20 X 60				
% Fraction	1.7	76.1	22.1	100.0
% Whole coal	0.5	21.2	6.2	27.9

TABLE VI. ASH DISTRIBUTION IN SO_2-TREATED LIGNITE SIZE/GRAVITY FRACTIONS
(calculated on a dry basis)

SIZE FRACTION	GRAVITY FRACTION 1.3 F	1.3 X 1.4	1.4 S	Total
10 X 20 Treated	2.05	3.69	28.6	5.52
20 X 60 Treated	2.83	2.93	20.9	6.90

TABLE VII. MACERAL ANALYSIS OF MARTIN LAKE LIGNITE
(volume % mineral-free basis)

Resinite	1.0	
Sporinite	2.2	
Cutinite	0.7	
Liptodetrinite	4.8	
Liptinites		8.7
Ulminite	18.5	
Hunodetrinite	51.7	
Gelinite	5.6	
Corpohuminite	2.2	
Huninites		78.0
Semi-inertinite	4.9	
Inertinite	2.5	
Inertodetrinite	5.9	
Inertinites		13.3

* values only significant to nearest whole number

Table VIII. Petrographic Analysis of Martin Lake Lignite
Size/Gravity Fractions
(volume % mineral-free basis)*

MESH SIZE	MACERAL NAME	GRAVITY FRACTION 1.3 F	1.3-1.4	1.4 S
+10	Resinite	1.1		2.5
	Sporinite	1.9		3.7
	Cutinite	0.1		0.6
	Liptodetrinite	1.8		3.3
	Liptinites	4.9		10.1
	Ulminite	31.8		8.8
	Humodetrinite	43.6		48.3
	Gelinite	4.1		8.5
	Corpohuminite	3.5		2.2
	Humnites	83.0		68.8
	Semi-inertinite	2.5		5.7
	Inertinite	3.5		4.1
	Inertodetrinite	6.1		11.3
	Inertinites	12.1		21.1
10 X 20	Resinite	1.3	0.8	1.4
	Sporinite	1.5	3.9	3.6
	Cutinite	1.2	0.2	0.1
	Liptodetrinite	3.3	2.6	3.2
	Liptinites	7.3	7.5	8.3
	Ulminite	31.2	19.5	12.4
	Humodetrinite	41.6	42.1	43.1
	Gelinite	7.6	6.2	8.6
	Corpohuminite	3.9	2.8	1.9
	Huminites	84.3	70.6	66.0
	Semi-inertinite	1.9	5.6	7.2
	Inertinite	3.0	6.1	4.9
	Inertodetrinite	3.5	10.2	13.6
	Inertinites	8.4	21.9	25.7
20 X 60	Resinite	2.0	1.1	0.9
	Sporinite	1.6	1.4	2.0
	Cutinite	0.4	0.7	0.1
	Liptodetrinite	2.7	1.8	2.9
	Liptinites	6.7	5.0	5.9
	Ulminite	30.3	27.9	20.1
	Humodetrinite	48.5	47.6	46.4
	Gelinite	7.1	9.2	5.1
	Corpohuminite	2.2	3.1	1.2
	Huminites	88.1	87.8	72.8
	Semi-inertinite	0.6	1.3	4.6
	Inertinite	0.8	3.0	6.9
	Inertodetrinite	3.8	2.9	9.8
	Inertinites	5.2	7.2	21.3
-60	Resinite	2.2		1.4
	Sporinite	1.0		3.2
	Cutinite	0.6		0.4
	Liptodetrinite	3.6		2.8
	Liptinites	7.4		7.7
	Ulminite	18.6		11.9
	Humodetrinite	60.0		45.5
	Gelinite	8.1		4.1
	Corpohuminite	0.9		0.9
	Huminites	87.6		62.4
	Semi-inertinite	0.6		3.6
	Inertinite	0.3		9.2
	Inertodetrinite	4.1		17.2
	Inertinites	5.0		30.0

* Values are only significant to the nearest whole number.

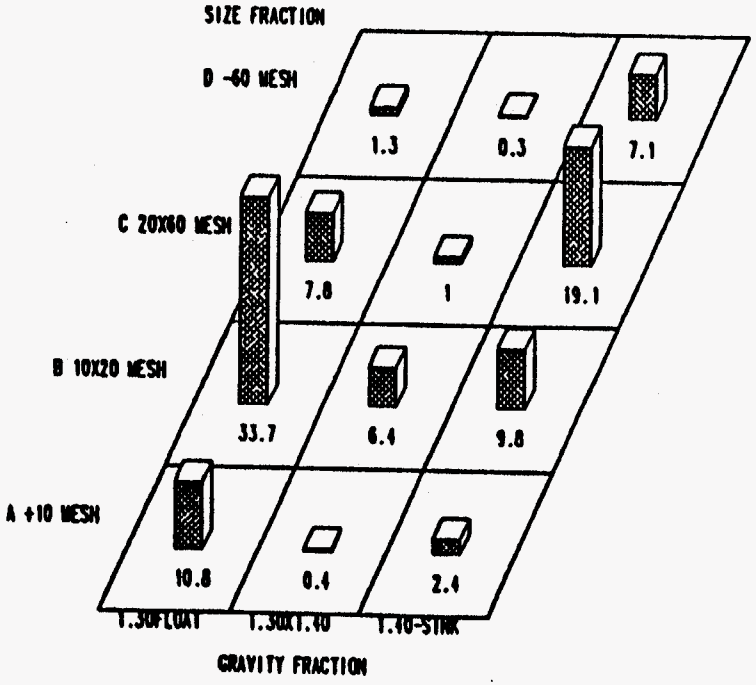
TABLE IX. PETROGRAPHIC ANALYSIS OF SO_2 TREATED MARTIN LAKE LIGNITE SIZE/GRAVITY FRACTIONS
(volume % mineral-free basis)

MESH SIZE	MACERAL NAME	GRAVITY FRACTION 1.3 F	1.3-1.4	1.45
10 X 20	Resinite	3.0	0.5	2.4
	Sporinlte	2.0	2.8	5.4
	Cutinite	0.8	0.5	0.2
	Liptodetrinite	4.5	3.3	4.2
	Liptinites	10.3	7.1	12.2
	Ulminito	25.6	24.8	6.5
	Humodetrinite	55.6	48.7	41.1
	Gelinite	3.2	4.4	11.5
	Corpohuminito	1.5	2.3	1.5
	Huminites	85.9	80.2	60.6
	Semi-inertinite	0.8	2.5	6.9
	Inertinite	0.5	2.1	3.7
	Inertodetrinite	2.5	8.1	16.6
	Inertinites	3.8	15.2	27.6
20 X 60	Resinite	4.5	1.4	1.7
	Sporinite	3.0	1.5	3.9
	Cutinite	0.4	0.7	0.6
	Liptodetrinite	5.7	2.3	2.1
	Liptinites	13.6	5.9	8.3
	Ulminite	27.1	21.6	10.3
	Humodetrinite	50.3	52.0	47.4
	Gelinite	3.3	7.5	4.3
	Corpohuminite	2.4	1.4	1.1
	Huminites	83.1	82.5	63.1
	Semi-inertinite	0.6	2.9	7.4
	Inertinito	1.6	1.0	5.1
	Inertodetrinite	1.1	7.7	16.1
	Inertinites	3.1	11.6	28.6

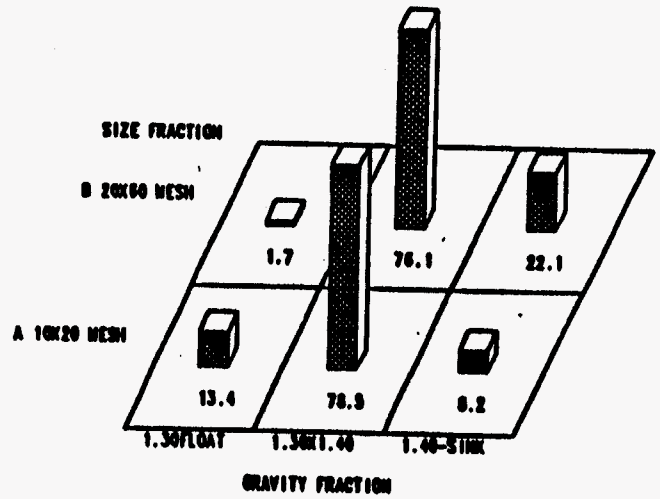
*Values only significant to nearest whole number

Figure 1

Yield Distribution of the Size/Gravity Fractions of Raw and SO_2-Treated Lignite



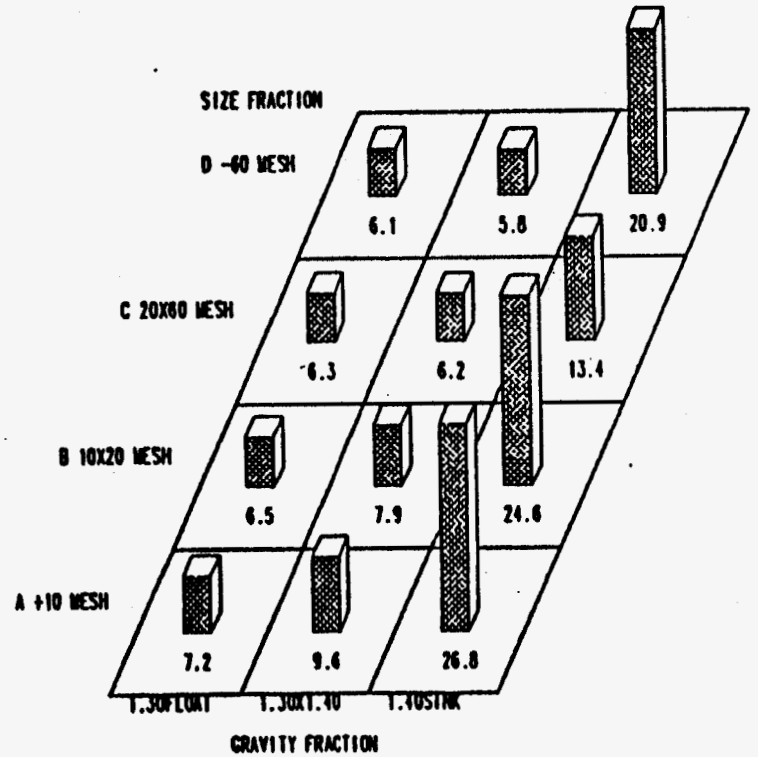
Raw Lignite



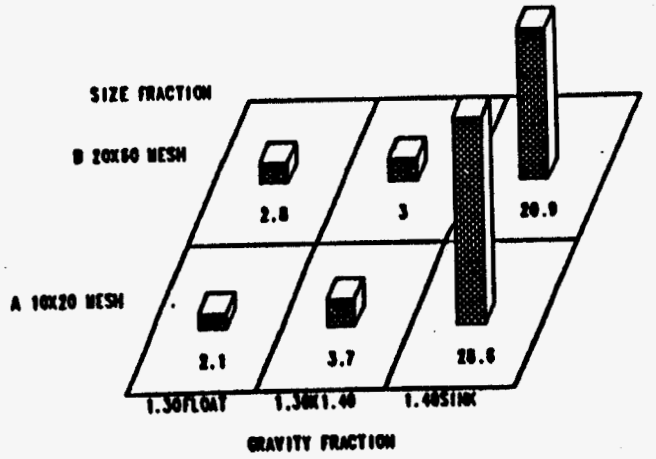
SO_2-Treated Lignite

Figure 2

Ash Distribution of the Size/Gravity Fractions of Raw and SO_2-Treated Lignite



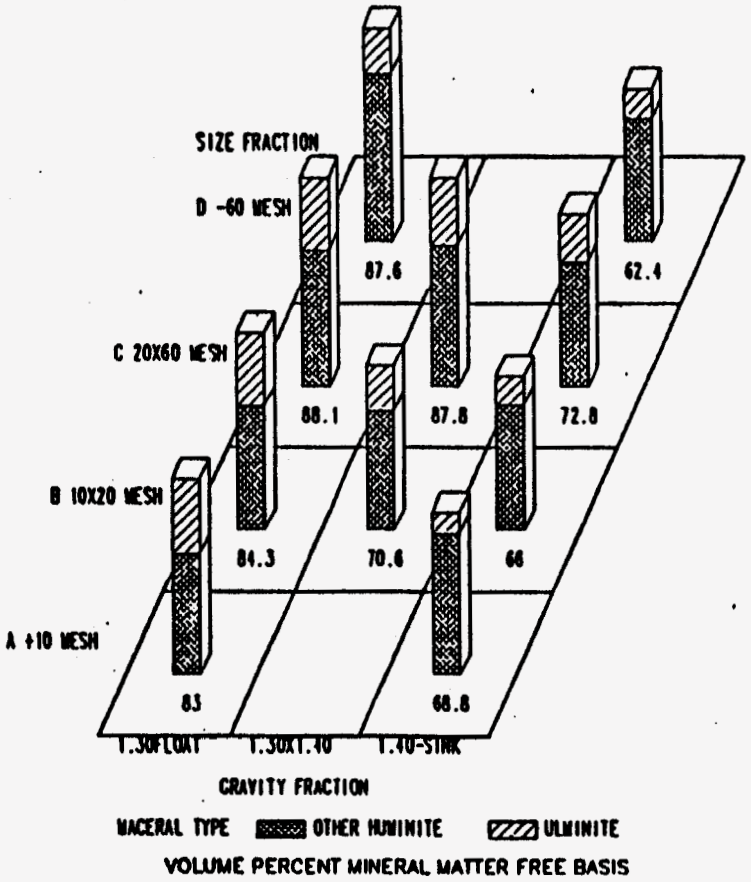
Raw Lignite



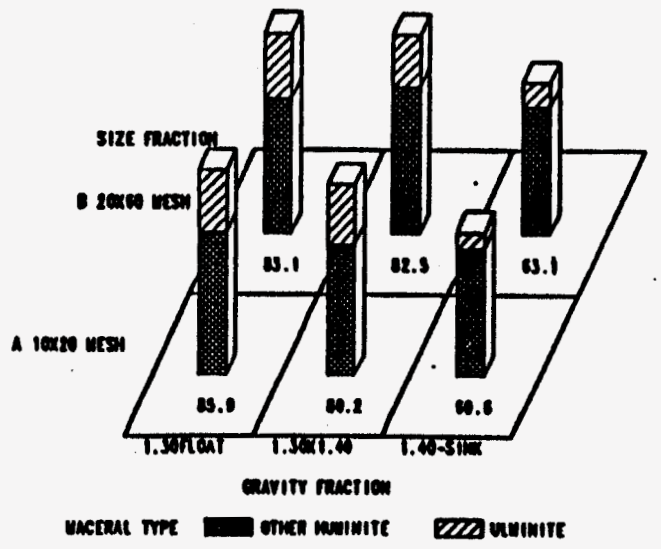
SO_2-Treated Lignite

Figure 3

Vitrinite Distributions in the Size/Gravity Fractions of Raw and SO_2-Treated Lignite



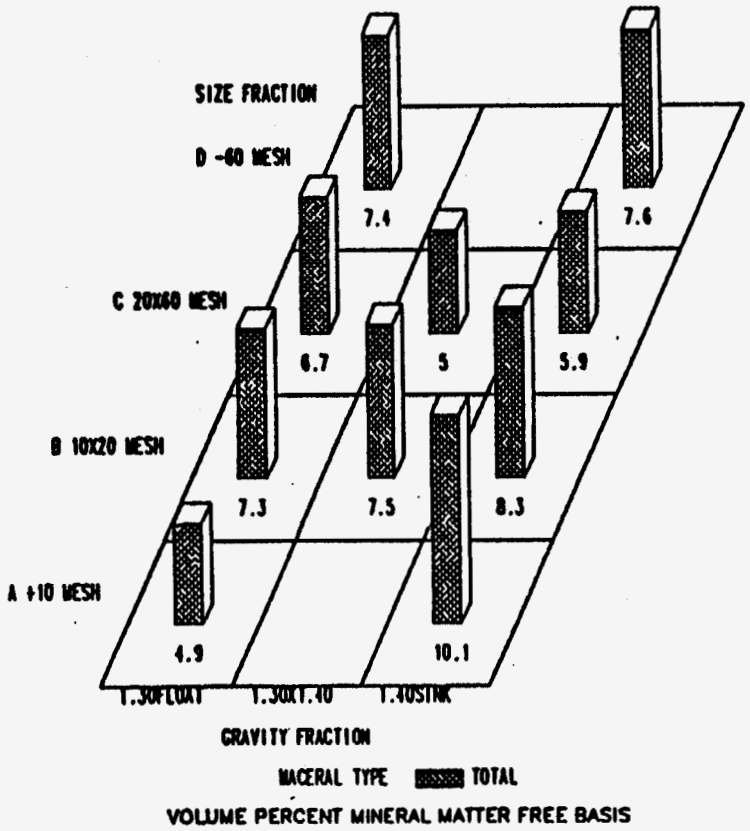
Raw Lignite



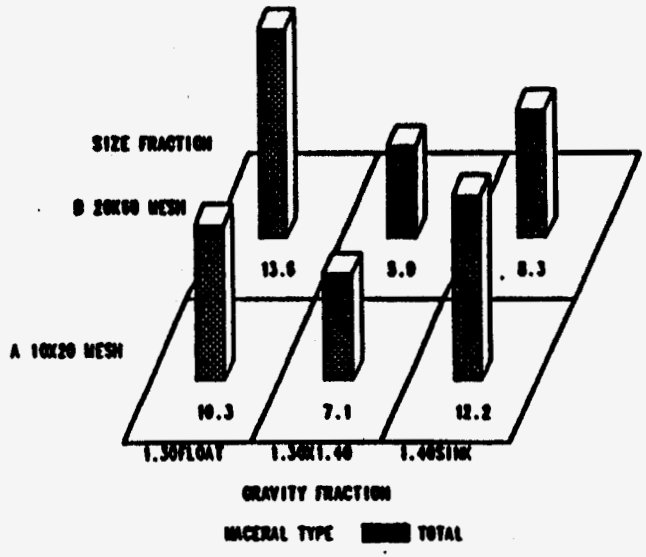
SO_2-Treated Lignite

Figure 4

Exinite Distributions in the Size/Gravity Fractions of Raw and SO_2-Treated Lignite



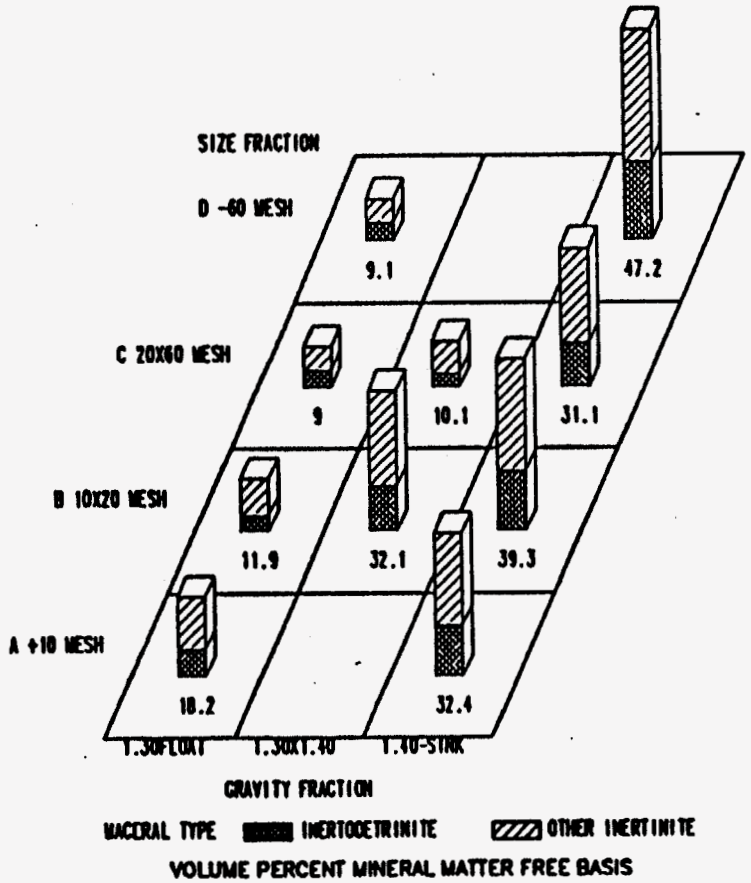
Raw Lignite



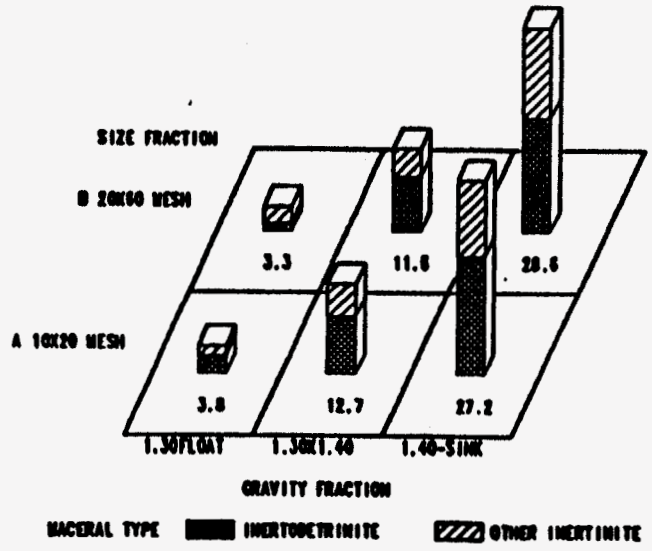
SO_2-Treated Lignite

Figure 5

Inertinite Distributions in the Size/Gravity Fractions of Raw and SO_2-Treated Lignite



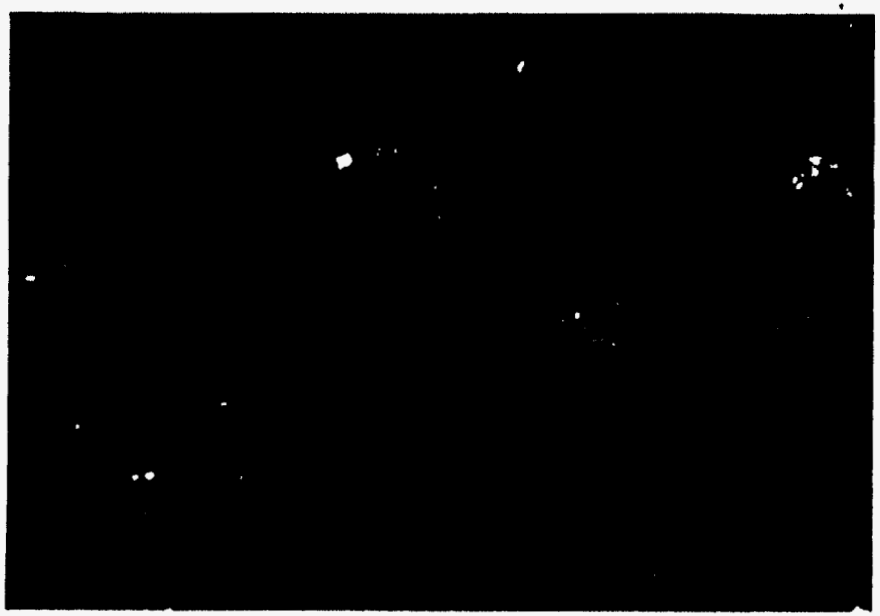
Raw Lignite



SO_2-Treated Lignite

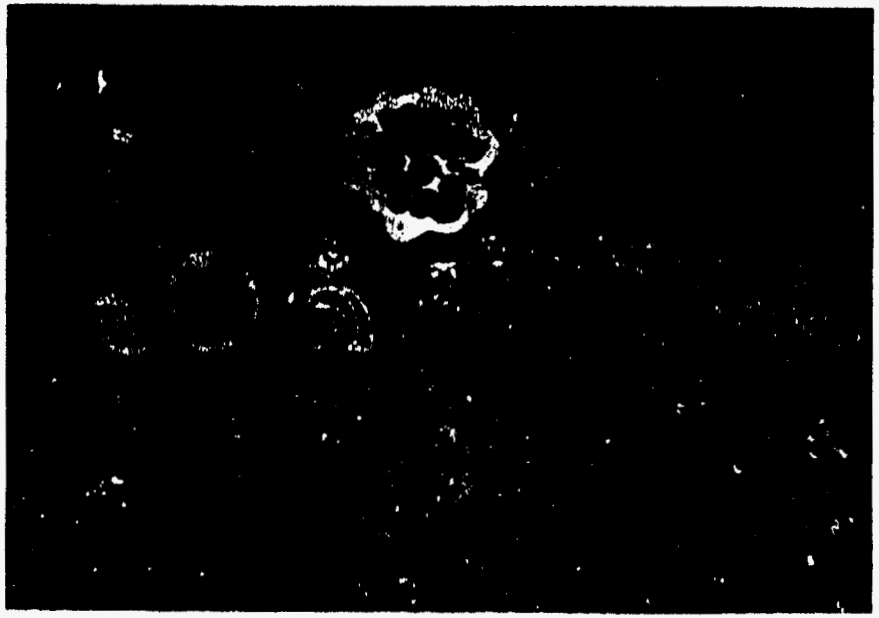
Pl 1

Representative huminite macerals



ULMINITE (texo-ulminite type)

ULMINITE (eu-ulminite type

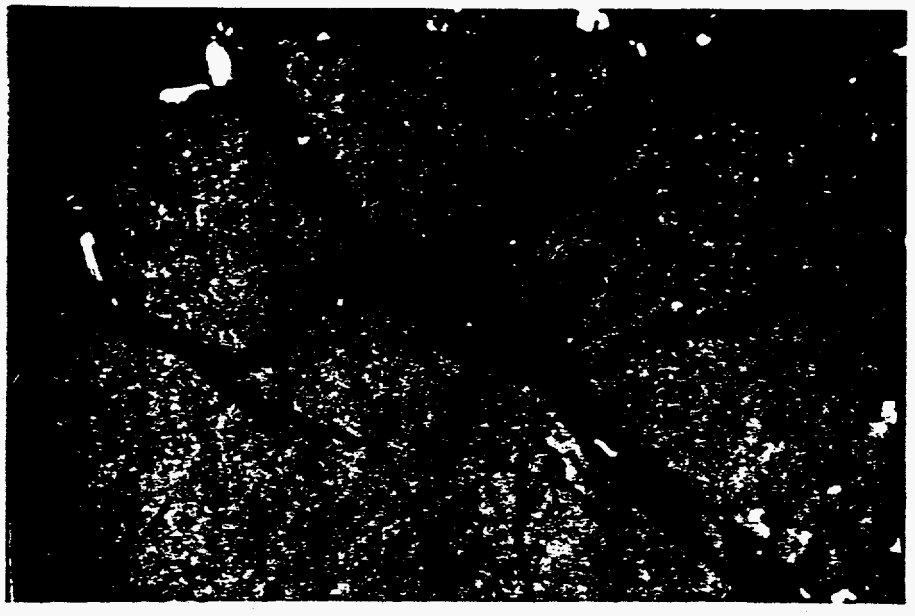


HUMODETRINITE

Plate B

Representative gelinite macerals

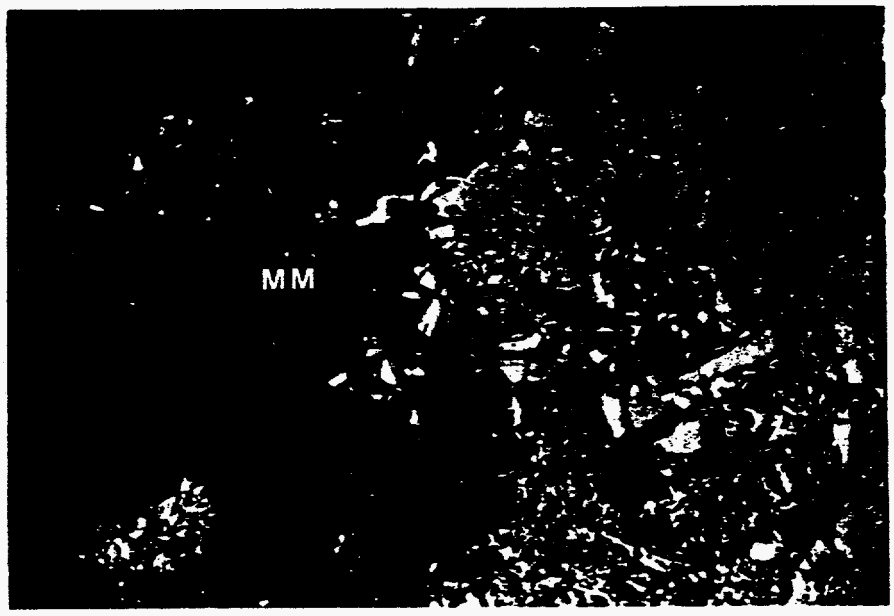
GELINITE (porigelinite type)



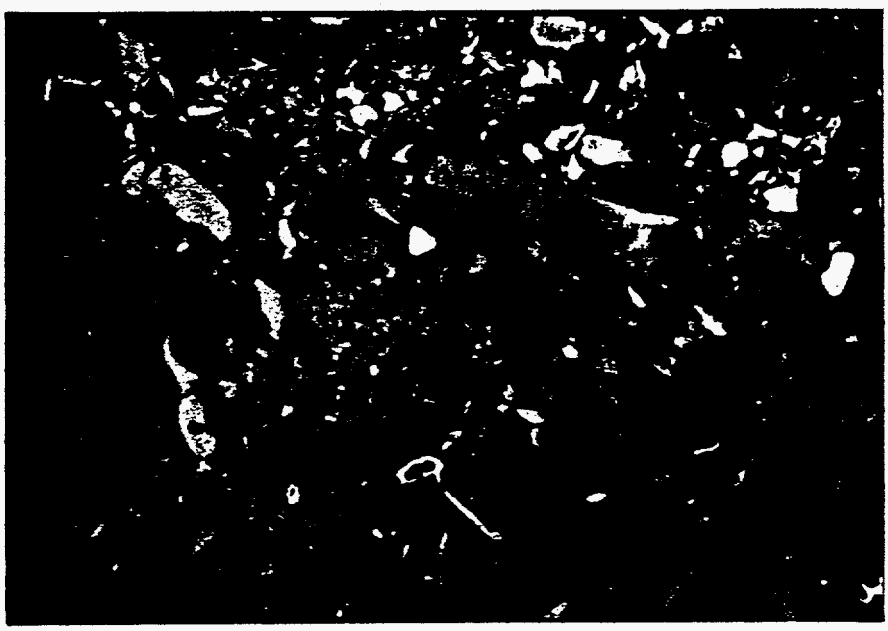
GELINITE (levigelinite type)

Plate C

Representative inertinite macerals



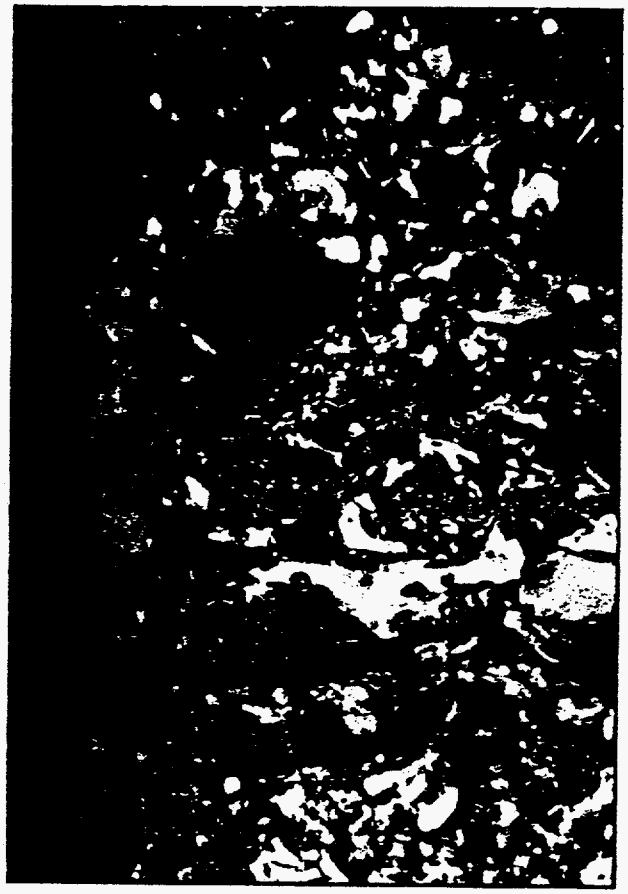
INERTINITE (fusinite, white)
(note mineral matter "MM")



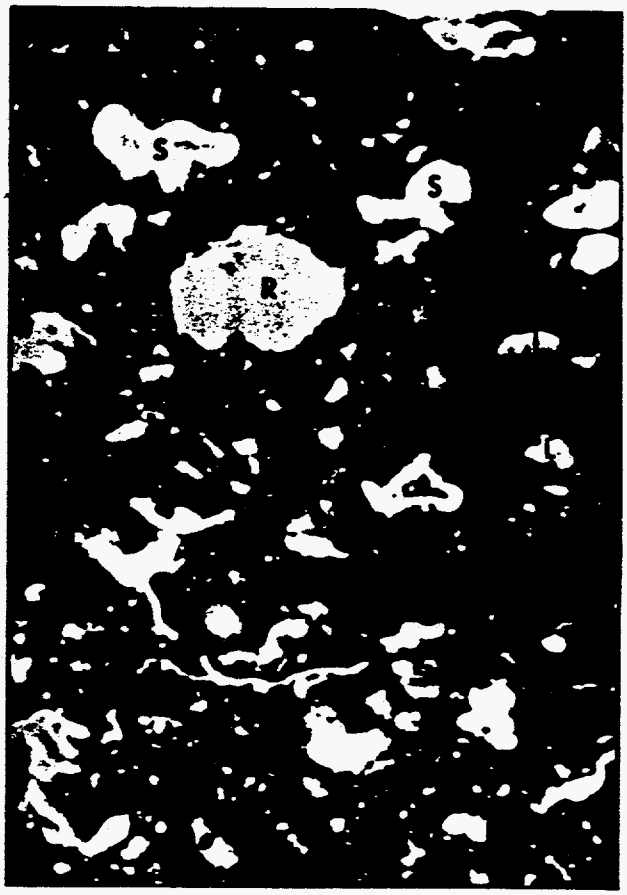
INERTODETRINITE (small bright white fragments)

Plate D

The effect of using fluorescence in observing exinite macerals



White reflected light image



Blue excitation, fluorescent image

Note the better recognition of fluorescent liptinite group macerals in the fluorescent image. "R" resinite "S" sporinite "L" liptodetrinite

APPENDIX B

TABLE B-1

C/C Liquefaction of Black Thunder Subbituminous Coal: Material Balances

	REFERENCE BLACK THUNDER SUBBITUMINOUS											AIR OXIDIZED		SOLVENT CORRECTION[a]	
SAMPLE PERIOD	4	5	6	7	8	10	13	14	15	16	17	19	20	25	26
NET PRODUCT YIELDS (WT% MAF COAL OR EQUIVALENT)															
OILS	89.2	82	86.4	96.5	81.9	86.1	76.3	83.4	79.7	78.3	79	83.4	77.5	16.7	17.4
ASPHALTENES	-27	-21	-25	-26	-22	-24	-17	-24	-21	-19	-21	-21	-16	-19	-20
PREASPHALTENES	-.40	-1.5	-1.6	-2.5	-1.1	-.87	0.54	-.42	0.03	0.07	-.22	4.03	2.16	-1.9	-2
H2S	.	.	.	.	0.48	.	.	0.50	.	.	.	.	0.45	.	0.04
NH3	.	.	.	.	1.66	.	.	1.57	.	.	.	.	1.50	.	0.56
CO + CO2	2.33	2.28	1.88	2.07	2.76	1.99	3.26	.	.	2.65	.	2.37	2.38	0.22	.
H2O	.	.	.	.	17.7	.	.	18.4	.	.	.	.	15.2	.	1.27
C1 TO C3	12.8	11.1	10.6	13.1	12.3	11.8	11.4	.	.	13.5	.	11.7	10.8	4.10	.
C4 TO 360	31.6	11.8	12.3	.	9.76	14.5	15.1	13.8	14.2	14.5	11.7	13.4	15.5	5.58	4.76
360 TO 650	49.4	45.3	51.3	.	47.5	52.4	48.2	45.9	53.4	45.7	54.8	49.3	45.4	14.6	13.2
650 TO 975	8.46	24.2	28.7	.	19.3	1.86	-2.3	2.83	13	5.90	11.7	0.96	4.04	-14	-13
975+	-11	-22	-32	.	-18	-7.9	-1.5	-3.5	-22	-6.9	-20	2.68	-1.5	-10	-9.9
C4 TO 650	64	57.1	63.1	.	57.3	66.8	63.4	59.7	67.6	60.2	66.5	62.7	61	20.2	18
C4 TO 975F	72.4	81.3	91.8	.	76.6	68.7	61.1	62.5	80.5	66.1	78.2	63.6	65	6.18	5.49
UNCONVERTED COAL	11.8	15.5	15.5	12.2	15.2	14.2	15.1	15	14.5	13.7	15.9	8.37	14.3	1.25	1.13
ASH	-.93	-.32	-3.1	.	-1.2	-1	-.81	-1.5	-1.6	-2.3	-1.4	-2.6	-.56	.	.
HYDROGEN	.	.	.	.	-9	.	.	-8.9	.	.	.	.	-8.2	.	-2.7
PRODUCT MATERIAL BALANCES															
% OVERALL BALANCE	94.6	95.3	89.8	86.9	103	89.2	95.7	87.5	95.4	90.9	99.2	87.9	90.9	96.1	92.3
% ASH BALANCE	87.5	95.7	57.8	.	83.4	86.4	89.2	79.9	78	69	80.6	64.7	92.4	.	.
HETEROATOM REMOVAL (% OF HETEROATOMS IN FEED)															
SULFUR	.	.	.	.	72.7	.	.	75.1	.	.	.	.	68	.	33.8
OXYGEN	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
NITROGEN	.	.	.	.	41.8	.	.	39.6	.	.	.	.	37.8	.	29.4

a) Net yields for solvent only periods were multiplied by the average ratio of solvent to MAF coal for this run to get solvent corrections that can be subtracted from yields from periods with coal to correct for solvent reactions.

b) Yields are expressed as percents of moisture, ash-free (MAF) coal. Calculations in this table assume that there was no conversion of solvent.

TABLE B-2

C/C Liquefaction of Martin Lake, Texas Lignite: Material Balances

	REFERENCE MARTIN LAKE LIGNITE									AIR OXIDIZED		SOLVENT CORRECTION		LIGNITE REFERENCE	
SAMPLE PERIOD	2	4	6	7	8	9	10	11	13	15	16	18	19	21	22
NET PRODUCT YIELDS (WT% MAF COAL OR EQUIVALENT)															
OILS.....	102	77	89.8	85.6	116	88.8	92.9	91.2	75.6	73.6	67.2	11.7	11.7	85.3	72.7
ASPHALTENES.....	-38	-31	-29	-27	-29	-29	-36	-36	-22	-21	-17	-16	-16	-26	-20
PREASPHALTENES.....	-3.8	0.65	-1.3	-2.4	1.93	-2.7	1.64	-1.6	-1.2	1.99	-2.4	-.70	-.65	-3.4	-.05
H2S	.	0.93	.	.	.	.	1.11	.	.	.	1.10	.	0.00	.	1.35
NH3	.	2.20	.	.	.	.	2.95	.	.	.	2.35	.	0.59	.	2.62
CO + CO2.....	.	2.39	.	3.32	2.96	3.80	4.33	.	3.81	6.22	7.97	.	0.35	4.62	.
H2O	.	15.9	.	.	.	.	.19	.	.	.	14.3	.	0.50	.	18.8
C1 TO C3	.	3.43	.	7.59	14.2	13.3	14.4	.	14.1	14.5	19.3	.	4.27	15.6	.
C4 TO 360	.	3.94	17.7	15.8	.	21.3	20.2	22.1	15.6	19.7	20.3	4.71	6.50	-3.6	18.4
360 TO 650	.	24.4	44.6	47.8	.	54.1	56.4	48.5	55.7	43.5	54.3	14.4	17.6	46.1	40.1
650 TO 975	.	8.77	3.71	22.9	.	1.06	-.29	23.8	-4.6	-16	-21	-14	-9.8	16.8	-2.2
975+	.	9.78	-6.6	-30	.	-19	-18	-41	-14	7.11	-5.1	-9.7	-19	-3.4	-4
C4 TO 650	.	28.3	62.3	63.4	.	75.4	76.6	70.5	71.4	63.2	74.7	19.2	24.1	42.5	58.5
C4 TO 975F	.	37.1	66	86.4	.	76.5	76.3	94.3	66.7	47.1	53.4	4.84	14.3	59.3	56.3
UNCONVERTED COAL	9.72	36.1	12.3	20	2.53	14.7	11.4	15	18.3	15.6	16.6	0.32	1.23	12.6	15.1
ASH	-1.3	-.67	-7.9	2.82	0.80	1.41	-.84	-.64	0.09	-.30	-2.4	.	.	-6.3	-5.1
HYDROGEN	.	-7.8	.	.	.	.	-11	.	.	.	-9.9	.	-2.4	.	-10
PRODUCT MATERIAL BALANCES															
% OVERALL BALANCE.....	79.8	113	109	98	95.5	105	97.1	94.4	98	97.6	95.9	98.5	102	116	106
% ASH BALANCE	92.8	96.2	55.4	116	105	108	95.3	96.4	101	98.3	86.5	.	.	64.8	71.3
HETEROATOM REMOVAL (% OF HETEROATOMS IN FEED)															
SULFUR	.	41.7	.	.	.	.	49.6	.	.	.	49.1	.	1.25	.	60.7
OXYGEN	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
NITROGEN	.	40.7	.	.	.	.	54.4	.	.	.	43.4	.	30.9	.	48.4

a) Net yields for solvent only periods were multiplied by the average ratio of solvent to MAF lignite for this run to get solvent corrections that can be subtracted from yields from periods with lignite to correct for solvent reactions.

b) Yields are expressed as percents of moisture, ash-free (MAF) lignite. Calculations in this table assume that there was no conversion of solvent.

TABLE B-3

C/C Liquefaction of Illinois No. 6 Coal: Material Balances

	REFERENCE ILLINOIS NO. 6 COAL										SOLVENT CORRECTION	
SAMPLE PERIOD	2	3	4	6	8	10	12	14	16	18	20	21
HOURS ON STREAM	38	61.3	89.8	131	178	225	273	320	360	408	448	471
NET PRODUCT YIELDS (WT% MAF COAL OR EQUIVALENT)												
OILS	71.1	64.9	41.7	49.4	52	36.3	43.4	42.3	37.3	35.6	2.48	5.20
ASPHALTENES	-1.4	2.05	12.4	7.20	8.51	8.86	8.40	10.1	12.2	13.8	-14	-11
PREASPHALTENES	4.26	5.89	6.39	12.8	13.6	15.6	18.1	15.6	10.7	12	2.78	1.16
H2S	.	2.92	.	.	2.48	.	.	.	.	2.38	-.07	.
NH3	.	1.26	.	.	0.71	.	.	.	.	0.56	0.26	.
CO + CO2	1.19	1.19	1.45	1.56	1.28	1.27	1.37	1.16	1.68	1.67	0.25	0.25
H2O	.	11.6	.	.	11.6	.	.	.	.	10.8	0.21	.
C1 TO C3	8.53	8.22	11.4	11.8	8.86	8.77	9.50	8.05	11.6	11.5	3.02	2.96
C4 TO 360	.	9.47	.	11.4	6.91	.	5.65	3.31	7.08	17.2	0.85	0.44
360 TO 650	.	36.1	.	37.1	34.5	.	32.1	26.6	28.5	27.4	8.68	7.78
650 TO 935	.	11.9	.	-13	5.27	.	0.46	5.20	5.03	-14	-6.3	-1.8
935 +	.	15.9	.	34.6	27.9	.	32	33.4	20.1	30.6	-11	-11
C4 TO 650	.	45.5	.	48.4	41.4	.	37.9	29.9	35.6	44.8	9.53	8.22
C4 TO 935	.	57.4	.	35.3	46.7	.	38.4	35.1	40.6	31.2	3.26	6.40
UNCONVERTED COAL	7.50	9.68	6.61	7.41	6.50	7.42	8.66	11.6	16.3	17.7	5.71	2.31
ASH	.	-1.6	1.71	0.74	2.80	1.71	0.83	2.00	1.80	1.67	0.89	0.28
HYDROGEN	.	-7.6	.	.	-5.6	.	.	.	.	-5.9	-1.1	.
PRODUCT MATERIAL BALANCES												
% OVERALL BALANCE	98.9	102	116	102	86.6	106	101	84.7	81.7	81.4	89.1	90.1
% ASH BALANCE	.	84.2	116	107	127	116	108	119	117	116	.	.
HETEROATOM REMOVAL (% OF HETEROATOMS IN FEED)												
SULFUR	.	72.5	.	.	61.5	.	.	.	.	59.2	-41	.
OXYGEN	.	.	.	.	.	.	.	.	.	.	.	.
NITROGEN	.	39.3	.	.	22.2	.	.	.	.	17.5	18.9	.

a) Net yields for solvent only periods were multiplied by the average ratio of solvent to MAF coal for this run to get solvent corrections that can be subtracted from yields from periods with coal to correct for solvent reactions.
b) Yields are expressed as percents of moisture, ash-free (MAF) coal. Calculations in this table assume that there was no conversion of solvent.