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ADVANCED DIRECT LIQUEFACTION CONCEPTS for PETC GENERIC UNITS

Phase I Final Report

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

Mark Dvorscak 10/30/95

by Office of Intellectual Property Counsel, DOE Field Office, Chicago — Date

University of Kentucky
Center for Applied Energy Research

Sandia National Laboratories

CONSOL Inc.

LDP Associates

March 1995

Prepared for

The U. S. Department of Energy

Under Contract No.

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Executive Summary

The Advanced Concepts for Direct Coal Liquefaction program was initiated by the Department of Energy in 1991 to develop technologies that could significantly reduce the cost of producing liquid fuels by the direct liquefaction of coal. One of the contracts awarded under this program was a collaborative effort between the University of Kentucky Center for Applied Energy Research (CAER), CONSOL, Inc., LDP Associates and SANDIA National Laboratories that began in August 1991. Although there had been significant advances both in improving the technology for converting coal to liquid fuels as well as improving the economics, the cost was still far greater than for fuels produced from petroleum. The advanced 2-stage liquefaction technology that was developed at Wilsonville over the past 10 years has contributed significantly toward decreasing the cost of producing liquids from coal to about $33/bbl. It remains, however, the objective of DOE to further reduce this cost to a level more competitive with petroleum based products. This project, among others, was initiated to investigate various alternative approaches to develop technologies that might ultimately lead to a 25% reduction in cost of product.

In this project a number of novel concepts were investigated, either individually or in a coupled configuration that had the potential to contribute toward meeting the DOE goal. The concepts included mature technologies or ones closely related to them, such as coal cleaning by oil agglomeration, fluid coking and distillate hydrotreating and dewaxing. Other approaches that were either embryonic or less developed were chemical pretreatment of coal to remove oxygen, and dispersed catalyst development for application in the 2-stage liquefaction process.

This report presents the results of this project. It is arranged in four sections which were prepared by participating organizations responsible for that phase of the project. A summary of the overall project and the principal results are given in this section. First, however, an overview of the process economics and the process concepts that were developed during the course of this program is presented.

Base Case Assessment - LDP ASSOCIATES

A technical assessment of the test results from this program was developed by comparing the new process concepts developed during this project with state-of-the-art Two Stage Liquefaction (TSL) technology. The 6 ton-per-day Wilsonville proof-of-concept (POC) operation with Black Thunder subbituminous coal was chosen as the basis for defining state-of-the art TSL technology. During Wilsonville Runs #262 & 263, conducted in 1991-1992, the POC operated in the so-called hybrid mode with dispersed iron and molybdenum catalysts used in the first reaction stage and a supported nickel-molybdenum catalyst used in the second-stage reactor. Material balance period #263J was chosen as the basis for developing a baseline conceptual commercial plant case against which the results of the program could be compared.

An all-distillate product base case was formulated in which resid extinction was achieved in the system via a reduction in reactor space velocities as predicted by first order reaction kinetics. It was anticipated that the distillate product from liquefaction in this program could differ from

the distillate product obtained at Wilsonville during Run#263J. As a result, all liquefaction distillates are assumed to be upgraded to a common basis (all-gasoline finished product) so that consistent comparisons are assured.

The base case conceptual commercial plant is an all-coal facility located at a mine-mouth Wyoming location. The hydrogen needed for liquefaction is generated by water slurry gasification of ash concentrate from the ROSE unit and coal. Light hydrocarbon gases produced in liquefaction and upgrading are used to close the fuel gas balance. Any excess gas is used to generate hydrogen via the steam reforming process. It is assumed that the electricity needed to help operate the plant is purchased from a nearby utility power plant.

The capital and operating cost estimates for the base case were developed using the relevant portions of previous liquefaction plant studies, as well as in-house LDP Associates information.

The base case plant converts 17,929 T/D of Black Thunder coal (mf basis) into 68,100 BPSD of gasoline product. An additional 5,204 T/D of coal is be gasified in order to meet the plants hydrogen requirements. Overall Maf coal conversion for the base case is 92%. The per pass conversion of resid and IOM in the first and second stage reactors is relatively low at approximately 23.5% and 18%, respectively. A high process solvent to coal ratio of 2.33 is employed since significant quantities of both IOM and ash are recirculated. Recycled ash is approximately 3.3 times the quantity of ash rejected from the process via the ash concentrate. The ash recirculation rate results in a 3.3 concentration effect for both the molybdenum and iron dispersed catalysts. As a result, the effective concentration of molydenum on coal to liquefaction is approximately 430 ppm at the base case fresh addition level of 100 ppm.

A once-through first stage reactor design has been assumed. Four reactor trains in parallel are required to process the 17,929 T/D of coal. The first stage reactor is refractory lined in order to maximize the cross sectional area per reactor. Reactor gas rates were determined based on the estimated average reactor partial pressures which existed during Wilsonville Run #263J and the recycle hydrogen gas purity. Actual reactor residence times and space velocities were also based on estimated WR#263J operation with appropriate corrections for the required resid plus IOM conversion level. Organic rejection (i.e. resid, IOM & DAS) from the liquefaction process amounts to 14.5% on an mf coal basis.

Significant investment cost areas for the base case process units ($2.563 billion) include the liquefaction reaction system, vacuum fractionation system, the hydrogen recovery and recycle system, the makeup hydrogen generation system and the upgrading system. No one particular system dominates process unit investment cost. Offsite unit investment costs ($0.903 billion) are widely distributed among the various units. Working capital, start-up costs and the costs of initial catalyst and chemicals adds an additional 10% to the total capital requirement of $3.842 billion. Assuming a capital charge factor of 15%, the annualized capital costs are $26.45 per barrel of gasoline product.

Total operating costs for the base case are approximately $20/bbl of gasoline product including

a $1/Bbl. credit for ammonia, sulfur and phenol byproducts. The significance of liquefaction system additives and purchased electrical power costs and the relative insignificance of coal cost is noteworthy. Liquefaction additives costs are approximately $5.20/Bbl. of gasoline, with the iron and molybdenum dispersed catalysts accounting for more than half of this total. Coal costs are low because of the low $5/ton-wet mine mouth price for Black Thunder coal. On this basis, assuming a capital charge factor of 15%, the base case required gasoline product selling price is $46.46/Bbl.

Case Analysis of the Advanced Concepts - LDP ASSOCIATES

An "Advanced Concepts Case" (ACC) was formulated which includes three process variations from the base case. The objective was to increase product yield per unit of coal feed while reducing solvent recycle rate and liquefaction system additive costs.

- Coal Impregnation With a Molybdenum Salt via Incipient Wetness: As pointed out in the base case the cost of dispersed iron and molybdenum catalysts accounts for almost $3/Bbl. of gasoline product selling price. A significant portion of this cost results from the use of an expensive molybdenum source, the oil soluble Molyvan L. At $3.20/lb. and an 8.1 wt.% molybdenum concentration, the cost per pound of molybdenum is $39.50. By using a molybdenum salt such as ammonium octamolybdate (available in tonnage quantities), the raw material cost per pound of molybdenum could be reduced to $7.30. Even when processing costs for preparing the salt solution, impregnating a small portion of the feed coal to liquefaction and driving off the extra water added to the coal are added, the cost of the impregnated molybdenum is still only about 25% of the cost of using Molyvan L. When using a molybdenum source in this way, the cost of using molybdenum drops below the cost of using particulate iron oxide at the 1 wt.% on MF coal dosage level of the base case. Using iron at a 1 wt.% level also adds to the ash in the liquefaction system and increases the organic rejection due to the assumed constant solids content of the ash concentrate. Therefore, for the purposes of this assessment, iron catalyst was not used, although test results to date have not proven that iron is unnecessary.

- Oil Agglomeration at Low pH: Results to date indicate that the use of oil agglomeration at low pH can remove approximately 50% of the ash in Black thunder coal. Ash reduction at the front end of the liquefaction process reduces organic rejection at the back end of the process, thereby increasing potential product yield. It also reduces the ash recirculation rate within the process while still maintaining the same catalyst recycle enhancement factor as in the base case. In effect, front end ash removal purges useless inerts from the system. At low pH, potential supported catalyst poisons, such as calcium, sodium, magnesium and potassium are also removed. For this assessment it has been assumed that the second stage reactor supported catalyst replacement rate can be reduced by 30%. Tests to date have also indicated that impregnated iron and molybdenum are retained on the coal during agglomeration.

The oil agglomeration process is well suited for liquefaction. Distillate recycle solvent can be used as the agglomerating agent. Sour water can be used as makeup water to the system and the slurry reject of solids and dissolved salts can be utilized in the gasification slurry mixing systems. In fact, the dissolved salts may even act as a catalyst in the gasification process. Of

course, the use of oil agglomeration adds capital and operating costs to the process. While, the capital cost for low pH oil agglomeration is expected to be moderate ($60 million assumed for the ACC), a definitive process design and estimate is required to better estimate costs for the process. The cost for sulfuric acid consumed in the unit is also significant.

• Distillate Solvent Quality Improvement: For the ACC, three process steps are used to treat the waxy distillate recycle solvent used in the base case. These processes are Solvent Extraction, Solvent Dewaxing and hydrotreating. In combination, these processes effectively remove and recover the waxy material from the distillate solvent and enhance its donor solvent capabilities. Both solvent extraction and solvent dewaxing are commercial processes used in the petroleum refining industry.

The benefit of applying these three processes are:

1. Reduction of distillate solvent recycle while improving quality
2. Recovery of a valuable byproduct wax
3. Increased potential product yield via coal conversion improvement.

It is estimated that the wax yield on MAF coal is 4 wt %. However, this wax builds up in the distillate recycle solvent until its cracking rate equals its production rate. Based on Wilsonville Run#263 data the wax concentration in the distillate recycle solvent is estimated to be approximately 24 wt %. Therefore, when a substantial portion of the wax in the distillate solvent is removed, the distillate solvent recycle, now almost free of recirculating wax, could drop by almost 20% provided that the resultant feed coal slurry is still pumpable (i.e. provided it meets viscosity criteria). In the ACC the coal concentration in the feed slurry to liquefaction increases to 34.4% from 30% in the base case. Total solids (coal+IOM+ash) concentration in the feed slurry in the ACC is slightly less than in the base case (43.1% vs 44.3%). It is recommended that coal slurry feed viscosity measurements be made on projected ACC type material, in Phase II of this program, to verify that the assumed reduction in distillate solvent recycle rate is feasible. The wax that is removed and recovered is a valuable material with a current estimated selling price (34¢/lb) more than double that of gasoline. The ability of the wax market to absorb the significant quantity of wax produced by an ACC size plant is a key consideration.

The solvent extraction process is used upstream of the solvent dewaxing process as a means of significantly reducing the feed rate and therefore the cost of the much more expensive solvent dewaxing process. In the solvent extraction process, a solvent such as furfural or N-methyl-2-pyrrolidone is used to absorb aromatics from the feed stream. The paraffinic wax is not absorbed and passes through the unit. For the ACC, approximately 70% of the distillate solvent feed to the extraction unit is absorbed, thereby reducing the solvent dewaxing unit feedrate by a factor of 3. In the solvent dewaxing process, the paraffinic wax is separated from the feed stream by chilling, precipitation and filtration in the presence of a suitable solvent such as methyl ethyl ketone (MEK). When wax production is desired, as in the ACC, a three stage filtration system is used. In addition, a wax finishing step is also required.

Conventional fixed bed hydrotreating is used to make the final improvement in distillate solvent quality. For the ACC, a single train system operating at conditions favorable for hydrogenation of the aromatics (650 to 750°F & 1800 psig) is anticipated.

In the Process Simulation Testing (PST) phase of the program, average MAF coal conversion improved 2.4 percentage points when the distillate recycle solvent was fully dewaxed and hydrotreated as compared to using the as-is distillate solvent. Hydrogen uptake in the small scale hydrotreating runs for the PST's was less than half of the 1 wt % expected based on Exxon EDS operation. Therefore, for the ACC it is assumed that the full dewaxing and hydrotreating of the distillate recycle solvent will improve MAF coal conversion by 3 percentage points (95% vs 92% in base case). Such an improvement further increases the potential product yield and reduces the IOM recycle rate.

The benefits of reduced feed ash and improved coal conversion are evident. While the solids concentration in the ash concentrate remains the same, organic rejection is reduced to 8.5% on mf coal. At the same time, the recycle solvent rate is reduced by 20% because of wax removal and lower ash and IOM recirculating rates. Molybdenum catalyst recirculation enhancement remains at the same 3.3 factor as in the base case. In order to achieve the higher product yield, the required per pass resid plus IOM conversion increases in both reaction stages. Since reaction temperatures are not changed, this increased conversion is achieved by reducing space velocity (predicted by first order kinetics) by approximately 15% versus the base case. Although reactor space velocities are lower, reactor weights are only slightly higher due to the offsetting effect of lower recycle solvent rates.

In this configuration gasoline product rate increases by 4.5% while a significant quantity of the valuable wax byproduct is also produced. Hydrogen consumption increases in proportion to the increased product rate. Because of the significant decrease in organic rejection, additional gasification of coal is required to close the hydrogen balance. The total electrical power requirement for the ACC increases by approximately 12% due to increased gasification quantities and the requirements of the added units.

Process unit investment increases by $432 million due to the added units and the increased gasification requirements and total capital required increases by $520 million over the base case. Net operating costs drop by approximately $140 million/year due to the lower liquefaction system additive costs and the significant impact of byproduct wax revenue. If a 15% capital charge factor is used, the required gasoline product selling price is $41.82/Bbl or $4.64/Bbl less than in the base case.

Dispersed Catalyst Development - CAER

Probably the greatest success in converting low-rank coal to distillate fuels was achieved at Wilsonville in Runs 263J, when operating in a thermal-catalytic mode with the addition of a dispersed Fe-Mo catalyst to the first stage. This run, which operated on Wyodak coal from the Black Thunder Mine, was the last run ever made at that pilot plant. Whether this same catalyst system could provide equivalent performance with a higher rank bituminous coal is not known.

Because the emphasis in this program was directed toward low-rank coals, it was decided that the performance of any dispersed catalyst system should be related to Run 263J, which was adopted as the base case of this program. In order to relate performance of any experimental system to the base case, it became necessary to develop a standard laboratory scale test that could be used for testing various catalysts and other concepts.

Since the base case operated with a process generated recycle solvent, it was necessary to use an equivalent solvent in order to closely simulate the conditions in Run 263J. The recycle solvent in that run contained about equal parts 1050 °F- distillate and 1050 °F+ resid along with about 20% recycled solids that were approximately equal parts unconverted coal and mineral matter. A significant amount of iron and molybdenum catalysts had accumulated in this stream and were present as pyrrhotite and molybdenum sulfide, respectively. The first challenge in developing a representative test and using this solvent was to understand how the solvents behaved and affected coal during liquefaction.

It immediately became apparent that liquefaction of Wyodak coal in the lab consistently gave THF conversions in excess of 100%. This suggested that the IOM contained in the recycle solvent was solubilized during the reaction. After considerable work, this problem was traced back to the presence of an easily converted THF insoluble fraction that was present in the Wilsonville solvent. In time it became apparent that this same pattern was observed for all the Wilsonville solvents that were evaluated in our laboratory which were obtained from Runs 258K, 260, and 262E. All of these samples had been stored for 2-4 years after they were originally produced, and each of them had IOM concentrations that had increased over this period. It was also observed that this additional accumulated IOM could be easily resolubilized by a rather mild thermal treatment. It was also found that the same solubilities observed for the original materials could be attained by using refluxing pyridine, a somewhat stronger solvent than either cresylic acids or THF that were originally used. The higher coal conversions that were observed when running in these solvents were concluded to be an artifact of the analysis technique and not evidence of facile conversion of unconverted coal materials in the recycle stream.

Another problem that plagued the early work with plant-derived recycle solvents was the presence of the catalyst that had accumulated. The contribution of these catalysts to the overall reaction was not readily apparent. Only when results were obtained using solvents from different Wilsonville runs did the magnitude of the problem become clear. The liquefaction of Black Thunder Wyodak coal in solvents that contained accumulated Mo, in addition to the Fe that was present in all these solvents, was always significantly greater than in solvents which contained only iron. Not only was the activity of the Mo-containing solvent very high, but it also masked the activity of freshly added catalyst.

The early efforts to develop a simulated 1st-stage catalyst screening test using Wilsonville solvents were complicated by this background contribution of the recycled Mo catalyst. A test protocol that simulated resid conversion using microautoclaves was selected that operated at 440 °C for 22 min with 1000 psig cold hydrogen. The coal concentration and the solvent to coal ratio was the same as used in Run 263J. Although the 565 °C+ resid conversion was higher

than actually observed at Wilsonville, for convenience the test protocol remained the same throughout the program. In fact, the resid conversion values obtained under these test conditions, with the 1 wt % Fe_2O_3 and 100 ppmw Mo (as Molyvan L) base case catalyst, as used in Run 263J, was 30-32 wt %, versus a target value of 24 wt %. The significant activity of the recycled Mo became apparent when, with a Mo-free recycle solvent (V-131B) from Run 258K, resid conversions were obtained that were less than 20 wt %.

These results also showed quite clearly that the activity of the accumulated recycled iron (pyrrhotite) was considerably less than that of the Mo component. Further, equivalent resid conversions could only be achieved with fresh Mo catalyst by adding twice the amount that was present in the recycle solvent. In all these cases, fresh iron as iron oxide was added with the Mo. It was later found that the activity of added Mo in the absence of any fresh iron was considerably enhanced, or as finally realized, was actually less inhibited. Although the inhibiting effect of iron has not been widely studied, the present status suggests that iron oxide, sulfate and nitrate all inhibit the Mo activity while pyrrhotite has either no effect or a very small one, at most.

After the economic base case had been developed, it became apparent that the cost of the dispersed catalyst (~$2.60 bbl/gasoline) was quite substantial. Most of the cost could be attributed to the cost of the Molyvan L, which is an oil-soluble molybdenum organophosphorodithioate. A substantial fraction of the cost is associated with the preparation or manufacture of the material. Although the preparative cost could be reduced somewhat, manufacturing costs would still cause a considerable markup over the price of the basic Mo metal. A considerable amount of experimental work in this program was devoted toward impregnating metal catalysts in the form of water-soluble salts onto the coal, eliminating the need for organically soluble catalyst precursors. A whole range of catalyst impregnated coals was prepared with Fe and Mo salts at different concentrations. In the end it appeared that for the Fe-Mo system the reaction was most strongly affected by the concentration of the metals on the coal. In fact, it was also found that the metals could be impregnated on as little as 10% of the coal and perform just as well as if dispersed onto all the coal, an approach that is referred to as the Vector approach in the report.

The technique of catalyst impregnation can substantially reduce the cost of the dispersed catalyst from ~$2.60 bbl/gasoline to ~$1.10 bbl/gasoline. Surprisingly, more than half of the remaining cost (~$0.60) is attributable to the soluble ferrous sulfate that was used in the impregnation. Attention then turned towards either eliminating or reducing the concentration of the iron catalyst. As already mentioned, in the 1st-stage liquefaction screening test, the performance of the Mo in the absence of added Fe was clearly better than when Fe was present. In fact, the level of activity approached the activity found in the base case with the highly active recycled Mo. Other data substantiated this result, including comparative runs with Fe-Mo and Mo-catalysts in deashed resid-containing recycle solvent. Assuming then that Mo alone will give a performance equivalent to the Fe-Mo catalyst, the cost of the dispersed catalyst can be further reduced to about ~$0.40/bbl gasoline, which is even less than the cost of the iron oxide in the base case.

Another interesting catalyst lead that developed in this program was the response of Mo catalysts to the presence of small amounts of nickel. Coals that were co-impregnated with Ni and Mo, both in the presence and absence of Fe, repeatedly gave better coal conversions while continuing to give resid conversions and distillate yields that were equal to those obtained in the Ni-free system. Since enhanced conversion appears to be quite similar to the effect of Fe in the system, the balancing of the catalytic selectivity by using Ni at a considerably lower concentration can be achieved while reducing cost. In most of the catalysts that were tested, the Mo/Ni molar ratio was 4/1. The cost of adding this level of Ni to 100 ppm Mo, where no Fe was used in the system, would be only $0.03, which is still less than the cost of the 1% iron oxide used in the base case.

Another family of catalysts that were investigated during the course of this study were sulfated hematites that are prepared by base precipitation of solutions of soluble iron salts. Other researchers had found that particulate sulfated-hematites, as well as various metal promoted ones, were exceptionally active in liquefaction. A number of these materials were prepared and tested in this program. The results with these catalysts were somewhat scattered, showing, at times, exceptional activity, while, at others, producing resid conversions that were significantly less than obtained in the base case. Unfortunately, it isn't known whether an activation factor or a variable in the synthesis procedure was responsible for this scatter in the data.

A preliminary process and economic evaluation of the preparation of this type of catalyst showed that the cost of a Mo-promoted hematite, used at a level equivalent to the Fe and Mo concentrations in the base case, with a distillate product yield equal to that of the base case, would cost about ~$1.90/bbl gasoline. Reducing the Fe by half while maintaining the same 100 ppm Mo level decreases the cost of the catalyst to ~$1.20 bbl/gasoline. Additional process benefits that could be derived from using these catalyst would further reduce that cost. Therefore, based upon the very positive results that have been observed elsewhere, as well as our own lab results, suggest that this approach deserves further attention.

During the project as the performance and economic evaluation of individual concepts progressed, the integration of several of these individual concepts was investigated. The individual steps of coal preparation, solvent modification, and dispersed catalyst addition were combined and evaluated in a series of experiments using the 1st-stage liquefaction test that was discussed above. In addition to the effect of adding the Fe-Mo-impregnated catalyst to the system, dewaxing and hydrotreating distillate recycle solvent gave an improvement in resid conversion of up to 4.6% along with a 3.2% increase in THF conversion. The corresponding change in distillate yield calculated from the material balance is approximately twice the resid conversion value. For the impregnated catalyst, when combined with oil agglomeration and dewaxing-hydrotreating, coal conversion increased by 2%. By itself, as expected, oil agglomeration had little effect on resid or THF conversions. The benefit of coal cleaning could only be observed in a recycle mode where the concentration of catalyst in the recycle catalyst would increase.

Chemical Coal Pretreatment - CAER

Various methods were examined during the course of this program to chemically modify the coal to provide a product that would react more readily in the liquefaction process as well as have a reduced oxygen content. Increasing the reactivity of the coal would enhance conventional 2-stage liquefaction. In the base case, that would be equivalent to a reduction of about 10% in the cost of the gasoline product or about $3 to $4/bbl gasoline. This would occur if the oxygen were removed as CO_x in lieu of water. Accompanying this reduction in water production would be other complementary process benefits, all of which could further improve process economics.

The reactions of Black Thunder mine coal was examined in a variety of thermal and hydrothermal process conditions at temperatures typically up to about 350 °C. The resulting products were analyzed and material balances were determined as outlined in detail in the main report. The major findings from this work were:

- Hydrothermal treatment of a Wyodak coal can remove up to about 40% of the oxygen both as water and a mixture of CO and CO_2 (CO is a minor product) along with a solid product that is deficient in hydrogen.
- Hydrothermal treatment of this coal in the presence of a base causes a small increase in the amount CO_2 that is produced which corresponds with a slight increase in the removal of oxygen.
- Hydrothermally treating coal with CO in the presence of a Na or K salt (hydroxide, carbonate, bicarbonate, formate) removes up to 75% of the oxygen which, based upon elemental balances, is removed as CO_2. The hydrogen content of the solid product increases, and the heating value is 26% greater than the original coal. The characteristics of this reaction are:

    * Oxygen rejection is strongly influenced by reaction temperature.
    * The composition of salt in the aqueous salt solution (formate or bicarbonate) depends on temperature and salt equilibrium.
    * Solubilities of the solid product as high as 94% in pyridine and up to 78% in THF were obtained.
    * THF solubilities increased with CO conversion and correlated with the amount of hydrogen consumed.
    * Increased solubilities reflect significant changes in the coal structure.
    * The solid product had a higher liquefaction reactivity than untreated coal.

- Hydrothermal reaction of coal is unaffected by the presence of hydrogen at temperatures up to 340 °C.

These results have shown that the hydrothermal treatment of coal with CO can selectively remove a very large amount of the oxygen from low rank coals as CO_2. The economic benefit from attaining this goal could result in a significant decrease in gasoline price. The reaction is very selective and utilizes the unique donor properties of the formate ion resulting in a high

degree of reaction specificity. Since this approach is still very embryonic, in order to exploit this approach, additional laboratory work is needed to more precisely define the conditions under which this reaction will occur.

Fluid Coking - CONSOL/CAER

Fluid coking was investigated as an alternative method to the ROSE process for removing ash and unconverted carbon from the 2-stage liquefaction process. Experimental coking runs were made in a bench-scale continuous coking unit at the CAER and its products were analyzed at CONSOL. The key results from that program were:

- Tar yield increased proportionately from 43 to 53% over a steam/resid ratio of 4-13 lb/lb.
- Essentially all of the overhead product (98%) was soluble in THF. Elemental analyses were the same as the starting deashed resid (V-130), except for a several percent increase in oxygen content. The phenolic −OH concentration was slightly lower.
- Proton distribution analyses indicate that the products are somewhat less paraffinic, slightly less naphthenic, and slightly more aromatic than the THF solubles in the feedstock.
- Coker overheads result from steam distillation of the feedstock.
- Relative to the Lummus run, coker overhead yields were similar (44%) but the product contained less aromatics and more hydrogen.

It was concluded that since the experimental results were essentially the same as the Lummus results, per analysis by CONSOL, additional experimental results would be of no further benefit for economic analysis.

EXECUTIVE SUMMARY - CONSOL

MAJOR ACCOMPLISHMENTS

CONSOL acquired, documented, prepared, analyzed, stored and distributed the Wilsonville two-stage liquefaction samples that were used by all the participants in this program. The principal samples were from Wilsonville Run 262E and included:

- Black Thunder coal
- V-1074 heavy distillate
- V-130 deashed resid
- V-1082 ashy resid
- iron oxide and Molyvan-L catalysts

Three dewaxing methods (ketone, liquid extraction, and thermal) were tested to remove the wax component from the distillate portion of recycle solvent from two-stage coal liquefaction. Dewaxing was shown to improve the hydrogen donor solvent quality of the recycle distillate alone, or in combination with hydrogenation of the dewaxed distillate.

Ketone dewaxing of the Wilsonville Run 262E V-1074 heavy distillate was tested with acetone, MEK, toluene and various mixtures of these at temperatures from -35 °C to 0 °C. The degree of dewaxing was found to be a function of solvent composition and temperature. Significant findings are:

- Solvent quality improves rapidly with dewaxing up to ~20 wt % wax removal and then levels off.
- Black Thunder coal conversion increases from ~87 wt % to 90 wt % when dewaxed distillate is substituted for the untreated distillate in the Wilsonville Run 262E solvent in 5-min microautoclave tests at 824 °F, 1.5 S/C, 1500 psig (cold) H_2.
- Hydrogenating the dewaxed distillate further improves coal conversion to ~91 wt %.
- Clean wax byproduct, similar to commercial petroleum based waxes, is produced by de-oiling the slack wax that is removed from coal-derived distillate.
- The slack wax properties indicate that it should be an excellent feedstock to produce high yields of light products in an FCC.

N-methyl-2-pyrrolidone (NMP) and furfural were used at ambient temperatures to extract the aromatics from the heavy distillate fraction of the recycle solvent. Significant findings are:

- The slack wax yield is greater, but the wax is of lower quality than that from ketone dewaxing (>40 wt % vs ~20 wt %).
- The extracted material is more aromatic than the ketone dewaxed distillate (~30% aromatic hydrogen vs ~20%).
- The residual extraction solvent is difficult to remove completely from the aromatic fraction.
- The solvent quality of the aromatic fraction is the same as that of the feed distillate.
- Hydrogenation of the aromatic fraction is expected to improve solvent quality.

Thermal dewaxing was tested by heating the heavy distillate to over 900 °F for five minutes to selectively crack the aliphatic compounds. Significant findings are:

- Dewaxed oil yield is ~75 wt % at 925 °F, and lower.
- Gas yield is <5 wt % at 925 °F, and lower.
- The dewaxed material is more aromatic than most ketone dewaxed distillates (~25% aromatic protons in 925 °F dewaxed distillate).
- Hydrogenating the dewaxed (925 °F) distillate produces an improved liquefaction solvent (Black Thunder coal conversion increases by 2 wt % when this hydrogenated thermally dewaxed distillate is substituted for untreated distillate in recycle solvent).

Oil agglomeration using the heavy recycled distillate as the agglomerating oil was successful in reducing the ash content of the feed coal to liquefaction. Significant findings are:

- Coals of rank from lignite through bituminous are reduced in MF ash content through agglomeration by 15 to 75 % relative to the feed coal, as shown below:
  - Black Thunder subbituminous coal at low pH: 3.7% MF product ash; 46% rejection.
  - Black Thunder coal at natural pH: 4.6% MF product ash; 31% ash rejection.
  - Clean Burning Star 2 coal: 7.6 wt % MF product ash; 38% ash rejection.
  - Kemmerer subbituminous coal: 1.9 wt % MF product ash; 50% rejection.
  - Martin Lake lignite: 9.9 wt % MF product ash; 28% rejection.
  - Beulah-Zap lignite at low pH: 2.5 wt % MF product ash; 75% rejection.
  - McKinley subbituminous coal: 4.6 wt % MF product ash; 64% rejection.
- An empirical model was created to relate agglomeration physical deashing performance of coal of various ranks with silica content.

Oil agglomeration was found to be a suitable recovery method for pretreated coal. This was demonstrated by recovering coal at temperatures of 50 to 175°C from: 1) coal which had been pretreated by CAER at temperatures greater than 300 °C with CO in basic slurry (agglomerated from slurry and from dry coal); 2) wet coal which had been impregnated with Fe by CAER by ion exchange; 3) wet coal which had been impregnated with Fe and Mo by CAER by incipient wetness; and by 4) successfully agglomerating various coals using several oils over a range of pH, temperature, and slurry concentration.

Oil agglomeration was shown to be effective for recovery of catalyst impregnated coals as

demonstrated by complete retention of Fe and Mo in incipient-wetness-treated Black Thunder coal agglomerates, and retention of 71% of the Fe in ion-exchanged coal.

Other significant findings of the oil agglomeration research include:

- Nearly quantitative recovery of the coal and oil as the agglomerates was demonstrated.

- The reactivity of Black Thunder coal was demonstrated to be unchanged by agglomeration, within measurement limits.

- Agglomeration water requirements were estimated, and the agglomeration coal slurry concentration was increased to decrease the water requirement and associated costs; this modification was also found to improve deashing.

- The benefits of integrating agglomeration into liquefaction were identified. Development needs to refine costs and benefits and to resolve uncertainties of process integration were defined. Key development topics include:

  ▸ Water availability and use (sour water use, recycle and integration possibilities).

  ▸ Drying (how much needed, where in process).

  ▸ Continuous liquefaction testing, which is needed to quantify/validate expected benefits.

- The potential for physical cleaning of several coals (Black Thunder, Burning Star 2, and Martin Lake) was assessed by float/sink tests, and by column flotation (Black Thunder only).

Significant accomplishments in solids separation were:

- The composition and yield of light ROSE-SR deashed resid was simulated using cyclohexane extraction of Wilsonville deashed resid.

  ▸ This material should be amenable to hydrogenation to improve solvent quality.

  ▸ Most of the resid components which are detrimental to the hydrogenation catalyst are removed in this operation.

  ▸ Possible flow rates were estimated.

- Segregation of the feed coal into a lower ash cleaned coal product that can be fed to liquefaction and a higher ash reject that can be gasified to produce hydrogen was

shown to be an potentially attractive option to improve liquefaction economics.

- Several additional solids separation concepts were tested, which offer some potential for future development. However, they are not ready for Phase II development.

SPECIFIC ACTIVITIES

Sampling and Analysis

CONSOL obtained, prepared, analyzed, stored and distributed the Wilsonville feed coal and process-derived materials that were used in this project. Descriptions and chemical analyses of key samples are summarized in this report. Complete sample descriptions and analyses can be found in References 1-12.

Dewaxing and Solvent Improvement

Solvent dewaxing was examined as a means of improving coal liquefaction economics through solvent upgrading. The purpose of dewaxing is to remove paraffinic (and naphthenic) materials from the recycle distillate in the coal liquefaction process. Coal liquids, and subbituminous coal liquids in particular, contain a paraffinic wax component. Because of their relative inertness, these paraffins tend to concentrate in the recycle solvent over time. These aliphatic materials dilute the hydrogen donors in the process recycle solvent, and are poor physical solvents for the coal reaction products. Therefore, they can contribute to the retrograde reactions which are thought to impair the dissolution and upgrading of low rank coals. In addition, removal of the paraffins as a wax stream reduces the burden on the reactors to crack them to light distillate products. The reduced reactor burden may translate into higher reactor throughput. The gas production and hydrogen consumption that must accompany the paraffin cracking also are avoided.

Three dewaxing schemes were evaluated for potential use in removing the wax from the recycle solvent in a coal liquefaction plant. The features and benefits of each of these dewaxing routes are summarized below.

Ketone Dewaxing

Features

- All or part of the heavy distillate stream is dewaxed in a ketone-based solvent.
- Dewaxed distillate is recycled, as is or after hydrogenation, to the first stage liquefaction reactor.
- The extent of dewaxing is easily selectable by the choice of conditions.
- Ketone dewaxing is commercially proven technology.

- The removed wax is either purified and sold as a high-value by-product or it is converted to product distillate in an FCC unit.

Benefits

- Ketone dewaxing produces a nearly paraffin-free distillate that is an improved donor solvent that may allow.

  - Improved coal conversions at current liquefaction conditions. Experimental data suggest 3-4 wt % improvement in coal conversion is possible. An increase in single pass coal conversion from 87 to 91 wt % could result in about an 6 wt % decrease in rejected organics and a similarly improved product yield.

  - Operation at lower severity conditions (lower T, P, RT) while maintaining current levels of performance.

  - Operation at higher severity conditions by reduction of retrograde reactions (increases in coal conversions of ~4 wt % were obtained by ~50 °F higher reaction temps); could improve throughput.

- Paraffin-rich wax can be upgraded to a salable clean wax product or fed to an FCC unit for conversion to distillate product. Sale of clean by-product wax can help defray processing costs.

Liquid Extraction Dewaxing

Features

- All or part of heavy distillate stream is dewaxed by liquid extraction with N-methyl-2-pyrrolidone (NMP), furfural or similar selective solvent prior to hydrogenation and recycle to the liquefaction plant.

- Commercially proven technology for removal of aromatics from paraffinic lube oils but not for paraffin removal from aromatic-rich distillates.

- Operation at modestly elevated temperatures (100-200 °F) and atmospheric pressure.

Benefits

- Produces highly aromatic, nearly n-paraffin-free distillate that should be easily hydrogenated.
- Operating costs estimated by LDP Associates to be lower than those of ketone dewaxing.
- With hydrogenation, coal conversion improvements should equal those obtained by ketone dewaxing plus hydrogenation (~3-4 wt % with Black Thunder coal); associated cost benefits of increased product yield through less IOM rejection or

lower severity operation are expected.

Thermal Dewaxing

Features

- All or part of heavy distillate stream is heated to >900 °F for several minutes to thermally crack paraffins and naphthenes.
- The light cracked product is removed as net product and the aromatic-rich heavy distillate is recycled to the liquefaction reactor with or without prior hydrogenation.
- Very simple process flow sheet.
- Similar to British coal "satcracking"; should be easy to demonstrate in bench-scale continuous unit.

Benefits

- Waxes are removed as distillable oils and gases.
- Produces highly aromatic distillate that should be easily hydrogenated (in a separate hydrogenation reactor or in the first stage liquefaction reactor) to produce a superior donor solvent with similar benefits to other dewaxing methods.

Agglomeration and Coal Cleaning

CONSOL studied coal agglomeration as a potential means of ash rejection and catalyst incorporation with the goal of improving liquefaction economics by increasing yields and lowering catalyst requirements. Several agglomeration scenarios are presented to summarize this work. These scenarios include: agglomeration at natural pH; agglomeration of low-rank coal at natural pH, with pretreated coal recovery; agglomeration at natural pH, with catalyst impregnation; agglomeration of low-rank coal at low pH; and segregation of feed coal based on ash content for liquefaction and gasification.

There are three basic issues to be addressed in developing agglomeration as an integrated component of a coal liquefaction process. These are:

- What is the agglomeration performance at a given set of conditions?
- What is the cost of agglomeration at those conditions?
- What is the liquefaction benefit and economic value of the agglomeration?

The first question can be answered by a few definitive lab experiments. For the most part, the Phase I work falls into this category. The latter two questions deal more directly with development and scale-up of the process, and will be addressed more specifically in Phase II

work. The latter issues are sensitive to the specific liquefaction plant concept, especially to how the liquefaction process is operated with the lower-ash feed, and to the degree of integration of agglomeration within the overall plant. These are where the major uncertainties lie, and are expected to be better defined as the process is scaled up and tested. The underlying problem is in choosing an environment or scenario that makes the whole process economically attractive. This requires that the three basic issues be addressed in an integrated or overlapping fashion, rather than as separate issues. The liquefaction benefits are not easily measured in the lab, thus requiring testing at the larger scale.

Agglomeration at Natural pH

Features

- Coal ranging in rank from lignite through bituminous can be reduced in MF ash content by ca. 15 to 64 relative percent.
- Natural pH or minor adjustment to pH ≈6-8.
- Oil dosage of ca. 15 to 35%, 50-65 °C, coal slurry concentration of 20-43%.
- Uses sour water (low pH may enhance ash rejection from some coals).
- Dissolved salts bled to Texaco gasifier.
- All organics, most iron, and pretreated catalyst retained.
- Some silica and ≈50% of sodium rejected from low-rank coals
- No coal reactivity loss.

Benefits

- Lower organic rejection results in perhaps a few percent higher MAF distillate yield.
- Lower ash content feed lowers viscosity and allows:
  - ▸ Reduced solvent/coal ratio to perhaps 1.6, or
  - ▸ Higher internal ashy recycle and reduced size of ROSE-SR unit.
- Reduced make-up of disposable catalyst with increased ashy recycle.
- Catalyst exposure to metal poisons may be reduced (especially Na in low-rank coals), resulting in lower catalyst replacement rate.
- Recovers coal from any aqueous pretreatment

In this scenario, coal is slurried with waste sour water from liquefaction and recycled water,

and it is agglomerated with heavy distillate. The agglomerates are rinsed over screens, blown with air to remove surface moisture, and sent to liquefaction. Additional drying prior to liquefaction is optional and depends on other factors (i.e., it is not a requirement of agglomeration). A slipstream of the agglomerate rinse water with mineral matter is used to slurry ash concentrate and coal for Texaco gasification. The remaining agglomerate rinse water with mineral matter is treated to remove solids, and then recycled for slurrying coal and rinsing agglomerates. Any additional water requirement would use gasification sour water, and any excess agglomeration waste water would go to water treatment with the gasification sour water. Liquefaction should be a net producer of water, both from coal drying, and from hydrogenation. Depending on implementation, it is anticipated that there can be an adequate water supply for agglomeration. In the Bechtel low-rank design case, liquefaction is a net consumer of water, with cooling (evaporation) being the biggest sink. For agglomeration, cost of water use and treatment will be minimized by using waste streams wherever possible.

Agglomeration of Low-Rank Coal at Natural pH, with Pretreated Coal Recovery

Features and Benefits

- Any aqueous coal pretreatment will require a recovery step.

- Recovery of coal from CO-pretreatment (as dry coal and as slurry) was demonstrated in Phase I work.

- Recovery of coal after two types of catalyst impregnation steps was also demonstrated in Phase I work. This avenue is pursued further in the discussion of agglomeration at natural pH, with catalyst impregnation, below.

- Other features and benefits are as generally described in the discussion of agglomeration at natural pH.

This concept differs from that of untreated coal recovery by agglomeration at natural pH in that aqueous coal slurry from a pretreatment step is agglomerated, instead of using sour water to slurry the coal. This concept is not restricted to any particular pretreatment, but was demonstrated in Phase I with CO-pretreated coal, and with catalyst-impregnated coal. Any use of sour water in the pretreatment or agglomeration steps depends on the specific pretreatment requirements. It is possible that rinsing of agglomerates with sour water could be done. Although not limited to any particular coal rank, it is anticipated that pretreatment will be most useful when low-rank coal is the feedstock.

Agglomeration at Natural pH, with Catalyst Impregnation

Features and Benefits

- Catalyst impregnation involving aqueous coal pretreatment can be followed by agglomeration for recovery, or impregnation can be incorporated into the

agglomeration step.

- Other features and benefits are as generally described for agglomeration of untreated coal and pre-treated coal at natural pH.

In this concept, the agglomeration feed could be a pretreated coal, or a pretreated coal slurry (as in agglomeration of low-rank coal at natural pH, with pretreated coal recovery, above), or an untreated coal for treatment during part of the agglomeration process. This concept is not restricted to any particular pretreatment, but it was demonstrated in Phase I with two methods of catalyst impregnation of coal, and catalyst impregnation is a likely pretreatment step. Any use of sour water in the pretreatment or agglomeration steps depends on the specific pretreatment requirements. It is possible that rinsing of agglomerates with sour water could be done. Although not limited to any particular coal rank, it is anticipated that pretreatment will be most useful when low-rank coal is the feedstock.

Agglomeration of Low-Rank Coal at Low pH

Features

- Coal ranging in rank from lignite through subbituminous can be reduced in MF ash content by ca. 50 to 76 relative percent.
- pH of 1 or 2 using H_2SO_4.
- Oil dosage of 21 to 54%, 50°C, coal slurry concentration of 20 to 43%.
- Uses sour water (low pH may reduce acid requirement).
- Dissolved salts bled to Texaco gasifier.
- All organics and most iron retained; perhaps pretreated catalyst also retained.
- Some silica and ≈90% (projected) of Na, K, Ca, Mg rejected.
- No coal reactivity loss.

Benefits

- Lower organic rejection results in perhaps a few percent higher MAF distillate yield (estimated to be about 4% for Black Thunder coal).
- Lower ash content feed lowers viscosity and allows:
  - ▸ reduced solvent/coal ratio to perhaps 1.3, or
  - ▸ increased internal ashy recycle and reduced size of ROSE-SR unit.
- Reduced make-up of disposable catalyst with increased ashy recycle.

- Supported catalyst exposure to metal poisons, especially Na and Ca, significantly reduced, resulting in lower catalyst replacement rate by 30% (est.).

- Recovers coal from any aqueous pretreatment.

- Reduced mineral/salt deposition in liquefaction system.

In the low pH agglomeration scheme, low-rank coal is slurried with waste sour water from liquefaction and pH-adjusted recycled water and agglomerated with heavy distillate. The agglomerates are rinsed over screens, blown with air to remove surface moisture, and sent to liquefaction. Additional drying prior to liquefaction is optional and depends on other factors (i.e., it is not a requirement of agglomeration). A slipstream of the agglomerate rinse water with mineral matter is used to slurry ash concentrate and coal for Texaco gasification. The remaining agglomerate rinse water with mineral matter is treated to remove solids and re-establish low pH, and then recycled for slurrying coal and rinsing agglomerates. Any additional water requirement would use gasification sour water, and any excess agglomeration waste water would go to water treatment with gasification sour water. Because liquefaction is a net producer of water, both from coal drying, and from hydrogenation, it is anticipated that there will be an adequate water supply for agglomeration. The cost of water use and treatment will be minimized by using waste streams wherever possible.

Segregation of Feed Coal Quality for Liquefaction and Gasification

Features

- Column flotation or other fine-coal cleaning method.

- For bituminous and subbituminous coals.

- No reject, as discussed here.

Benefits

- Reduces ash content of liquefaction feed coal from 6.3 to 3.8% MF while increasing gasifier feed coal ash to 14.7% MF for fine Black Thunder coal (not SO^3-free).

- Reactive maceral enrichment improves coal conversion by 1% MAF (est.).

- Increases product yield by 3.5% MAF (est.) by reducing deasher reject.

- reduced solids loading allows:
  - lower solvent to coal ratio, or
  - higher solids recycle, which reduces deasher size by 1/5 (est.) and make-up of dispersed catalyst.

In this scenario, the ground feed coal to the plant is fed to a fine-coal cleaning plant to produce two streams: A low-ash liquefaction feedstock and a higher ash gasifier feedstock. Since the gasifiers process all the coal ash fed to the plant anyway, either as native coal ash or as ROSE bottoms ash, this step does not burden the gasifiers with additional ash, but does substantially reduce the ash burden on the liquefaction section.

Solids Separation

Another possible improvement to current liquefaction practices that CONSOL examined was the recovery and utilization of light deashed resid during ash removal. In this scheme, the ROSE-SR unit would be operated in stages to produce a "light" deashed resid (LDAR) stream for hydrogenation with the distillate to improve solvent quality prior to recycle. The "heavy" deashed resid (HDAR) will be recycled without additional treatment and IOM/ash component will be partially recycled and partially rejected. Such operation provides a hydrogenation feed which is amenable to hydrogenation, but is not high in heteroatomic components which are detrimental to the hydrogenation catalyst, and is not high in paraffinic components which are poor hydrogenation feeds.

Solvent Improvement by Staged ROSE-SR Operation

Features

- Three-stage ROSE-SR unit operated to produce light (44-75%) and heavy (25-56%) deashed resid.
- For all coal ranks.
- Light resid is fed with distillate to solvent hydrogenation.
- Heavy resid is recycled to slurry with ash concentrate.
- A portion of the ash concentrate is gasified.
- All V-1082 is deashed; as much light resid as possible recycled back.
- Up to 57 wt % of recycled soluble resid is sent through solvent hydrogenation.
- The light resid cut (yield and properties) is determined by choice of deashing solvent and conditions.
- Light resid has a moderate content of aromatics and paraffins and is low in phenolic -OH concentration, indicating its suitability as a hydrogenation feedstock.

Benefits

- Provides a solvent component which is amenable to hydrogenation to improve solvent

quality, without most of the components which are detrimental to the hydrogenation catalyst.

- Solvent quality improvements will improve conversion and yields.

Miscellaneous Concepts in Solids Separation

CONSOL also pursued research on several solids separation concepts which are not recommended for Phase II development. Most of this work concerned alternative methods for resid deashing. These concepts include resid deashing by low-temperature agglomeration, resid deashing by high-temperature agglomeration, alternate resid deashing schemes. A related concept, that of ash concentrate upgrading and utilization, was developed as the Phase I work progressed.

Each of the topics mentioned in this summary, pertinent supporting data and recommendations for future research are discussed in the attached final report.

EXECUTIVE SUMMARY - SANDIA

Sandia's portion of the Advanced Concepts for Direct Coal Liquefaction program focussed on evaluating new hydrotreating catalysts for use in preparing donor solvents and developing and evaluating new approaches for producing better hydrogen donor solvents to allow better control of initial coal dissolution reactions. This work also included evaluating the impact of generating H_2 with an in situ water-gas shift reaction, evaluating different process conditions for solvent hydrogenation and coal liquefaction and preparing donor solvent samples for evaluation by other program participants. Experiments were performed in batch microautoclave and a trickle-bed flow reactor.

CATALYSTS FOR IN SITU WATER-GAS-SHIFT SOLVENT HYDROGENATION

Sandia has been synthesizing and testing hydrotreating catalysts for solvent pretreatment reactors. These catalyst development efforts have involved testing hydrous metal oxide catalysts developed at Sandia and comparing results to those of commercial catalysts. The screening reactions were performed using a model compound mixture.

Commercial cobalt molybdenum catalyst:

- Without potassium promoter: 60% CO conversion at 275 °C
- With potassium promoter: 94% CO conversion at 275 °C
- Addition of potassium: reduced hydrogenation of aromatics from 38% to 6%
- Conclusion: No further evaluation of this catalyst due to potassium inhibition of hydrogenation.

Platinum hydrous titanium oxide (HTO) catalyst prepared as bulk catalyst:

- Calcining at 200 °C and testing at 275 °C gave 27% CO conversion & no aromatics hydrogenation.
- Calcining at 500 °C and testing at 275 °C gave 95% CO conversion and 56% aromatics hydrogenation, some deactivation observed, most likely due to sulfur
- Calcining at 500 °C and testing at 300 °C gave 95% CO conversion and 97% aromatics hydrogenation.
- Calcining at 500 °C and testing at 315 °C gave 96% CO conversion and 93% aromatics hydrogenation; no measurable deactivation; significant sulfur removal.
- Conclusion: Pt HTO bulk catalyst performed well in model solvent water-gas-shift hydrotreatment.

Nickel Molybdenum Catalyst Testing:

- The effect of gas velocity on solvent hydrogenation was negligible.
- Increased gas velocity gave significant decreases in the water-gas-shift reaction.
- On a catalyst weight basis, Shell 324M was somewhat more active for solvent hydrogenation than a thick film NiMo HTO catalyst in a large pore silica bead.
- On a weight of active metals basis, the coated NiMo HTO catalyst was more active.
- The water-gas-shift reaction was unaffected by the increase in aromatic feed rate.
- At weight hourly space velocities greater than 0.67, aromatic hydrogenation decreases significantly.
- A NiMo HTO coated on alumina (7.2% Mo) showed high activity comparable to Shell 324M (12.4% Mo) for both water-gas shift and solvent hydrogenation.

Conclusions for catalyst hydrotreating studies:

- Supported NiMo and Pt HTO catalysts showed excellent activity for hydrogenating aromatic compounds.
- The combined water-gas shift reaction effectively produced hydrogen from synthesis gas.
- In most cases, CO conversions were greater than 93%.

HEAVY DISTILLATE SOLVENT PRETREATMENT STUDIES

Sandia has developed and evaluated approaches to allow better control of initial coal dissolution reactions by producing and utilizing an improved hydrogen donor solvent. Hydrogen donor solvent improvements have been attained through solvent dewaxing at CONSOL and a variety of hydrotreating reactions at Sandia. Hydrogen donors have been extensively studied in direct coal liquefaction research and have been used effectively to stabilize thermolysis products in the preheater and first stage of liquefaction. The bulk of Sandia's work involves hydrogenation of heavy distillate liquefaction solvent including dewaxed process solvents and solvents selectively chosen to increase hydrogen donating ability. Initial solvent pretreatment work at Sandia consisted of solvent hydrogenation using the water-gas- shift reaction as the source of hydrogen. The aim of this work is to reduce reaction temperature and pressure for donor solvent hydrogenation, and to remove the requirement for the use of purified hydrogen.

Goal: To evaluate the response of V1074 heavy distillate feed and dewaxed feeds to low severity hydrogenation using the water-gas- shift reaction.

Results: At 300 to 325 °C and a hydrogen pressure of 1000 psig, the maximum increase in solvent hydrogen content was 0.8 wt% for V1074, -5 °C dewaxed V1074, and -35 °C dewaxed V1074. This increase in solvent hydrogen content should be sufficient to make notable improvements in coal liquefaction reactions. There is a kinetic rather than a thermodynamic limitation on the solvent hydrogenation reaction. Also significant catalyst activity losses were observed. Therefore, higher temperatures and hydrogen (without the water-gas-shift reaction) were used for subsequent testing.

Goal: To evaluate the response of -35 °C dewaxed V1074 to high severity hydrogenation.

Results: Reactions performed at 360 °C and 1300 psig H_2 showed that the level of hydroaromatic hydrogen was relatively unchanged when LHSV was increased from 0.7 hr^{-1} to 1.1 hr^{-1}. Hydrocarbon gases account for less than ~0.3 vol% of the gases in the effluent. Therefore, hydrogen consumption due to hydrocarbon gas formation is about 0.4% of the feed hydrogen. The hydrogen consumption was 460 scf/bbl.

Goal: To determine starting conditions for the Process Simulation Tests (PST) with V1 074

Results: The hydrotreated samples showed extensive hydrogenation and indicate that a nominal starting point for the PST could be LHSV = 1 hr^{-1}, temperature = 365 °C, hydrogen pressure = 1400 psig, and a hydrogen gas treatment rate >3000 scf/bbl.

Process Simulation Testing

Batch Hydrogenation Test to Evaluate Maximum Hydrogen Uptake

Batch hydrogenation tests were performed with dewaxed heavy distillate to evaluate the maximum hydrogen uptake. The maximum uptake with the -5 °C dewaxed heavy distillate was obtained at 396 °C, for 60 minutes, with 1400 psig H_2, and a solvent:catalyst ratio of 2:1. This sample experienced a 0.9 wt% increased in hydrogen. Proton NMR results showed decreases in aromatic protons with hydrotreatment at 355 °C, 372 °C, and 396 °C. The sample that was hydrogenated at 420 °C was poorly hydrogenated. This observation is consistent with model compound experiments that show dehydrogenation becomes more favored with increasing temperature at a given hydrogen pressure. The optimum hydrogenation temperature for batch experiments was about 400 °C. Four preparatory runs were made at about 396 °C to generate enough material for testing at CONSOL. Reaction time was 60 minutes with a solvent to catalyst ratio of 3:1 and an initial hydrogen pressure of 1400 psig.

Distillation Pretreatment and Batch Testing

Batch microautoclave testing was performed to determine the effect of the recycle distillate cut-point upon donor solvent quality. This was aimed at evaluating the concept of staging the

ROSE unit at Wilsonville to produce a recycle solvent enriched with donor precursors. CONSOL performed a distillation of the V1074 to produce 'light" and "heavy" distillates that were dewaxed at -35 °C. The dewaxed oil yields were 84.5% and 82.5% for the light and heavy fractions, respectively. These distillates were used in batch hydrotreating tests. Reaction products showed improved solvent quality as indicated by an increase in cyclic alpha and cyclic beta hydrogen content from 30.5% to 42.5%. This increases was due to the combination of distillation, dewaxing, and hydrotreating. These improved donor solvents were sent to CONSOL for coal dissolution tests with Black Thunder coal.

Goal: To increase the amount of donatable hydrogen in a reaction solvent.
Three solvents (Wilsonville run 258K distillate, Lummus pasting solvent, the -25 °C dewaxed slipstream solvent) were hydrotreated at 365-380 °C, 1400 psig H_2 , LHSVs of 1 hr^{-1} with Shell 324M. Results showed hydrogen increases of 1.0, 2.5, and 0.3 wt% respectively. Performing uncatalyzed coal liquefaction experiments with a nitrogen overpressure using both unhydrotreated and hydrotreated Lummus pasting solvents and both unhydrotreated and hydrotreated slipstream solvents yielded significant increases in THF coal conversion. The Lummus pasting solvent showed increased conversion from 25% to 78% at 400 °C and from 4% to 93% at 450 °C due to hydrotreating. The slipstream solvent showed increased conversion from 66% to 88% at 450 °C, whereas the conversion at 400 °C was 64%, which and was not affected by hydrotreating. A hydrotreated slipstream sample was sent to CAER for evaluation.

SECTION ONE

Center for Applied Energy Research
University of Kentucky

Summary

This section provides a detailed report of the work that was conducted at the CAER. It encompasses a review of the results that were obtained in the general areas of dispersed catalyst development, chemical pretreatment of coal, and fluid coking of vacuum tower bottoms. Chapters 1 though 6 cover the area of dispersed catalyst development. Chapters 8 and 9 covers chemical pretreatment of coal and Chapter 10 discusses fluid coking of vacuum tower bottoms. Chapter 7 discusses the experimental plan and results from the testing of the integrated concepts. Chapter 11 presents a reaction model that was developed.

Chapter 1 - Catalyst Testing in Resid Containing Recycle Solvents

One of the objectives of the Advanced Concepts for Direct Liquefaction Program was to identify and develop dispersed catalysts that would provide high conversion and distillate yields when processing low-rank subbituminous coals. Since the distillate yields that were obtained during Run 263J at the Wilsonville pilot plant were among the highest ever observed, it became an specific objective of this program to develop a catalyst having activity equal or better than the dispersed catalyst used in that run. In addition, this catalyst must provide this improved level of performance at a lower cost. In order to correctly assess the performance of various candidates relative to the base case catalyst, testing was performed in full-range ash-laden recycle solvents that had been generated at the Wilsonville pilot plant.

Numerous problems were encountered in evaluating catalyst performance in the full-range liquefaction recycle solvents. In a liquefaction plant in which only distillate products are produced, all of the resid that leaves the final processing stage that isn't converted is recycled back to the front end of the plant. In the configuration used at Wilsonville in Run 263J, about 1/3rd of the recycle solvent was residual hydrocarbonacious material that boiled over 1050 °F. In addition to this non-distillable material, the solvent also contained about 21% solids that were a combination of mineral matter and unconverted coal macerals. The distillate portion of the solvent was only about 45% of the total. Because of this high concentration of heavy viscous resid plus solids, the amount of recycle solvent needed to

paste the coal was quite high, namely 2.3 to 1. In the reactor feed, however, the actual distillate to coal ratio was less than one.

Liquefaction in all of the Wilsonville plant solvents that were tested in the lab gave THF conversions in excess of 100%. After considerable work, this problem was traced back to the presence of an easily converted THF insoluble fraction present in the starting solvent that was resolubilized during the testing procedure. When these recycle solvents were heated in the absence of any added coal, an actual decrease was observed in the amount of insoluble organic matter (IOM) present in the solvent. It was apparent from evaluating the solubilities of these samples that were reported soon after they were originally produced at the plant, that the concentrations of insolubles had increased over the 2 to 4 year period between when these materials were originally produced and when they were analyzed in our lab. Solubilities consistent with the original samples could be achieved either by a rather mild thermal treat or by using refluxing pyridine, as somewhat stronger solvent. For this reason, we concluded that these higher conversion values was merely an artifact of the analysis technique that was used to report conversions in these runs. In other words, if refluxing pyridine had been used as solvent in the analysis scheme, the conversion values would have been less than 100%.

Another problem that was encountered when using these ash-containing recycle solvents was obtaining an accurate measure of catalyst activity in the presence of the large amount of accumulated catalyst. The background catalyst masked the activity of fresh catalyst for coal dissolution, distillate yield and resid conversion. Since iron was added as catalysts for all the runs from which we had samples, these solvents contained sizable amounts of accumulated iron. Some of the samples that were produced at Wilsonville also contained molybdenum which was had been added as a co-catalyst. Comparative liquefaction runs made in Mo-free (Run 258K V-131B) and Mo-containing (Run 262E V-131B) solvents indicated significantly higher distillate yields and resid conversions in the presence of the recycled Mo catalyst.

A screening test was setup to provide comparisons between experimental catalysts and the

base case catalyst, which was equivalent to that used in Run 263J. A series of runs were made at 440 °C at residence times from 7.5 to 30 min to reproduce the resid conversion obtained in the 1st-stage reactor in Run 263J. These runs were made by adding 1 wt % Fe_2O_3 and 100 ppmw Mo as Molyvan L, based on dry coal, to a slurry of 30 wt % Black Thunder coal in Run 262E V-131B. The solvent was essentially the same as produced in the base case run. Analyses were done entirely by a solvent separation technique. Oil yields from this series from 7.5 to 30 min increased from 8.4 to 48.6% while THF conversions increased from 70.2 to 97.8%. From on that series a residence time of 22 min was selected for the simulated 1st-stage test procedure. Later results, based on vacuum distillation, showed that the 22 min residence time gave 31-32% resid conversion versus a target of 24% that was observed in Run 263J. However, since a considerable amount of data had already been collected, the test procedure reaction time was left at 22 min.

Because the recycle Mo was so active, it was decided to use a full range ash-containing Mo-free recycle solvent (V-131B) from Run 258K under the same conditions used above. Although a considerable concentration of recycled iron remained in the Mo-free solvent, the activity of the Fe was considerably less than the Mo. Using this solvent, a number of coals impregnated with Fe and Fe-Mo catalysts were tested by this procedure. In every case the concentration of added Fe was 0.7 wt % which was equivalent to the concentration in the base case. The concentration of Mo that was impregnated onto the coal varied up to 1000 ppmw. The results on these impregnated coals indicate that coal conversion, pentane solubles and 1050 °F- distillate increases as the Mo concentration increases. At the 1000 ppmw level the activity is approximately the same as observed with a recycled Mo concentration of 400 ppmw. Somewhat surprising, an exceptional level of activity was observed for the nanometer-size iron oxide (SFIO) in the absence of any Mo.

Chapter 2 - Surface Characterization and Liquefaction of Impregnated Coal

It has long been known that iron is a catalyst for the direct liquefaction of coal. A number of studies have also reported that increased dispersion of iron improves liquefaction. Cugini and coworkers found that FeOOH that had been finely divided and highly dispersed on coal

gave improved conversion and distillate yields. The FeOOH had been prepared by treating with base a coal that had been impregnated with an Fe salt by an incipient wetness technique. By contrast, Andres et al. reported that coals impregnated with aqueous solutions of $FeSO_4$ gave not only low catalytic activity but poor reproducibility in liquefaction. Against this background, we undertook a program to examine this approach for injecting catalysts into the liquefaction reaction.

Forming the FeOOH on the surface of the coals is a multi-step process involving first the impregnating the iron as well as the co-metals onto the surface of the coal by an incipient wetness technique followed by treatment with a basic solution to convert the iron to the oxyhydroxide. The overall scheme, starting with a low-rank subbituminous coal, would involve several steps, including coal preparation, filtration, washing, and drying. Any of these steps could influence the liquefaction of the coal. Also the form of the salts used in the impregnation could affect both performance and cost of the catalyst. In this program a study was undertaken to prepare both Fe and Fe-Mo impregnated coals and to determine their liquefaction performance. A further objective of the study was to determine the effect of the preparation technique on the metals, their chemical form, their concentration and their dispersion on the coal.

The surface composition and chemistry of coals impregnated with 0.7-2.0 wt% Fe and 500-1000 ppmw Mo were studied by X-ray photoelectron spectroscopy (XPS). In general, the XPS results showed that the surface concentration of Fe increased with the increasing amount of added Fe. When ferric nitrate was used, the Fe concentrations on the surface was higher relative to when sulfate was used. For samples that had been treated with ammonium hydroxide solution, the anions of the impregnating salts were readily removed. However, for samples impregnated with sulfate salts which were not treated with base, the sulfur concentrations were higher than observed on the surface of the starting coal. The corresponding surface concentration of Fe on the Fe-Mo co-impregnated coals were intermediate between the nitrate and sulfate impregnated coals, regardless of whether nitrate or sulfate was used as the impregnating salt for the Fe. The $Fe_{2p\ 3/2}$ and Fe_{3p} peak positions

in the XPS spectra of the base treated coals corresponded with α-FeOOH while the positions in the non-base-treated sulfate-impregnated coals were consistent with the respective ferric or ferrous sulfate salts. Although ammonium hydroxide readily converted the Fe on the surface to FeOOH it had no impact on the relative surface concentration of the Fe. The sulfur concentration on the surface of non-base treated sulfate-impregnated coals was significantly higher than for the base treated coals indicating deposition of the sulfate ion. The splitting of the Fe_{2p} peaks and the position of the $Fe_{2p\ 3/2}$ and Fe_{3p} peaks confirmed the presence of iron sulfates.

The added Fe on the surface of the impregnated coals had a direct impact on the position of the O_{1s} peak shifting it to a lower energy position. Likewise the oxygen concentrations on the surface were strongly influence by the presence of Fe being significantly greater than for the as-received coal and always exceeding the bulk concentration. Overlap of the Mo_{3d} doublet by the S_{2s} peak required deconvolution based upon peak positions in reference materials. Mo was present on the surface as MoO_3 and its concentration was higher than in the bulk. These results support greater penetration of the sulfates into the coal particle relative to the nitrate salts.

The liquefaction performance of the Fe-impregnated samples was primarily related to the concentration of Fe impregnated on the coal. However, liquefaction of the Fe-Mo co-impregnated coals was always greater than for the Fe-only impregnated coals. Both the nitrate and sulfate-impregnated coals performed similarly with coal conversion and oil yield being unaffected by the form of Fe on the surface of the starting impregnated coal. Performance was also not affected the impregnating salt, a base treatment step, a predrying step, a washing step or the presence of anions on the final impregnated coal.

Chapter 3 - Catalyst Impregnated Vector Coals

Although metal-impregnated coals are excellent catalysts and would be considerably less expensive than the base case, impregnating the metal salts onto all of the feed coal would be a major materials handling problem. Cugini et al. recognized this problem and evaluated

putting the Fe onto only a portion of the feed coal. They "spiked" as little as 10% of the feed coal to an added Fe concentration sufficient to give a final Fe concentration of 5000 ppmw. Bockrath et al. reported a related "spiking" experiment involving Mo catalysts in which Mo was placed onto 5% of a coal feed, reacted and then combined with the remaining 95% of the coal.

In this study we investigated impregnating the metallic precursors onto only a portion of the coal, which has been referred to as the "Vector". In tetralin, using vector concentrations from 10 to 90% of the total feed appeared to perform just as well as the completely impregnated coal. In the 1st-stage catalyst screening test, the 10% Fe-vector actually out-performed the 100% case giving a 1050 °F- distillate yield of 38.2% versus 30.6% for the 100% case. The latter coal was considerably drier than the vector coal which could explain this unexpected difference. For Fe-Mo cases having 0.8 wt % Fe and 500 ppmw Mo on total coal feed, the 10% vector again gave better results than the 100% case, i.e. 47.9 wt % distillate versus 41.2 wt % for the 100% case. Although THF conversions, distillate yields, and H_2 consumptions for the vector cases often exceeded the non-vector cases, for whatever reason, it appears that addition of the catalyst using the vector approach does not adversely affect performance.

Using the vector approach, a significant amount of experimental work was directed toward understanding the lower activity of freshly added Mo versus the much higher activity of Mo contained in the recycle solvent. Adding additional sulfur to the feed improved the activity of the fresh catalyst but did not reach the activity of the recycled catalyst. It was also observed that pre-reacting the Mo-vector portion of the feed (a la Bockrath et al.) resulted in an increase in THF conversion and distillate yield. This suggested that the activation of the fresh Mo was either kinetically limiting or that the presence of freshly added Fe oxide was, in some way, retarding the activation of the Mo. Using the Vector approach, Mo in the absence of any fresh Fe, produced significantly greater distillate yield (55%) than when fresh Fe was present (48-51%). A comparative run with Molyvan L in the absence of any fresh Fe also gave much more distillate (54.6%) than when fresh Fe was added (47.9%). This

response of Mo in the absence of added Fe suggests that iron oxide is inhibiting complete activation of the Mo while the pyrrhotite in the recycle solvent has either no effect or a much smaller one.

Additional experiments were done by adding Ni to the coal either alone or in combination with Mo. These impregnated coals were all quite active. Coals having concentrations of Ni of 1000 ppmw, Mo of 500 ppmw or Mo/Ni of 500 and 125 ppmw gave nearly equal distillate yields and coal conversions. Although more data is need, Ni has promise because of its much lower cost than Mo. The strongest benefit may be an increase in THF conversion at the same distillate yield and H_2 consumption level.

An analysis of all the data that has been collected in the 1st-stage catalyst screen test is presented. All these runs were made at the standard conditions of 440 °C, 22 min, 1000 psig H_2 (cold), and a Run 258K V-131B solvent to coal ratio of 2.3/1. These data show a strong correlation between THF conversion and distillate yield. There is also a strong correlation between calculated hydrogen consumption and total THF conversion for these combinations. Regression analyses for both sets of data provided a correlation coefficient of 0.7.

Chapter 4 - Nanoscale Iron Catalysts

Two small particle iron catalysts that had been prepared by using a laser pyrolysis technique were evaluated relative to the activity of a superfine iron oxide that was obtained from Mach I. An iron carbide, Fe_7C_3, was prepared by pyrolyzing a flowing stream of ethylene at a pressure from 0.4-0.7 atm in a laser. The product had a particle diameter of 17 nm and surface area of 92 m^2/g. The iron sulfide was prepared by injecting H_2S into the ethylene stream. The solid product was characterized as $Fe_{(1-x)}S$ having a particle diameter of 14 nm with a surface area of 42 m^2/g. The Mach I material had a particle size of 3 nm and a surface area of 195 m^2/g. Liquefaction results for these materials in tetralin, using a solvent separation work-up procedure, showed that the oil yields from both the carbide and the sulfide catalysts were less than obtained for the Mach I material, while the THF conversions were nearly the same. Hydrogen consumptions were considerably less for the two

synthesized materials relative to the Mach I product while the hydrogen contribution from the tetralin was higher for the synthesized materials. There was no further evaluation of these two synthesized materials because of their low activity.

Chapter 5 - Promoted Sulfated Hematite

The objective of this project was to develop a particulate catalyst which would display a high activity for the liquefaction of a subbituminous coal. Iron based catalysts were investigated due to their low cost and ease of preparation and disposal. Nanoscale particles were utilized in order to maximize the activity of these catalysts. The high surface area to volume ratios associated with these particles results in more catalytic sites per unit mass. Several types of nanoscale iron based catalysts were synthesized and their activities were measured. The promoted sulfated hematites were identified during this process as strong candidates for further investigation based on their ease of synthesis and high activity.

The results of this program have shown the high catalytic activity of the nanoscale sulfated hematite particles. The addition of low concentrations of molybdenum has been shown to significantly enhance the activity of the sulfated hematite. The molybdenum exhibits a level of activity similar to that of a more expensive oil soluble precursor utilized at Wilsonville. In microautoclave tests using a process derived recycle solvent a molybdenum promoted sulfated hematite resulted in a resid conversion similar to that obtained using the base case catalyst while increasing the THF conversion by 6%.

The synergistic effect of nickel and molybdenum has been evident throughout this study. The use of nickel to reduce the amount of molybdenum required should result in substantial reduction in catalyst cost. A nickel - molybdenum promoted sulfated hematite and a molybdenum promoted sulfated hematite yielded identical conversions at similar loadings. This indicates the possibility of improving the activity of these catalyst by replacing a portion of the molybdenum with nickel, thereby reducing the cost of the promoter metal. There appears to be an optimum ratio of promoter metals which yields a maximum activity. Higher concentrations of nickel adversely effect the conversions.

The use of high molybdenum concentrations on the sulfated hematite have shown that the amount of catalyst may be reduced without sacrificing high activity. By increasing the molybdenum concentration by a factor of 2 the total catalyst loading could be reduced by a factor of 0.5 without any loss in activity. This results in significant saving in the volume of catalyst which must be handled for each run. It may also be possible to further enhance the activity of these catalysts by the use of high concentrations of nickel and molybdenum, in the proper ratio, thereby further reducing the cost of the catalyst.

This study has shown the high activity of both the molybdenum and nickel-molybdenum promoted sulfated hematites for coal liquefaction in a recycle solvent. However, the activity of these catalysts when used in a recycle mode has not been investigated. The results of the model compound studies indicate that the catalysts exhibited high activity after an initial period of low activity. This delayed onset of activity is presumably related to conversion to an active phase. Estimations of particle diameters from XRD spectra both before and after reaction indicate no significant increase in catalyst size. Given the slow rate of activation observed in the model compound experiments and the lack of particle growth and agglomeration, it is probable that the catalyst will exhibit higher activity in its recycled form than in its freshly added form. The higher activity of the recycled catalysts will allow the use of substantially lower catalyst addition rates.

Chapter 6 - Activity and Sulfur Activation of a Nanoscale Iron Oxide Catalyst for Coal Liquefaction

A commercially available nanoscale iron oxide was investigated as a dispersed catalyst for liquefaction of a subbituminous coal. Results reported in Chapter 1 showed that SFIO increased coal conversion and distillate yields when used as a catalyst in Wilsonville process derived recycle solvents. This exceptional activity initiated a more extensive study to understand the mechanism by which this catalyst was activated and how it affected both product yields and hydrogen consumption. The results from liquefaction with SFIO are compared with results from other catalyst precursors, including a coarser grade iron oxide (IO) and a carbon black, that exhibit some, but not all, of the characteristics of the nanoscale

iron oxide.

The IO precursor investigated is a powdered material that had been successfully used at Wilsonville in Run 263. This iron oxide was selected to represent a commercial grade iron oxide that would provide a comparison to the performance of the specialty SFIO described above. Additionally, liquefaction experiments were conducted using carbon black as a catalyst that would present a considerable non-Fe surface in the reaction, to investigate the importance of an Fe species present as the active catalyst, in addition to other catalyst factors that are examined for the two iron oxide precursors.

SFIO used in the absence of added sulfur was found to have a positive effect on both the kinetics and extent of coal dissolution at concentrations down to 3000 ppmw Fe. However, little hydrogenation activity was seen as evidenced by low yields of pentane-soluble product and hydrocarbon gas. Higher unsulfided SFIO concentration resulted in uniformly increasing improvements in solvent quality, utilization of dissolved hydrogen, and total coal conversion. Sulfiding the SFIO with dimethyl disulfide (DMDS) had a pronounced effect on the consumption of molecular hydrogen and product yields. Compared with the larger particle IO, use of the sulfided SFIO precursor increased coal conversion and total hydrogen consumption. Hydrogen selectivity changed by increasing direct consumption of gaseous H_2 while decreasing tetralin dehydrogenation. The increased conversion reported to the heavier THF fraction which was found to be enriched in hydrogen. No difference was observed in the yield of light product. While both of the iron oxides that were studied showed activity when compared with uncatalyzed runs, precursor size and follow-on dispersion appear to be key variables for further development. Clearly, product yields are enhanced by smaller particle size precursors, and more intimate mixing of catalyst and coal that results. The 90 m^2/g surface area carbon black added to the coal feed in a 9:1 ratio (coal: carbon black) had no effect on the liquefaction results or hydrogen consumption when used in the absence of DMDS, underlining the importance of the precursor's composition.

Differing degrees of hydrogenation ability were observed for each of the five catalyst cases

considered. At the lowest level is the ability to solubilize coal, even at the outset of liquefaction, which apparently requires little incremental hydrogen addition. Next is the ability to mobilize additional gaseous hydrogen (while either rehydrogenating naphthalene or reducing hydrogen abstraction from tetralin) to better produce the lighter pentane soluble fraction, an important function for a practical liquefaction plant catalyst. While SFIO used without DMDS clearly showed some ability to dissociate molecular hydrogen (in direct proportion to SFIO concentration), as did IO with DMDS, a much better product resulted from the combination of the small particle SFIO precursor used with DMDS. The presence of the larger size pyrrhotite alone was not sufficient to give the large effects desired, nor did the addition of carbon surface area from added carbon black have any effect on hydrogen consumption. The relative importance of hydrogen donated by tetralin solvent follows the order

$$\text{Carbon black} \approx \text{Thermal} > \text{SFIO} > \text{IO+DMDS} > \text{SFIO+DMDS}$$

where the SFIO experiments with added DMDS had the highest hydrogen uptake with the least dehydrogenation of the tetralin. We would speculate the high surface area SFIO's initial propensity to mobilize gaseous hydrogen is augmented by a more reactive hydrogen donor, or a better catalyst in the smaller pyrrhotite phase formed, or both.

Chapter 7 - Process Simulation Testing Program

During the course of this program after several different process steps had been evaluated by the individual groups, an integrated experimental plan was developed to evaluate the integration of several of these individual steps. Results from each of the individual steps of coal preparation, solvent modification, and catalyst improvement had indicated that together significant process enhancement might be realized. An experimental design was developed to assess the integration of removing ash from coal by oil agglomeration, testing both impregnated and particulate Fe-Mo catalysts, and modifying the solvent by dewaxing and hydrotreating. The option of subjecting all of the recycle stream or only 25% of this stream to dewaxing was also evaluated to assess the sensitivity of wax removal-hydrotreating on the process. Both Mo-containing and Mo-free

full-range Wilsonville process solvents were selected to be used with Wyodak Black Thunder coal. The Mo-containing solvent was a full-range reconstituted V-131B from Run 262E and the Mo-free solvent was a V-131B made up of 1050 °F+ bottoms from Run 258K V-131B and Run 262E V-1074 heavy distillate.

The individual steps involved in the evaluation were:

- Dewaxing of the distillate recycle solvent stream to remove the paraffinic fraction by treating either the entire distillate recycle stream (100% case) or a portion of the stream (25% slipstream case).
- Preparing a 25% slipstream distillate by blending heavy distillate and dewaxed distillate.
- Hydrotreating the 25% slipstream and 100% dewaxed distillate streams in a downflow fixed bed reactor.
- Agglomerating the coal using both the 25% and 100% dewaxed-hydrotreated distillate streams.
- Liquefying the as-received coal and the agglomerated coal using both a Mo- and a Mo/Ni promoted hematite particulate catalyst.
- Liquefying two different Mo-Fe impregnated coals.
- Liquefying two oil-agglomerated, Mo-Fe impregnated coals.

The liquefaction tests were performed at 440 °C in microreactors for periods of 5 minutes and 22 minutes. Products were analyzed by a workup procedure involving THF extraction and vacuum distillation to determine both resid conversion and distillate yield.

In the Mo-free solvent, introduction of 250 ppmw Mo along with 1 wt % Fe_2O_3 as Fe-Mo-impregnated catalysts increased the 22 min resid conversion from 12.9% to 24.2%. When the Mo was increased to 500 ppmw, the conversion was further increased to 26.5%. THF conversions also showed a sizable change over this range. The activity of the particulate hematite catalyst that contained ~10% molybdenum showed an increase in resid conversion to 25.2% accompanied by a sizable increase in THF conversion. The corresponding activity of a

1% Ni and 1% Mo on hematite gave a somewhat smaller increase in resid conversion to 21.3%. On the other hand, increasing the Mo content in the Mo-containing solvent had little effect on resid conversion indicating that an apparent ceiling had been reached which was subsequently ascribed to the exceptional activity of the recycled Mo. Both catalysts showed quite high catalytic activity in this test.

Topping and reconstituting the Mo-free process solvent appeared to have a negative impact on both resid and THF conversions. Results obtained using recycle solvent from Run 258K V-131B without any separation resulted in a resid conversion of 16.7 wt % and THF conversion of 98.1. By merely changing the distillate fraction by the method described above in the absence of any added metal the resid conversion decreased to 12.9% and THF conversion decreased to 93.7%. In the presence of 500 ppmw added Mo the resid conversion decreased by 6.6% and THF conversion by 3%. This is a significant negative effect in both cases. It points out that an apparent mismatch in the solvent had a sizable effect on the results. Since a higher boiling cut was substituted for a lower boiling cut, the poorer donor quality of the replacement solvent may have affected the result.

The effect of dewaxing and hydrotreating the distillate was evaluated for both Fe-Mo-impregnated catalyst as well as the Mo-Ni particulate catalysts. It was later found that the hydrotreating had been done with a partially sulfided catalyst which appeared to incorporate less hydrogen into the product than expected. For those comparisons involving the Fe-Mo-impregnated catalyst, resid conversions improved by 1.9 to 4.6% and THF conversion improved by up to 3.2%. For the particulate catalyst, however, there was a slight decrease in resid conversion that was accompanied by an increase in THF conversion. The Mo-Ni particulate catalyst gave the same result for both the 100% and the slipstream cases. When oil agglomeration was combined with the dewaxing, resid conversion increased by a sizable amount. The data suggest that the impregnated catalysts benefit from the modified solvent, whereas all together, the result suggest little overall effect on resid conversion with a 2% increase in THF conversion.

The results on oil agglomeration indicate very little effect on resid or THF conversions as might be expected. This benefit from this step would be enrichment of the maceral concentration in the feed plus an alternative method for dispersing the catalyst onto the coal. Unfortunately, the large number of variables in this series limits the interpretation on these results but suggest that integrating these steps can have benefit.

Chapter 8 - Chemical Coal Pretreatment: Background and Review

One of the process concepts that was investigated during the course of this study was the modification of the structure of low-rank coals by low-temperature treatment under a variety of different condition. An objective was to determine if the increased cost associated with a low-temperature treatment could be off-set by increased product yield, improved selectivity or other product or process benefits. As work progressed in this area it became apparent that an enormous literature existed on several of the approaches that were being investigated as well as important literature in other areas that relates to such low-temperature thermal treatment of coal. This chapter reviews several areas that were important to the study that was conducted on chemical coal pretreatment.

A considerable amount of work has appeared in the recent literature on the hydrothermal treatment of coal at a variety of different pH values as well as on related model compounds. At temperatures up to the critical temperature of water, very significant changes have been observed in the structures of low rank coals. Sizable amounts of oxygen has been eliminated from coal that could lead to more efficient hydrogen consumption. The modification that occurs to the coal structure has resulted in increased volatility as well as enhanced solubility in a number of solvents. The resulting materials that have been isolated from these reactions are more easily hydrogenated to liquid product as well as more easily pyrolyzed to distillate tar products. A number of studies have been done at temperatures at and above the critical temperature of water over a range of different water concentrations. Many were done at relatively low partial pressures of water while in some cases sufficient water was present to generate a partial pressure equivalent to the critical pressure of water. In some cases a sizable amount of the coal was volatilized, although in many of the studies solubility of the total

material recovered from the treatment was used as a measure of coal transformation. A large number of related studies have been reported on conversions of model compounds under hydrothermal conditions. Multi-ring compounds both with and without a wide variety of different functional groups have been investigated under various hydrothermal conditions, such as in the presence of formic acid or formate salts.

A considerable amount of work has been done on the hydrothermal conversion of coal in the presence of CO. These reactions have been carried out for a range of different rank coals under a variety of conditions, both with and without the presence of various catalysts and reagents. Most of the earlier work was directed toward using this method to generate hydrogen which would then participate in the reaction with the coal in a variety of process type configurations. The benefit of this approach for direct liquefaction of coal was discovered in Germany in the early years of this century and has been applied for liquefying brown coal at the pilot scale in Australia in more recent years. Over the years this chemistry has been widely investigated over a wide range of temperatures from a few hundred degrees up to temperatures well in excess of conventional liquefaction temperatures. Most of the review presented here is concerned with temperatures at or below conventional liquefaction temperatures.

Background on the role that CO plays in this reaction is discussed. The considerable interest that developed in CO chemistry over the last several decades, especially in the area of homogeneous catalysis, has expanded our understanding of the role that CO plays in this reaction. The literature on the role of various catalyst types and the intermediacy of molecular species that are likely involved in the thermal chemistry in coal structures is discussed. Attention is drawn to the types of electron transfer reactions using these types of intermediates that has developed into a highly facile synthesis tool. An appreciation of the potential of this reaction system for manipulating selected chemical structures within the coal matrix can be related to the energetics of these reactions. The overall participation of the water-gas-shift reaction and the role of promoters in that reaction are discussed.

Water-Gas-Shift Reaction. In our preliminary micro-autoclave study, the water-gas-shift (WGS) reaction was evaluated in the absence of coal over a range of reaction temperatures (250-350°C) for one hour to gain some insight into the chemistry and intermediacy of the reaction. Sufficient water was added in these reactions to maintain an aqueous phase at reaction temperature. In the absence of a base, CO conversion to CO_2 and H_2 was very small, ~ 1% of CO feed at all reaction temperatures that were investigated. Adding NaOH (0.33 M) to the reactions promote the WGS reaction significantly. CO conversion reached a high of 34% at 350 °C. However, this value is significantly lower than the thermodynamically predicted value. The reason for this observation is still unclear.

Carbon oxide recoveries based on total recoveries, which are the sum of gaseous CO and CO_2 plus the assumed concentration of formate/bicarbonate species present in the aqueous phase were found to be experimentally close to 100%. Within experimental error, hydrogen balance is found to be consistent with CO_2 yield in most cases. However, in later experiments with added coal, hydrogen balance is significantly affected, due to hydrogen consumed by the coal reaction.

Measuring the pH of the aqueous phase at ambient temperature gave some idea of the Na+ species present in the reaction and assist in accounting for the CO_x, although it does not necessarily reflect on the chemistry at reaction temperature. It is interesting to note that pH measurements of the aqueous phases from the CO/water/NaOH reactions at 300 °C indicated a much lower value (pH 4.5) compared to the pH of a HCOONa solution (pH 7.8) based on an equivalent amount of Na+ salt used in the reaction. Similar observation was observed for the same reaction at 340 °C when compared to a solution containing only 25% HCO_3^- in a $NaHCO_3$/NaOOCH mixture (pH=7 vs 8.2 for the latter). Experiments with ^{14}C labelled CO suggests that the NaOOCH/$NaHCO_3$ solution might be buffered by a small excess of free acid (eg. formic or oxalic acid) formed in the reaction and this has been documented in the studies reviewed in Chapter 8.

Hydrothermal Reaction of BT Coal. The hydrothermal reactions of coal was studied as part of the investigation into the elimination of oxygen from coal. In the absence of a base, oxygen rejection as CO_2 increases with temperature from 4.1 wt%(maf coal) at 300 °C to 4.7 wt%(maf coal) at 340 °C. The amount of oxygen rejected as CO_2 and water appears about equal and is unaffected by the presence of either N_2 or H_2. Preliminary data indicated that the addition of base in these reactions substantially increases the amount of oxygen that is eliminated, with the increase being the amount of CO_2 that is formed. For example, at 340 °C, the amount of oxygen and CO_2 rejected in the presence of NaOH was 49 % and 30 % respectively compared to coal reaction without base which gave 42% and 22 % respectively.

The product from these reactions essentially have lower atomic H/C ratios than the parent coal. However, the presence of H_2 and/or the addition of NaOH appears to give a product that has a consistently higher H/C ratio than N_2/water reactions. The results are consistent with the selective removal of oxygen as CO_2 rather than water under these conditions.

Recovery of the solid material from these reactions were in the range of 90 to 97 wt% maf coal. However, thermally heating the coal under dry N_2 produced a material that has very little solubility in THF, reaching and levelling out between 5- 6% after an hour reaction at 340 °C. The addition of hydrogen gas did not appear to have any effect on both recovery and THF solubility of the solid material. There is no significant liquefaction activity at 340 °C. Adding NaOH, however, decreases the solids recovery to 82-83% but increases both the THF solubility and humic acid material by 3-4 %. The apparent increase in THF solubility was largely due to the formation of alkaline soluble humic acid material.

Hydrothermal reaction of BT coal in the Presence of CO. Unquestionably CO has a big impact on the hydrothermal treatment of coal as the THF solubility of the solid products increases dramatically when CO is present. The presence of CO, however, did not have a significant impact on the removal of oxygen from the coal. The amount of oxygen removed is comparable to the N_2 or H_2 reaction at a given temperature. Adding sufficient water to maintain a liquid phase increases CO conversion and the initial CO partial pressures appear to be critical

in attaining a product that is soluble in THF. For example at 300 °C, the THF solubility of the solid material generated increases from 23% at 300 psig CO to 28% at 800 psig at 0.91 mmol NaOH/g maf coal loading. Moreover, increasing the reaction temperature and NaOH concentration drive the WGS reaction further to the right and this coincides with a significant increase in the coal reaction as the solid material recovered decreased dramatically over the temperature range 300-340 °C. A strong correlation was found between the THF solubility of the solid products and CO conversion. This correlation was found over a wide temperature, CO pressure, water and NaOH concentration range indicating that the quality of the products, as measured by THF solubility criteria, and to a lesser extend the coal conversion is directly influenced by the WGS reaction.

Support for this observation came from three separate sources:

(1) available results indicate a good correlation between the H/C ratio of the product and CO conversion.

(2) it is consistently observed that the solid material with the higher H/C ratio also has a higher THF solubility. The solid material recovered from the $CO/H_2O/NaOH$ reactions has a significantly higher H/C ratio ($H/C > 0.8$ range) than those obtained from CO reactions without base and, hydrothermal reactions without CO ($H/C \leq 0.8$).

(3) a good correlation exists between the missing hydrogen which is presumably absorbed by the product and THF solubility of the recovered pretreated material.

In conclusion, the strong correlation observed between product solubility and CO conversion during treatment of BT coal further re-iterate the importance of the intimate association of the WGS reaction with coal reaction. It appears that hydrogen is transferred to the reaction product via the intermediacy of the formate ion which acts a H-donor. It is interesting to note that the intercept of the observed correlation is very close to the origin, where the THF solubility of BT coal is experimentally determined to be $\sim$ 1 %wt. (maf coal basis). The efficiency of the hydrothermal treatment reaction is underscored by the relatively small amount of CO conversion

during the reaction. This is between 15-20% of the CO charge at 800 psig initial CO pressure and 25-30% at 300 psig CO pressure.

Effect of Sodium salts. The effect of using other sodium salts (NaCl, Na_2CO_3, $NaHCO_3$, NaOOCH) in place of NaOH at a reaction of 300 °C gave very similar yields of water-insoluble products which had similar THF-solubility characteristics. The products were apparently unaffected by the initial pH value of the reaction mixtures, which were 13-14 for NaOH and 7.8-8.2 for NaOOCH and $NaHCO_3$ respectively. The THF solubilities of the solid material appears to correlate well with the degree of CO conversion. In the presence of NaCl, ammonium hydroxide or nitrate, the CO conversion was similar to the NaOH and Na_2CO_3 promoted reactions. However, the THF solubility of the solid material generated from these three reactions was significantly less than the NaOH or Na_2CO_3 cases. Perhaps, this can be partially explained by the low level of hydrogen uptake by the coal as a consequence of the WGS reaction. The missing hydrogen values calculated from WGS reaction ranges only from 20-51% for these reactions whereas the NaOH reactions were typically around 80%.

It is interesting to note that the THF solubility of the solid material generated from the NaCl reaction is surprisingly higher than expected based on perceived low concentration of formate and in addition to the low level of hydrogen consumption. This leads us to suspect that the intermediacy of a formate complex may be formed by the presence of this salt although conventional formate is not observed. HCOOH is not effective in promoting the coal reaction in the absence of CO. Decomposition of HCOOH to mainly CO_2 and H_2 during the reaction leads to a solid material which has little solubility in THF.

At higher reaction temperature (340 °C), the ammonium hydroxide reaction seemed to fall in line with other data (eg. NaOH, NaOOCH etc.) and this is surprising since we observed at 300 °C it deviates significantly from the results obtained from the other sodium salts. This occurs despite the fact that ammonium salts are quite unstable under these conditions, presumably decomposing to ammonia and CO. In summary, there is a good correlation between the THF solubility of the solid material obtained from the various salts (with the exception of ammonium

nitrate and hydroxide at 300 °C) and the CO conversion as promoted by these salts during the reaction.

Hydrothermal Treatment of Clovis Point Wyodak Coal. The effect of CO partial pressure was studied to evaluate the treatment of coal with CO. In the large number of experiments that were run, the yield of water-insoluble product ranged from 75-92 wt% while the maximum yield of water soluble product that was observed was 7 wt%. However, in many cases there was no water soluble product that was formed. Consistent with the BT coal runs, carbon balance is almost quantitative except for the carbon eliminated as CO_x gases. The product solubility in THF and pyridine and, H/C ratio of the solid material appears to increase as the CO partial pressure increases. The H/C ratio of the treated material reached a high of 0.94 at 800 psig initial CO pressure. The amount of oxygen removed from the coal during pretreatment is approximately 40% at 300 °C and a significant proportion of the oxygen rejected can be ascribed to decarboxylation as indicated by FTIR spectroscopy.

In addition, with increasing CO partial pressure, the amount of water soluble material (humic acids) appears to decrease. Elemental analysis of the humic acid material generated from a number of different reaction under N_2 and low CO pressures(200 and 400 psig) indicated that the oxygen content fell between 16 and 21 wt% and the hydrogen content were between 3.3 and 4.9 wt%. Surprisingly the oxygen content of these acid fractions was not enriched relative to the starting coal and cannot account for any of the (~40%) decrease in oxygen in the product.

The study into the effect of time indicated that at least for CP coal, a solid product that is more soluble in THF and has a higher H/C ratio can be obtained with increasing reaction time. Thus, at 300 °C after 120 min of reaction, the H/C ratio of the solid material obtained is 0.97 compared to 0.92 after 60 min. The product solubility in THF for the 120 min reaction is 37 wt% vs 20 for the 60 min reaction.

Scale-up Experiments. Scale-up reactions were carried out with Black Thunder Wyodak coal in a continuous stirred autoclave by two methods: (1) by hot-charging the coal in a 1-L

preheated autoclave and (2) by placing the coal and reaction mixture in a 300 ml. continuous stirred autoclave and heating into reaction temperature. In the hot-charge experiments carried out at 310±5 °C, water insoluble product recovery and carbon recovery for coal reaction with NaOH and Na_2CO_3 were high; 85 wt% maf coal and 90% respectively for both reactions studied. The H/C ratio of the material obtained for the NaOH and Na_2CO_3 reactions was 0.9 and 0.84 respectively, compared to 0.8 for the raw coal. The amount of oxygen removed from the coal corresponds to 41% for the NaOH reaction and 47% for the Na_2CO_3 reaction. It is interesting to note that there is a significant difference of about 20-30% between the solubility of the CO-generated material in pyridine and in THF. Elemental analysis of the pyridine solubles and insoluble fraction from these reactions indicated that the pyridine solubles fraction has less oxygen and more hydrogen than the insoluble fraction.

In the reaction of BT coal with NaOH at 340 °C in the 300 ml. autoclave, a material was obtained which was highly soluble in pyridine and THF; 94 and 78 wt% (maf coal) respectively. Elemental analysis of the material obtained from this reaction indicated that there is substantial oxygen removal (~75%) from the coal. Consistent with other results, there has been an increase in hydrogen content of the solid material (H/C=0.88 vs. 0.8 for the coal). Oxygen removal from the coal from the reaction without NaOH is similar but the H/C ratio is significantly lower (H/C=0.8). In addition, the heating values calculated for both solid material are significantly higher, by 26%, than the original coal. Elemental and forced mass balances performed on the products indicated that even with a number of assumptions, the removal of oxygen as CO_2 in lieu of water is apparent. From a process standpoint, this is directionally consistent with the program objective of removing oxygen with carbon than with hydrogen. The high solubility of the material in both THF and pyridine offers the potential for obtaining a "clean coal" feed by removing ash and other insoluble inorganic material prior to hydrotreating in a two-stage process development scheme.

Coal Morphology. Thermally heating coal in either N_2 or H_2 at the temperature range 300-340 °C produces a material which has a higher reflectance compared to the original coal when observed under the microscope. The huminite macerals essentially retained their angular shapes

indicating no major structural change has occurred during the reaction at least at 300 °C. As the reaction temperature approached 340 °C, there is indication of relatively more softening/melting and disintegration of the coal particles. Replacing either N_2 or H_2 with CO has a significant impact on the morphology of the coal particles. At 300 °C in the presence of NaOH and 400 psig CO pressure, the huminite maceral reacted extensively giving a rounded and porous appearance with no evidence of any botanical structures and layering features found in the original coal. Increasing the CO pressure to 800 psig gave a material which is completely altered where the particles were agglomerated, forming large coherent masses. These latter observations were seen for comparable reactions at higher temperatures in both the micro-autoclave and scale-up experiments in the 300 ml and 1-L reactor runs. In all the samples analyzed, the inertinites remained intact and the liptinites were less identifiable compared to the raw coal at higher temperatures (340 °C). The impact of other salts such as NaCl, NaOOCH, $NaHCO_3$ and acid (HCOOH) are less extensive as the product shows a substantial number of particles with smooth surface area. In addition, there appears to be a good correlation between the reflectance measurement of the samples generated from a number of different reactions and the H/C ratio of those samples.

In summary, the structural modification in the coal morphology as observed under optical microscopy is consistent with the significant improvement in THF and pyridine solubility of the material produced as a result of the coal reacting with CO. The good correlation between the reflectance and H/C ratio of the samples is in agreement with previous studies on coal liquefaction residues which showed that more effective liquefaction occurs in residues with low reflectance. In short, optical microscopy is a useful tool in evaluating the hydrothermal reaction of coal.

FTIR spectroscopy. FTIR analysis of the solid samples generated from hydrothermal reactions of BT coal with N_2 and CO in the presence and absence of a base indicated a significant reduction in intensity in the carbonyl region (1700 cm-1) of the spectra. This is consistent with other studies mentioned in the background and review (Chapter 8) which showed decarboxylation as one of the major pathways for the evolution of CO_2. In addition, there also appears to be an

increase in intensity of the 2910 cm-1 region for the higher H/C solid material compared to the coal. This is consistent with the suggestion that hydrogen has been added to the organic part of the coal. Hydrogen addition to an aromatic moiety would certainly increase the intensity in this region of the spectra.

Thermogravimetric analysis (TGA). TGA analysis of the water-insoluble samples from the reaction of BT coal at 315 °C with NaOH and Na_2CO_3 indicated the volatility of the solids are greater than the untreated coal. Since higher volatility would correspond to the presence of smaller molecules or weakened bonds, it can be concluded that coal treatment with CO results in molecular weight reduction.

Liquefaction of hydrothermally treated Coal

Liquefaction in Tetralin. Material generated from the reaction of Clovis Point and BT coals in the presence of NaOH and Na_2CO_3 at 300 and 315 °C for an hour were liquefied with tetralin and distillate from Wilsonville Run 262E (V-131B).The following observations were made for reactions with tetralin and hydrogen at 400 °C.

(1) THF conversions obtained from the reaction with the treated material at both 15 and 60 min. were 8-12 wt % maf coal higher than for the untreated coal. At 15 min. the increase in conversion reported mainly to the PA+A whereas at 60 min. the increase in conversion reported mainly to the oil+water fraction.

(2) The liquefaction of coals treated with steam and low CO pressure or without CO gave slightly lower conversion than the untreated coal.

(3) The CO+CO2 yields for all treated coals were significantly lower and is in agreement with the reduced oxygen content.

(4) In the presence of Shell 324, THF conversion is similar for both the treated and untreated coal. However, there is a significant selectivity toward oil production for

treated coal reaction.

(5) In the presence of Nanocat, there is a significant improvement in both the conversion and oil yield over the untreated case.

(6) Lower hydrogen consumption was observed for the CO(800 psig)/H_2O/NaOH treated coal compared to the untreated coal.

Liquefaction in Wilsonville Process Solvents. The results from the liquefaction reaction of the treated material with Wilsonville Process solvents over a range of reaction temperatures (415-440 °C) can be summarized as follows:

(1) The reaction of the treated coal material in the presence of 1 wt% Mo as shell 324 gave a substantial improvement in oil yield (~9 wt% maf coal) over the untreated coal.

(2) In the presence recycle oil from Wilsonville Run 262, the pretreated material yielded a resid conversion (by established distillation method used at the CAER) of 22.3% compared to 19.5 % for the untreated coal. A comparable base case for BT coal with added Mo and Wilsonville iron oxide at 1% Fe gave a resid conversion of 23.5 wt%.

The most significant conclusion that can be drawn from these experiments is that hydrothermal treatment of low-rank coal with CO and water in the presence of a base produced a material that has been chemically and structurally modified. This new material is significantly more reactive and appears to be a better feedstock for liquefaction than the untreated coal. In addition, there appears to be a lower hydrogen consumption in the liquefaction process and a selectivity toward oil production. It is suggested that retrogressive reactions competing for hydrogen during liquefaction apparently has been quenched.

The implication of this work on a process standpoint is that there are significant potential savings associated with oxygen removal from coal, improved liquefaction activity of the treated material,

product selectivity, hydrogen consumption and overall plant operability. Although this work has made progress in demonstrating the beneficial impact of hydrothermally treating coal with CO, further fundamental work has to be carried out in order to answer numerous questions concerning the subject.

Chapter 10 - Fluidized Coking

An alternative method to the ROSE process for removing ash and unconverted carbon from the system that was investigated in this program was fluid coking, which at the outset had a lower estimated cost relative to critical solvent deashing. In a configuration where the vacuum bottoms would be coked, distillate product would be recovered and recycled back to the liquefaction stage. Related studies have been conducted by Exxon Research and Engineering in the late 1970s and, more recently, Lummus-Crest Inc. The latter found the distillate to be a poor donor solvent. However, upon hydrotreating the solvent quality increased quite dramatically. This approach offered a potentially lower cost option removing ash from the system and providing liquids that could be hydrotreated to give an improved recycle solvent.

A 3 inch fluidized retort at the CAER was modified to evaluate the coking of vacuum bottoms (V-1082) to determine coking yields and product quality of the coker overhead. Samples were produced at the CAER and then distributed to both CONSOL and Sandia National Laboratory for analysis and further treatment. In the coking experiments the V-1082 was cooled in liquid nitrogen, ground, mixed with a sintered alumina and transported pneumatically in nitrogen to the reactor fluidized bed. The particles immediately melt coating the alumina. The bed was fluidized (0.3 m/s) with a mixture of steam and nitrogen which was preheated to 500 °C. The height of the fluidized bed zone was controlled by varying the length of an overflow tube in the center of the reactor and coked particles were continuously withdrawn from the bottom of maintain the reactor inventory. A thick aerosol formed which was then collected in the sample recovery train. The residence time of gas in the reactor under these conditions was ~0.25 sec while the average solids residence time was 15 to 20 min. The latter corresponds to the residence time of the unconverted resid in the bed.

The tar yield appeared to be proportional to the steam/resid ratio which varied over a range of 4-13 lb/lb. Over this range as the steam/resid ratio increased the tar yield increased from 43 to 53%. Essentially all of the product (98%) was soluble in THF. Elemental analyses were the same as the starting deashed resid (V-130), except for a several percent increase in oxygen content. However, the phenolic −OH concentration was slightly lower. The proton distributions indicate the products are somewhat less paraffinic, slightly less naphthenic, and slightly more aromatic than the THF solubles in the feedstock. This suggests loss of paraffins or alkyl side chains accompanied by some aromatization.

The absence of any significant differences from the feedstock indicates that these overheads are not products from cracking but were produced by steam distillation of the starting material. Solvent quality values did not differ from those of the starting materials. Solubility fractionation also gave generally similar results for each of the products with no clear trend. Comparison of these results with the Lummus run, which was conducted at 544 °C, gave coker overhead yields which were quite similar (44%) but the product contained somewhat less aromatics and more hydrogen. It was concluded that since the experimental results were essentially the same as the Lummus results, per analysis by CONSOL, additional experimental results would be of no further benefit for the economic analysis.

Chapter 11 - Reaction Model Development

A kinetic model was developed based upon data taken at 415 °C in both tetralin and Wilsonville Run 262E recycle solvent. The model comprises a series of ordinary, first order, linear differential equations to describe the reaction rates for five reactants and products which are coal+IOM, PA+A, oils, carbon oxide gases, and hydrocarbon gases. In the model, IOM is converted to PA+A (k1), oils (k3) and CO_x(k5), and PA+A are converted to oils (k2) and both PA+A and oils are converted to HC gases (k4). An unreactive IOM fraction, $I\omega$, is included to define the IOM remaining at maximum coal conversion in a specific solvent at a particular reaction temperature. This parameter is important since it determines the agreement of the IOM model with the data at 60 minutes reaction time, which is about 8 half-lives with respect to the disappearance of IOM. Data taken at 7½, 15, 30, or 60 minutes were used to develop the

simultaneous solution of this set of equations for which R^2 values were calculated.

In tetralin an R^2 value of 0.941 was obtained which was improved by using a Iω value taken from the 60 minute IOM measurement. Using the Iω value improved the fit giving an R^2 value of 0.994. The k1 rate constants, which is the dissolution of IOM to PA+A, that was obtained for an impregnated Fe coal showed a 46% increase over a non-catalyzed case with smaller changes being observed in the other rate constants. This significant increase is a reflection of the catalytic effect of the iron for promoting coal dissolution.

In Wilsonville Run 262 recycle solvent, that contains both Mo and residual pyrrhotite, the best fit was obtained using an Iω value of 7.9 which gave an R^2 of 0.977. Runs with 1.0 wt % added Fe as Mach I superfine iron oxide (SFIO) gave an R^2 value of 0.991. Since a portion of the IOM in the Wilsonville solvent is immediately soluble, even at short times at 300 °C, going primarily to PA+A, the effect of adjusting the IOM and PA+A concentrations on the rate constants was determined. The biggest change was in the values of k2 and k3 which increase and decrease by 20%, respectively, along with a 5% increase in k1. The fit of the adjusted case appears to be little changed.

Adding SFIO in the Run 262E solvent increased the values of all the rate constants except for k4, the formation of HC gases. The biggest change was an ~40% increase in k2 while both k1 and k5 increased by ~20%. The level of Fe addition of the SFIO was only about 1/4 the amount of Fe already present in the recycle solvent. This would suggest that the fresh Fe significantly enhances the liquefaction rate even though recycled Mo is already present in the solvent. This is somewhat surprising based upon later results that showed that the recycled Mo is quite an active catalyst.

Chapter 1
Catalyst Testing in Resid Containing Recycle Solvents

Summary

Numerous problems have been encountered in evaluating catalyst performance in full-range liquefaction recycle solvents that contain sizable amounts of resid, unconverted coal and ash. In a liquefaction plant in which only distillate products are produced, resid is recycled to extinction. In such a configuration the feed to the plant will contain a distillate to coal ratio of less than one with the remaining portion of the solvent made up of residual material having reduced donor capacity. In recycle solvents obtained from the Wilsonville pilot plant, which were produced when running in the distillate-only mode, the presence of an easily converted THF insoluble fraction was found in the residual fraction of all the Wilsonville recycle solvents that have been tested in our laboratory. When using these recycle solvents for evaluating catalysts, conversion of the residual fraction leads to abnormally high coal conversions even under the mildest of conditions. The presence of catalysts that accumulated in some of the recycle solvents masks the effect of added fresh catalysts on both dissolution of the coal and 565 °C$^+$ resid conversion. Results from this study have shown that catalyst testing in these systems requires careful control of the components in the residual fraction.

Results from liquefaction of Wyodak coal in recycle solvents containing up to 1060 mg freshly added Mo per kg maf coal indicates that coal conversion, pentane solubles and 565 °C$^-$ yields increase as Mo concentration increases. Activity of recycled Mo is much higher than freshly added Mo. Exceptional activity with nanometer-size iron oxide in the absence of any Mo was observed.

Introduction

Since the early 1980's, the objective of liquefaction processing has changed from making primarily a low-sulfur residual product to producing exclusively distillate product.[1] Since resid conversion to distillate product does not proceed to any significant extent in the absence of

catalyst,[2,3] the major technological challenge has become to develop catalysts that will convert the residual fraction. To meet this challenge, a considerable amount of recent work has been directed toward developing catalysts for conversion of coal to distillate product. At the same time there has been continued interest in upgrading petroleum-derived resids to make distillate products.[4,5,6] The criteria for optimizing resid conversion is to maximize distillate yields at low hydrogen consumption levels while limiting gas make. This, however, does not discount the need to also attain maximum coal dissolution in order to develop an economically viable process.

Both particulate and highly dispersed catalysts have been used for converting residual feeds to distillate products.[7] At Wilsonville, various Fe and Fe-Mo catalysts have been used along with particulate catalysts for processing coal slurries through thermal and ebullated-bed reactors. Runs 260, 262 and 263 were made in which a dispersed molybdenum catalyst (Molyvan L) plus iron oxide were fed with coal through a thermal reactor followed by an ebullated catalytic reactor containing a particulate nickel-molydenum on alumina catalyst.[8] This reactor configuration with dispersed molydenum gave among the highest C_4^+ distillate yields ever observed at the Wilsonville facility.

In order to develop catalysts for these resid conversion applications, a microautoclave screening test was developed. This test which is run at temperatures equivalent to those used in the first stage at Wilsonville measures catalyst performance in ash and resid containing process solvents that were obtained from the Wilsonville plant. A measure of distillate production and coal conversion to THF solubles is provided. In addition, C_1-C_3 hydrocarbon, CO and CO_2 gas yields and H_2 consumption are measured. In this chapter, the development of this test is discussed including results from scoping studies that defined the test conditions. Results from evaluation of several catalyst candidates are used to illustrate results from this test.

Experimental

Recycle Solvents - The recycle solvents were all produced at Wilsonville when the plant was operating on Wyodak coal. The Run 258K V-131B (II) and the V1067 low-pressure flash bottoms from Run 260 were used as supplied. Run 262 recycle solvent (I) was prepared by

blending V-1074 heavy distillate (**I-HD**), V-130 deashed resid (**I-DR**), and V-1082 ashy resid (**I-AR**) in the ratio used during the material balance period Run 262E.[9] Analyses of these recycle solvents given in Table 1-1 show that all of the recycle solvents contain sizable concentrations of iron resulting from addition of iron oxide to these feed slurries. **I** also contained a sizable concentration of accumulated Mo which had been introduced into the process as MVL. Mo concentrations were 300 mg/kg in **I-AR** and 53 mg/kg in **I-DR**. The iron is present in combination with sulfur as pyrrhotite.[10,11] The molybdenum was presumed to be present as MoS_2. Each of the recycle solvents was characterized by separating into the following fractions: tetrahydrofuran (THF) insoluble material, which included insoluble organic matter (IOM) and ash, THF soluble-pentane insolubles (PA+A), and pentane solubles (oils) (see Table 1-2). The calculated concentrations of the individual fractions agreed with the concentrations of these fractions that were determined by solvent separation of **I**. A sample of THF insoluble material in **I-AR** was isolated by exhaustively extracting in a Soxhlet extractor with THF for 2 days and drying overnight at 40 °C at 125 torr.

Table 1-1. Recycle Oil Characterization (wt%)

	I[a]	II	III
566 °C⁻ Distillate	44.2	46.6	N.A.[b]
Ash[c]	8.1	8.1	8.2
THF IOM	13.0	15.1	17.8
PA+A	18.7	22.1	24.0
Oils	60.2	54.7	50.0
Iron	1.7	1.2	N.A.
Molybdenum, mg/kg	163	3	N.A.

a. Prepared by blending **I-HD**, **I-DR** and **I-AR** in ratio 42.7:6.6:50.7 wt%, respectively.
b. Not available
c. SO_3-free basis

Reaction Conditions - These experiments that are described here were conducted in 50 cc microautoclaves that were pressurized with 1000 psig cold hydrogen. In a typical experiment, 5.4 g of solvent, catalyst and dimethyl disulfide were added to the reactor. In coal runs 3 g of coal were also added to the reactor. Particulate catalysts IO and SFIO and organically dispersed Molyvan L (MVL) were added to the reactor. The reactor was placed in a fluidized sandbath set at the specified temperature and continuously agitated at a rate of 400 cycles per minute. At the end of the reaction period, the reactor was quenched to ambient temperature and the gaseous products collected and analyzed by gas chromatography. The solid and liquid products were scraped from the reactor using THF and the mixture was extracted in a Soxhlet extraction apparatus for 18 hours. The THF insoluble material was dried (80 °C at 125 torr) and weighed. The soluble fraction was concentrated by removing excess THF in a rotary evaporator and subjected either to solvent separation or vacuum distillation. Material balances using the solvent separation method are based upon a forced ash balance wherein oils are calculated by difference and includes water and any experimental error. Net product yields are calculated by subtracting the amount of each fraction contained in the feed from the corresponding amount found in the product. The total net product equals the amount of moisture and ash free (maf) coal in the feed and reflects the net make (or loss) of each of the solubility fractions.

Distillation Procedure - Vacuum distillations were performed using a modified ASTM D-1160 procedure starting with the soluble product from THF extraction of the total reactor effluent.[12] The apparatus used in the distillation consists of a distillation flask equipped with a thermowell, a distillation head equipped with a thermometer, an adapter connecting the distillation head to the receiver flask and equipped with a sidearm, and a receiving flask. A 2.1 cm Teflon coated magnetic stir bar is placed into the distillation flask. A known weight of vacuum grease ($\sim$0.2 g) is applied to the ground glass joints. A Thermix magnetic stirrer is used to drive the magnetic stir bar. A GlasCol heating mantle and two-2 ft 1/2 inch wide heating tapes are used to apply heat to the distillation flask and distillation head. The apparatus is liberally wrapped in Fiberglas insulation. The THF soluble solids-free product from the microautoclave is placed into the distillation set-up. While stirring, the flask is slowly heated to $\sim$120 °C at $\sim$0.5 atm

to remove light material including any remaining THF and any entrapped air. During this period care must be taken to prevent bumping. At ~120 °C the vacuum is increased slowly to 1 Torr while stirring. The temperature is increased from near ambient to the final cut point over a period of 1.5 to 2 hours, depending on the amount of residual THF present. Once the cut point has been reached, heating of the apparatus is discontinued. The flask is allowed to cool while caution is taken to prevent liquids collected in the ice trap from backing into the distillation apparatus. Once the apparatus has returned to ambient temperature, the weight of each individual section is obtained. The contents are then calculated assuming that grease contained on the joint connecting the distillation head and the adapter remains on the distillation head. The holdup in the distillation head is then assigned as follows: 66.7 wt % to the residual fraction and 33.3 wt % to the distillate fraction. The atmospheric equivalent temperatures (AET) is calculated from the actual cut point obtained in the microdistillation apparatus by the following equation

$$AET, °C = \{(748.1 * A)/[1/VT+(0.3861*A)-0.00051606]\}-273$$

where:

A = ([5.9991972-(0.9774472*log P)]/[2663.129-(95.76*log P)])

VT = is vapor temperature in Kelvin

P = is pressure of system in mm of Hg (Torr) observed when the vapor temperature is read

The AET for an observed distillation temperature of 331 °C at 1 torr is 566 °C (1050 ° F) simulates the temperature obtained in the vacuum tower at the Wilsonville Advanced Coal Liquefaction Facility. Material balances and product distributions are calculated in the usual manner. Material balances are based upon a forced ash balance with any loss and error being accounted for in the distillate product. Product distribution using the distillation method are calculated by subtracting the weights of gases, residue, ash and IOM from the weight of each in the feed. Resid conversion was calculated as follows:

$$Resid\ Conv = 100\ [\ 1 - \frac{[IOM\ +\ 565^oC^+\ Resid\ (maf)]_{Products}}{[Coal\ (maf)\ +\ IOM\ +\ 565^oC^+\ Resid\ (maf)]_{Feed}}]$$

In both the distillation and solvent separation cases, coal conversion equals 100 minus the yield of IOM.

Results

Reactivity of Recycle Solvents - In order to assess the action of catalysts, it was necessary to understand the composition of the solvents and the reactions that occur to them both in the presence and absence of catalysts. These recycle solvents that were used contained ~45 wt % of 370 to 565 °C heavy distillate and ~32 wt % of 565 °C$^+$ THF soluble organic material. The remaining material included ~8 wt % ash in addition to IOM (see Table 1-2). Almost half of the resid from **I** (**I-R**) and one quarter of the resid from **II** were soluble in pentane.

Table 1-2. Recycle Oil Characterization (wt%)

	I[a]	II	III
565 °C$^-$ Distillate	44.2	46.6	N.A.[b]
Ash[c]	8.1	8.1	8.2
THF IOM	13.0	15.1	17.8
PA+A	18.7	22.1	24.0
Oils	60.2	54.7	50.0
Iron	1.7	1.2	N.A.
Molybdenum, mg/kg	163	3	N.A.

a. Prepared by blending **I-HD**, **I-DR** and **I-AR** in ratio 42.7:6.6:50.7 wt%, respectively.
b. Not available
c. SO_3-free basis

The IOM fractions in all these recycle solvents decreased when heated. As shown in Table 1-3,

up to 20% of the IOM concentration in **I** became soluble in THF after heating at 415 °C in the presence of H_2 for periods ranging from 3.8 min up to 60 min. The concentration of IOM was also observed to decrease at temperatures as low as 300 °C, both in the presence and absence of hydrogen. In **I-AR**, which contained a higher concentration of THF insolubles, a similar level of IOM conversion was also observed after heating at 415 °C in H_2 (see Table 1-4). The IOM decreased from an initial 26.7 wt % to 20.7 wt %. In the presence of NiMo/alumina, the changes to either **I** (see Table 1-5) or **I-R** (see Table 1-4) were essentially the same indicating that catalysts had minimal impact on IOM conversion. Likewise, adding 1.4 wt % fresh Fe as SFIO or 0.6 wt % Mo as molybdenum naphthenate gave essentially the same yield of IOM as in the absence of any added fresh catalyst (Table 1-5).

Table 1-3. Disappearance of IOM from **I**

Temperature (°C)	Gas[a]	Time (min)	THF IOM[b]
415	-	0	13.0
415	H_2	3.8	11.4
415	H_2	7.5	11.2
415	H_2	15	10.9
415	H_2	30	10.9
415	H_2	60	10.3
300	H_2	15	11.1
300	N_2	15	11.8

a. Pressure 6.89 MPa (cold).
b. Weight percent ash-free solvent on SO_3-free ash basis.

In a separate experiment the IOM was separated from **I-AR** by exhaustively extracting with THF. When the isolated material was then heated in tetralin and H_2 at 415 °C for 15 min only 5.2 wt % would dissolve in THF. This level of solubilization was far below the 23 wt % of the IOM that dissolved when **I-AR** was treated under the same condition. Since **I-AR** has negligible hydrogen-donor capacity, hydrogen transfer reactions are not involved in the solubilization of this material. The important thing for solubilization appears to be the presence of coal derived material.

Table 1-4. Reaction of Resids at 415 °C				
	No catalyst		NiMo/alumina[a]	
	I-AR	Product at 15 min[b]	I-R	Product at 60 min[c]
Products (wt% af)				
HC Gases	-	0.24	-	0.7
$CO+CO_2$	-	-	-	-
Oils	35.4	43.9	39.2	64.2
PA+A	37.9	35.1	37.2	18.2
IOM	26.7	20.7	23.6	16.9
IOM Conv	-	23	-	29
PA+A Conv	-	7	-	51

a. Shell 324, 7.2 wt% on ash-free feed (1.0 wt% added Mo on ash-free feed).
b. No coal, 5.4 g **I-AR**, 6.89 MPa H_2 cold.
c. No coal, 3.3 g **I-R**, 6.89 MPa H_2 cold, 1.0 wt% Mo on feed.

Table 1-5. Conversion of I at 415 °C for 60 min[a]					
	Starting Material	Catalyst			
		none	NiMo/ alumina[b]	MoN[c]	SFIO[d]
Products (wt% af)					
HC Gases	-	0.3	0.5	0.6	0.7
$CO+CO_2$	-	0.1	<0.05	-	-
Oils	65.6	68.0	77.9	76.9	70.3
PA+A	20.3	21.3	11.3	13.4	19.6
IOM	14.1	10.3	10.3	9.1	9.4
IOM Conv	-	27	27	35	33
PA+A Conv	-	-5	44	34	3

a. No coal, 5.4 g **I**, 6.89 MPa H_2 cold.
b. Shell 324, 4.5 wt% on ash-free feed (0.6 wt% added Mo on ash-free feed).
c. Contains 0.6 wt% added Mo on ash-free feed.
d. Contains 1.4 wt% added Fe as SFIO on ash-free feed.

Lower IOM concentrations were also obtained when **I-AR** was extracted with either pyridine or mixed cresylic acids, both of which are known to be better solvents than THF for vacuum tower bottoms and ROSE-SR ash concentrate.[13] The insolubles in pyridine, using a Soxhlet extraction technique where the temperature was held either at 84 °C or at reflux at 114 °C, were 23.1 wt % and 21.4 wt %, respectively. The cresylic acid insoluble fraction, determined by the procedure used at the Wilsonville pilot plant,[14] was 24.0 wt %. All were less than the 26.7 wt % IOM in **I-AR** (see Table 1-4), with the amount insoluble in refluxing pyridine being only slightly higher than the 20.7 wt % observed after heating **I-AR** at 415 °C for 15 min in H_2. This contrasts with the nearly equivalent values obtained with cresylic acids and THF on freshly prepared **I** and **II** (see Table 1-6).[9,15,16,17]

Table 1-6. Composition of Wilsonville Recycle Solvents (wt%)

Solvent	Analysis Laboratory	Analysis Date	Distillate + Resid	Unconverted Carbon	Ash[a]
II	Wilsonville	Oct 1989	80.7	9.6[c]	9.7
	CONSOL	Oct to Dec 1989	80.0	9.3[b]	9.8
	UK/CAER	1993	76.8	14.2[b]	9.0
I	Wilsonville	Sept. 1991	80.3	9.3[c]	10.4
	CONSOL	Jan to Mar 1992	79.0	10.0[b]	10.5
	UK/CAER	1993	79.1	10.7[b]	10.2
	UK/CAER	Corrected to 15 min, 415 °C data	80.6	9.1[b]	10.3

a. Proximate ash values, dry coal basis.
b. THF insolubles.
c. Cresylic acid insolubles.

It appears that solubilization of the IOM in these aged recycle solvents results from disassociation of agglomerates that form over a period of time as opposed to dissolution of unreacted coal macerals. As shown in Table 1-6, the IOM concentration of both **I** and **II**, as measured in our laboratory, was greater than measured at the time this material was produced in the pilot plant.[15,18] Increased agglomeration over the interim three year period between the time **II** was produced in the pilot plant and when it was used in our laboratory resulted in formation of additional THF insoluble material. The IOM measured on fresh **II** was at least 4% lower than measured in our laboratory 3-4 years later. The differences for **I** were less reflecting the shorter aging period.

We are aware of only one previous report on increased IOM in pilot plant derived materials.[19] A reactive pyridine insoluble fraction was observed in samples of ash concentrate obtained from the Wilsonville critical solvent deashing (CSD) unit. A sizable amount (17%) of this material became pyridine soluble when heated at 450 °C for 40 min. It was originally thought that this behavior was the result of changes caused by the CSD. However, based upon results reported here, the resolubilized material is the result of retrogressive reactions of the originally solubilized coal product that was occluded on the solids reject.

The composition of **I-HD**, which contained a small amount of IOM, also changed when heated. The IOM fraction decreased from 3.1 wt % to 1.8 wt % after heating at 300 °C in hydrogen for 15 minutes. Since distillate was such a large component of the reactant mixture, this small change in IOM concentration had a sizable impact on coal conversion.

Converted IOM went into both the PA+A and oil fractions, in lieu of forming hydrocarbon gases, which were less than 1 wt %, as shown in Table 1-5. No significant formation of carbon oxides was observed. Added NiMo/alumina or molybdenum naphthenate increased the conversion of PA+A resulting in an increase in the amount of oils that were produced from **I**, as shown in Table 1-5, and **I-R**, as shown in Table 1-4. In the presence of Mo, the concentration of PA+A in **I** decreased from 20.3 wt % to 11 to 13 wt %, whereas in the

absence of a catalyst the PA+A concentration was actually greater than in the starting material. In **I-R**, conversion of PA+A in the presence of NiMo/alumina was 51 wt % versus only 7% in the absence of added catalyst (see Table 1-4).

Reactivity of the Recycle Solvents in Presence of Coal. When recycle solvents that contained reactive IOM were heated in the presence of Wyodak coal, higher than expected THF conversions were observed, some being in excess of 100%. At 415 °C for 60 min, liquefaction of Wyodak coal in **I, II,** and **III** resulted in a net loss in IOM. Negative IOM yields of -5.4, -5.3, and 0 wt %, respectively, were obtained compared to IOM yields of 14.5 and 15.9 wt % in **I-HD** and tetralin, respectively (see Table 1-7). Distillate solvents under these conditions exhibit little reactivity.[20] Although the THF insolubles that had been isolated from **I-AR** are only slightly reactive when placed in tetralin under these same reaction conditions, in the presence of coal the solubility of the IOM increased resulting in a net loss of IOM (-5.8 wt %). The reason there was a net loss of IOM in the presence of coal was that the coal derived products that formed during liquefaction solubilized the IOM fraction. In the absence of IOM, coal conversion in solvents containing both distillate and resid are comparable to those obtained in distillate alone.[3]

Table 1-7. Effect of Solvent on IOM Yield in Liquefaction with Wyodak Coal[a]

Solvent	Time (min)	IOM Yield (wt% maf coal)[a]
I-HD	60	14.4
Tetralin	60	15.9
I	60	-5.4
III	60	-5.3
II	60	0
Tetralin + THF Insolubles from **I-AR**[b]	60	-5.8
Tetralin + THF Insolubles from **I-AR**, No Coal	15	5% of IOM in THF Insols Converted

a. Conditions: 415 °C, 60 min, 6.89 MPa H_2 cold.
b. THF insolubles is equal to concentration of THF insolubles in **I**.

Screening Test. Since the desired product from this liquefaction process is distillate, this requires that all of the coal and intermediate residual material be converted to distillate, to gas, or be rejected from the process with the ash concentrate as unconverted carbon and residual material. The role of dispersed catalyst is to promote conversion of resid to distillate product and influence coal solubilization. Resid conversion, which measures the disappearance of coal, unconverted carbon, and resid, provides a measure of the activity of catalysts for promoting this reaction. However, these values can be compared only for essentially the same conditions of IOM and resid in the recycle solvent and concentration of coal in the feed. This value was determined using the vacuum distillation technique.

In establishing the conditions of the test, the initial runs were analyzed by the solvent separation technique. The change in pentane soluble product provides an indication of the conversion of coal and resid to lighter molecular weight product. The temperature for this test was chosen as 440 °C based upon run temperatures at Wilsonville and safety considerations with regard to the particular microautoclave equipment used in the study.

Conversions and product yields were determined for the liquefaction of Wyodak coal in I at 440 °C for residence times up to 30 min in the presence of added fresh iron and Mo catalysts (see Table 1-8). The total concentration of Fe and Mo in these runs, on a maf coal basis, was 4.4 wt % and 440 mg/kg coal, respectively. Additional DMDS was added to sulfide the catalyst. Under these conditions, THF conversion increased from 74 wt % at 7.5 min to 102 wt % after 30 min (Figure 1-1). The corresponding oil yields over this same time span increased from 8.4 wt % to as high as 49 wt %. Recalculating the THF conversions assuming that the input recycle solvent had an initial IOM concentration equivalent to that observed in I after being heated at 415 °C for 15 min (see Table 1-6), all the values decreased by approximately 4%, as shown in Table 1-8, bringing them much more in line with expected values. In this correction, it was assumed that all of the resolubilized IOM belongs in the PA+A fraction which has no effect on the yields of oils and gases or the magnitude of the resid conversions.

Figure 1-1. Effect of reaction time on liquefaction

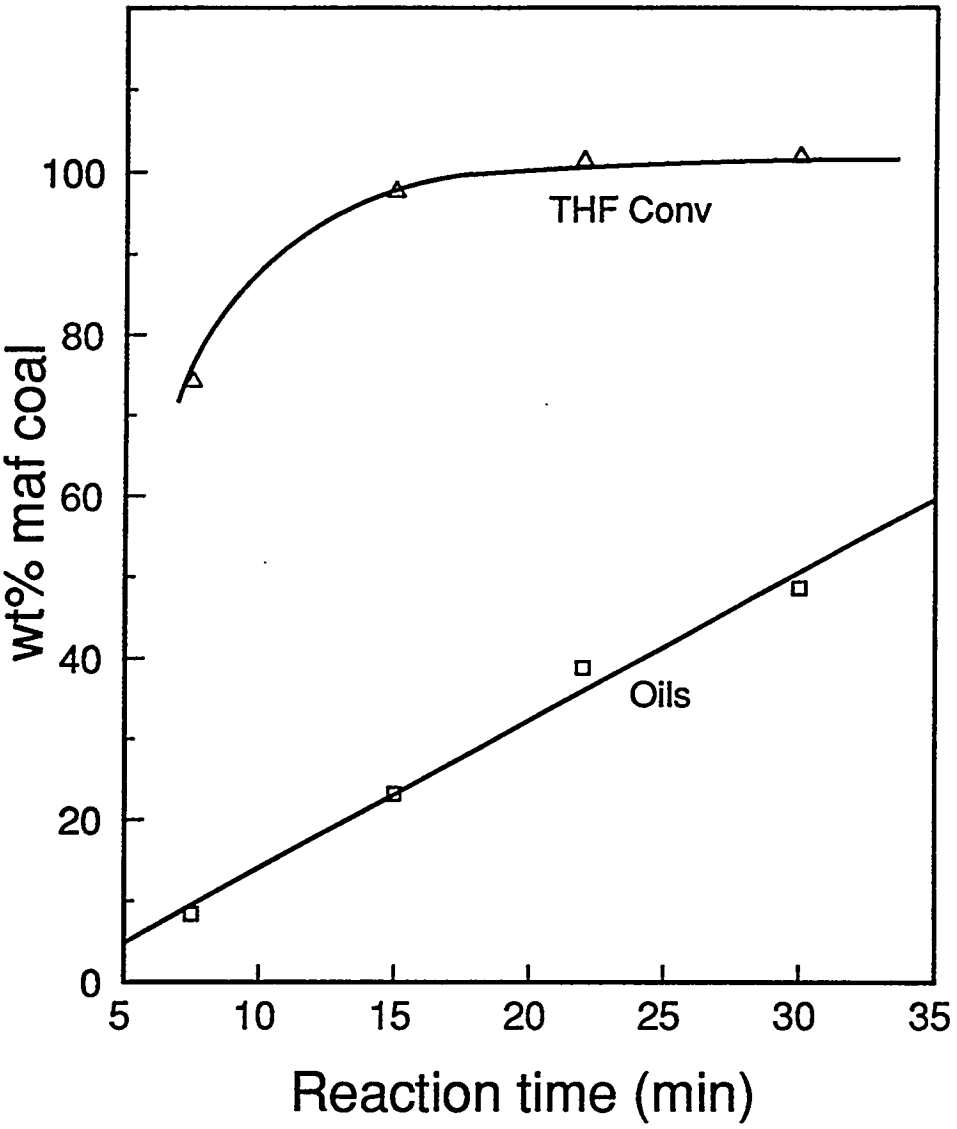


Table 1-8. Liquefaction of Wyodak Coal in I at 440 C[a]						
Reaction time (min)	THF Conv No Correction (wt%)	Gases (wt%)		Oils (wt%)	PA+A (wt%)	THF Conv, IOM Corrected (wt%)
		HC	CO_x			
7.5	74.2	0.9	5.2	8.4	59.7	70.2
15	97.6	1.0	6.0	23.2	67.3	92.3
22	101.3	2.5	5.6	38.8	54.4	97.3
30	101.8	3.2	5.7	48.6	44.3	97.8
a. 1% IO + 100 ppm Mo as MVL on dry coal						

Coal and resid conversions and oil yields were obtained for a series of iron and iron-molybdenum combinations at 22 min residence time. Concentrations up to 4.6 wt % Fe and 1060 mg Mo/kg coal, on a maf coal basis, were tested (Table 1-9). THF conversions increased sharply from a low of 95 wt % in **II**, in the absence of any added metal, up to values in excess of 100 wt % in the presence of additional Fe and/or Mo. Adding 20-30% fresh Fe to the Fe already present in **II** promoted a significant increase in THF conversion, suggesting that fresh Fe provides a catalyst that is more active than the Fe already present in the recycle solvent. Likewise, there appears to be little difference in activity between the different forms of Fe that were added to the reaction. Increasing the Mo concentration from 110 to 1060 mg/kg maf coal appears to increase coal solubilization.

The corresponding 565 °C$^+$ resid conversion values in **II** showed a steady increase with Mo concentration, as shown in Figure 1-2. Increases in distillate yields parallel this change. Addition of Mo to recycle solvent **II** increased resid conversion from 14 wt % to 31 wt % over this range. Resid conversions in **I**, that already contained 300 mg of recycled Mo/kg maf coal, were significantly better than obtained at comparable levels in **II**. This shows the higher activity of the recycled Mo relative to freshly added Mo, which agrees with previously reported results.[21] The increase resulting from addition of Mo to FeIII impregnated coals is shown by the line in Figure 1-2.

Item	Recycle Solvent	Form of added Catalyst[b]		Total Metal Conc.		THF solubles (wt%)	565 °C$^+$ (wt%)	565 °C$^+$ Resid Conv (wt%)
		Fe	Mo	Fe (wt% maf coal)	Mo (mg/kg maf coal)			
1	II	none	none	3.1	1	95	22	14
2	II	IO	MVL	3.9	110	102	28	18
3	II	FeIII	none	3.7	1	102	29	19
4	II	SFIO	none	4.0	1	104	50	28
5	II	FeIII	AM	3.9	270	101	41	23
6	I	IO	MVL	4.4	440	101	61	32
7	II	FeIII	AM	3.9	540	103	43	25
8	I	FeIII	AM	4.6	600	102	52	29
9	I	FeIII	AM	4.6	870	103	56	31
10	II	FeIII	AM	3.8	1060	106	53	31

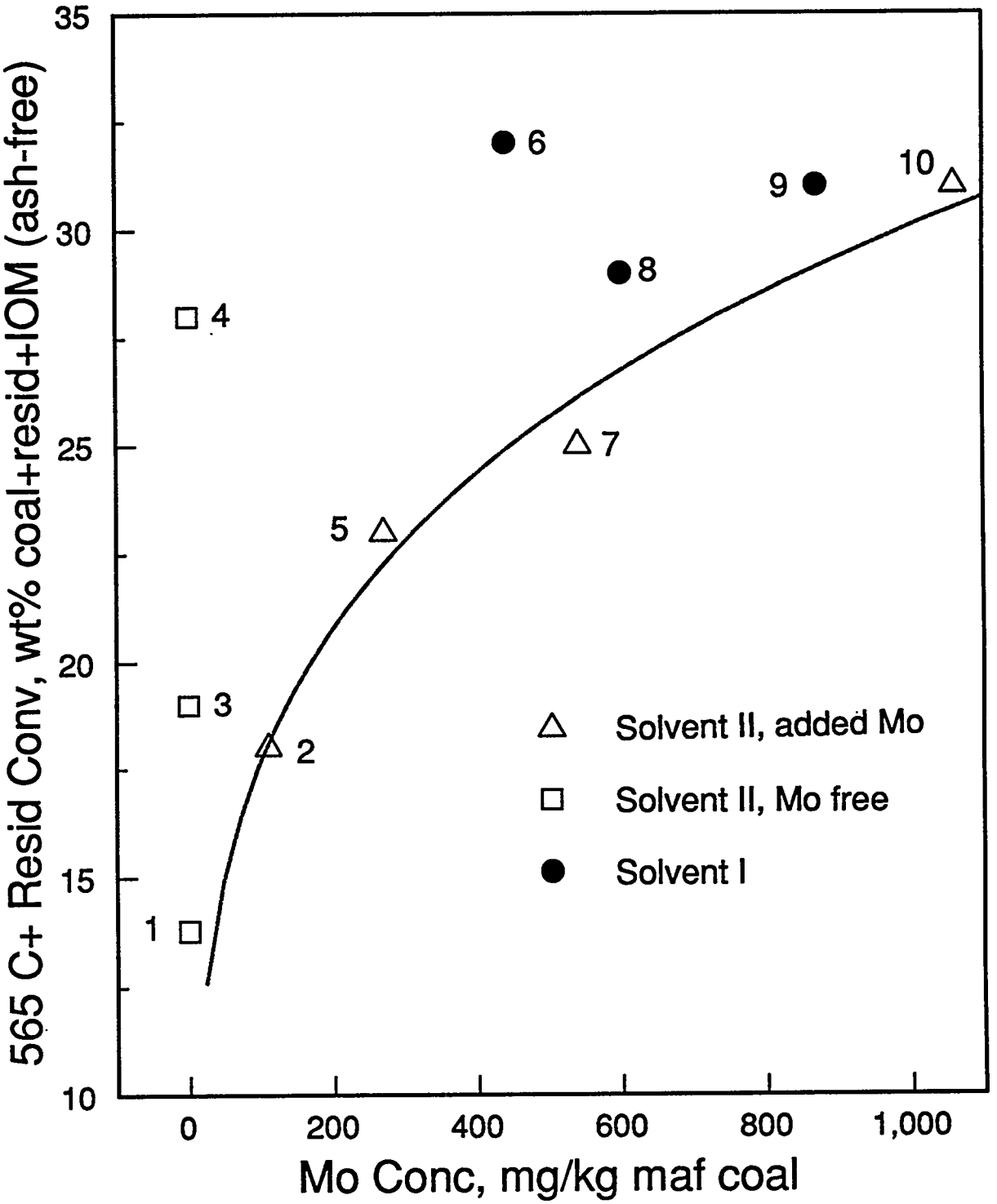
Table 1-9. Wyodak Coal Liquefaction in Recycle Solvents[a]

a. Weight basis expressed on moisture and SO_3-free-ash-free coal.
b. IO added as particulates; MVL added to feed recycle oil; FOH = FeOOH formed by base precipitation of ferric nitrate impregnated on coal; SFIO added as particulates; AM = ammonium molybdate impregnated as aqueous solution on coal; FeIII = $Fe_2(SO_4)_3 \cdot 5H_2O$ added as aqueous solution impregnated on coal.

Very high coal conversion and distillate yields were obtained in the presence of SFIO to which no Mo had been added. Although only 20% of the 1.2 wt % Fe present on total maf feed was present as SFIO, the 565 °C$^+$ resid conversion was equivalent to addition of approximately 600 mg Mo/kg maf coal to **II**. This increase in catalytic activity by this nanometer size iron-based material suggests that the activity of Fe catalysts can be improved relative to low surface iron oxides.

Impregnating the coal with a comparable amount of Fe as ferric sulfate also gave higher resid conversion in **II**, although the incremental increase was only half that of the SFIO. The relative particle size of the active iron catalyst, which presumably is pyrrhotite, isn't known at present. Also, how the particle size in the catalyst relates to the size of the Fe in the recycle stream is not known.

Fig. 1-2. Effect of Mo concentration on resid conv



Conclusions. Assessing the activity of fresh catalysts for liquefaction of Wyodak coals in pilot plant derived recycle solvents is complicated by the presence of resid, unconverted coal, ash and accumulated dispersed catalyst. Retrogressive reactions, that apparently occur over a period of time, were observed in all the plant derived solvents that were used in this study. The presence of a THF-insoluble fraction that easily converts at or above 300 °C in an inert atmosphere to THF-soluble material results in apparent coal conversions in excess of 100%, even under the mildest of conditions. Solubilization of this material in refluxing pyridine at 114 °C approached that observed by heating these solvents at 300 °C or above. Treating this IOM material in tetralin/H_2 at high temperature does not convert this material into a material which is soluble in THF. Addition of Mo to Mo-free recycle solvents resulted in increased THF-conversion and 565 °C^+ conversion. Accumulated Mo catalyst, that was present in recycle solvents that were produced in runs at Wilsonville, where dispersed Mo was being added, masks the effect of added fresh Fe or Mo catalysts. Catalyst testing in these systems requires careful control of the components in the residual fraction. Addition of 0.8 wt % Fe as SFIO to coal gave an increase in coal conversion, C_5 solubles and 565 °C^- distillate yield in Mo-free recycle solvent comparable to the presence of 500 mg fresh Mo/kg maf coal.

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Chapter 2

Surface Characterization and Liquefaction of Impregnated Coal

Summary

Results are presented from a study of the preparation and characterization of Wyodak subbituminous coal impregnated with iron and iron-molybdenum salts by the incipient wetness (IW) technique. X-ray photoelectron spectroscopy (XPS) was used to examine the surface composition and chemistry of coals impregnated with 0.7-2.0 wt% Fe and 500-1000 ppmw Mo. Various salts were used in preparing the impregnated coals including ferric nitrate, ferric sulfate, ferrous sulfate and ammonium molybdate. The surface concentration of Fe increased as the amount of added Fe increased, with higher concentrations being observed for the nitrate impregnated coals. The anions of the impregnating salts were readily removed from the samples that were treated with ammonium hydroxide solution. For samples impregnated with sulfate salts, which were not treated with base, higher sulfur concentrations were observed on the surface of the coal. The $Fe_{2p\ 3/2}$ and Fe_{3p} peak positions in the base treated coals correspond with α-FeOOH while the positions in the non-base-treated sulfate-impregnated coals are consistent with the Fe sulfate salts. The added Fe on the surface of the impregnated coals has a direct impact on the position of the O_{1s} peak shifting it to a lower energy position. Overlap of the Mo_{3d} doublet by the S_{2s} peak required deconvolution based upon peak positions in reference materials. The liquefaction performance of the impregnated samples is directly related to the amount of added Fe with THF conversion and oil yield increasing as Fe concentration on the surface increased. The liquefaction results with the Fe-Mo co-impregnated coals were better than the other coals prepared in this study.

Introduction

Highly dispersed iron-based catalysts have been extensively studied for direct coal liquefaction. The benefit of using smaller particle iron oxides as catalysts for coal liquefaction was observed by Anderson[1] who reported improved results when using 1 μm pyrite which had been ground to 75 μm. In recycle under SRC II conditions, total oil went from 17.8 up to 23% when using

the smaller pyrite. Cugini and coworkers[2, 3] found that finely divided and highly dispersed FeOOH-impregnated coals prepared by an IW technique had high activity in direct liquefaction by improving both conversion and distillate yields.[4] Pretreatment at lower temperatures was also found to provide increased liquefaction performance because of the more efficient conversion of the precursor oxide to pyrrhotite. These coals were prepared by impregnating the coal with a solution of ferric nitrate followed by treatment using an excess of NH_4OH. Cugini et al,[5] proposed that the deposited FeOOH coordinated with surface hydroxyl groups in a manner described by Yamashita et al.[6] They employed a gas-phase silylation technique to support the increased binding of surface hydroxyl groups on the coal with increased FeOOH addition.[7] The supposition was that the decrease in consumption of silylating agent by coals with increased FeOOH reflected increased coordination by added FeOOH. This assumes that interaction between the silylating agent occurs only with the hydroxyl groups on the coal surface and not with hydroxyl groups on the surface of the FeOOH group, although such reactions are well known.[8]

Liquefaction of Wyodak coal prepared with 5000 ppmw impregnated-Fe gave increased distillate yields compared to pigment grade iron oxide, both in the presence of added sulfur.[9] An SEM analysis showed that for coals impregnated with $FeCl_3 \cdot 6H_2O$, the Fe was primarily deposited on the surface.[10] Sulfidation during liquefaction was found not to result in any significant growth of the iron particles upon conversion to pyrrhotite,[11] thereby maintaining the advantage of the highly dispersed, small particle form of the metallic precursor.

In contrast to these results, others have reported not only low catalytic activity but poor reproducibility in liquefaction of coals impregnated with aqueous solutions of $FeSO_4$.[12] Possibly these differences could be related to the impregnation technique or to the application of base treatment. Impregnating coals by the IW technique is a multi-step process involving first the distribution of the metal solution onto the coal, after which the oxide is formed by increasing the pH, which precipitates the oxide at the point of contact with the base material. In addition, the IW procedure also includes coal preparation and filtration, washing, and drying steps. Any of these may influence the subsequent liquefaction performance of the impregnated coal. Among

the salts that have been used for impregnating Fe onto coals, the sulfates are preferable because they are the least expensive form of soluble iron that is available due to their abundance as a by-product from the iron and steel industry.

Considerable research has also been directed toward exploiting the improved liquefaction performance of mixed Fe and Mo catalyst.[13,14] Garg et al., found higher conversion and oil yields by simultaneously impregnating coal with 1% Fe and 0.02% Mo using solutions of 10% ferrous sulfate and 0.5% ammonium molybdate.[15] In related studies, Pradhan, et al.,[16] reported improved liquefaction of subbituminous coal with sulfated α-hematites containing small amounts of added Mo. Since Mo is expensive, its application in liquefaction will depend on maximizing activity at low concentrations while simplifying the preparation in order to minimize catalyst processing costs.

A study was undertaken during the course of this program to determine how impregnation technique affected liquefaction performance. The premise was that the metal function could be optimized by understanding the location of the impregnated catalytic metals on the coals, the degree of dispersion on the surface and their resulting chemical states. The importance of these variables on liquefaction would provide guidance on how best to prepare impregnated coal feeds. Numerous impregnated coal samples were prepared and characterized. Subsequently, they were subjected to liquefaction and their relative performance was evaluated The effects of several independent variables in the preparation scheme on metal deposition and chemical form were investigated using XPS. This technique has been used, not only to analyze the surface composition of coals,[17,18] but also to characterize the chemical state of the Fe-O system.[19,20,21]

Experimental

In this study, the Wyodak coal from the Black Thunder Mine in Wright, Wyoming, as provided by CONSOL Inc., was used throughout this study. The coal was ground to -200 mesh, riffled and stored under nitrogen at 4 °C. Proximate and ultimate analyses of the coal are presented in **Table 2-1.** Coals were prepared starting with reagent grade $Fe(NO_3)_3 \bullet 9H_2O$, $FeSO_4 \bullet 7H_20$ and $Fe_2(SO_4)_3 \bullet 5H_2O$, and ammonium molybdate (85% MoO_3), which were purchased from

Aldrich Chemical Co.

Impregnated Coal Preparation - Most of the coals prepared during the course of this program were prepared by the incipient wetness (IW) technique. Incipient wetness as a preparative technique has been extensively used for preparing supported metal catalysts. Milburn et al.[22] described "incipient wetness" as the point where unbound moisture is about to become available. At the IW point the onset of particulate bridging or agglomeration occurs as well as the volume of the material begins to expand significantly, i.e., the apparent density begins to decrease. The coals prepared by the IW preparative method involves a number of independent steps that can affect the performance of the resulting coal-catalyst combination. A flow chart showing the general synthesis method for preparing IW impregnated coals is shown in Figure 2-1. Preparation proceeds through a series of operations involving coal preparation, metals impregnation, base precipitation, filtration, washing, and drying, all of which can be altered in various ways. All the samples were prepared starting with either as-received coal or coal that had been predried. The moisture content and the volume of water used in the impregnation of as-received coal and coals that had been predried at 110 °C at 10 torr for 20 hrs are shown in Table 2-2.

The effect of mixing on dispersing the metals onto the coal by the IW procedure is not well defined. Presumably, the larger the volume of metal solution to be added to the coal, the less the problem will be for attaining better dispersion. In the lab preparations, which were done on coal samples of approximately 19 g, solutions containing either the nitrate or sulfate salts were added slowly in a dropwise manner to the coal while mixing to assure even distribution. As impregnation with the salt solution proceeds, the mixing of the dry coal particles became easier as well as the volume of the coal gradually increased. If the volume of water that was added during the preparation exceeded the IW volume, the volume of the coal decreased as a layer of water appeared and particle agglomeration occurred. After complete addition of the water, the particle size of the coal appeared to be about 1-2 mm. As the results presented below will show, dispersion in these samples were quite good. Although mixing problems may not have been observed at this small scale, at the larger scale the method of achieving uniform

Table 2-1. Proximate, Ultimate and Ash Analysis of Black Thunder Wyodak Coal		
	As Received	Dry[a]
Proximate, as-received basis		
Moisture	21.0	2.63
Ash	4.82	5.66
Volatile Matter	34.4	45.5
Fixed Carbon	39.8	46.2
Ultimate, Dry		
Carbon	69.97	72.15
Hydrogen	4.78	4.34
Nitrogen	1.43	1.23
Sulfur	0.56	0.53
Oxygen (diff)	18.21	16.94
Ash (SO_3-free)	5.05	4.81
Ash Composition, wt%[b]		
Fe_2O_3	6.62	-
CaO	25.79	-
Al_2O_3	19.05	-
SiO_2	38.05	-
MgO	5.20	-
Na_2O	0.58	-
K_2O	0.59	-
TiO_2	1.38	-
P_2O_5	1.16	-

[a] Dried 110 °C/20 hrs/10 torr. [b] Analysis provided by Consol Inc.

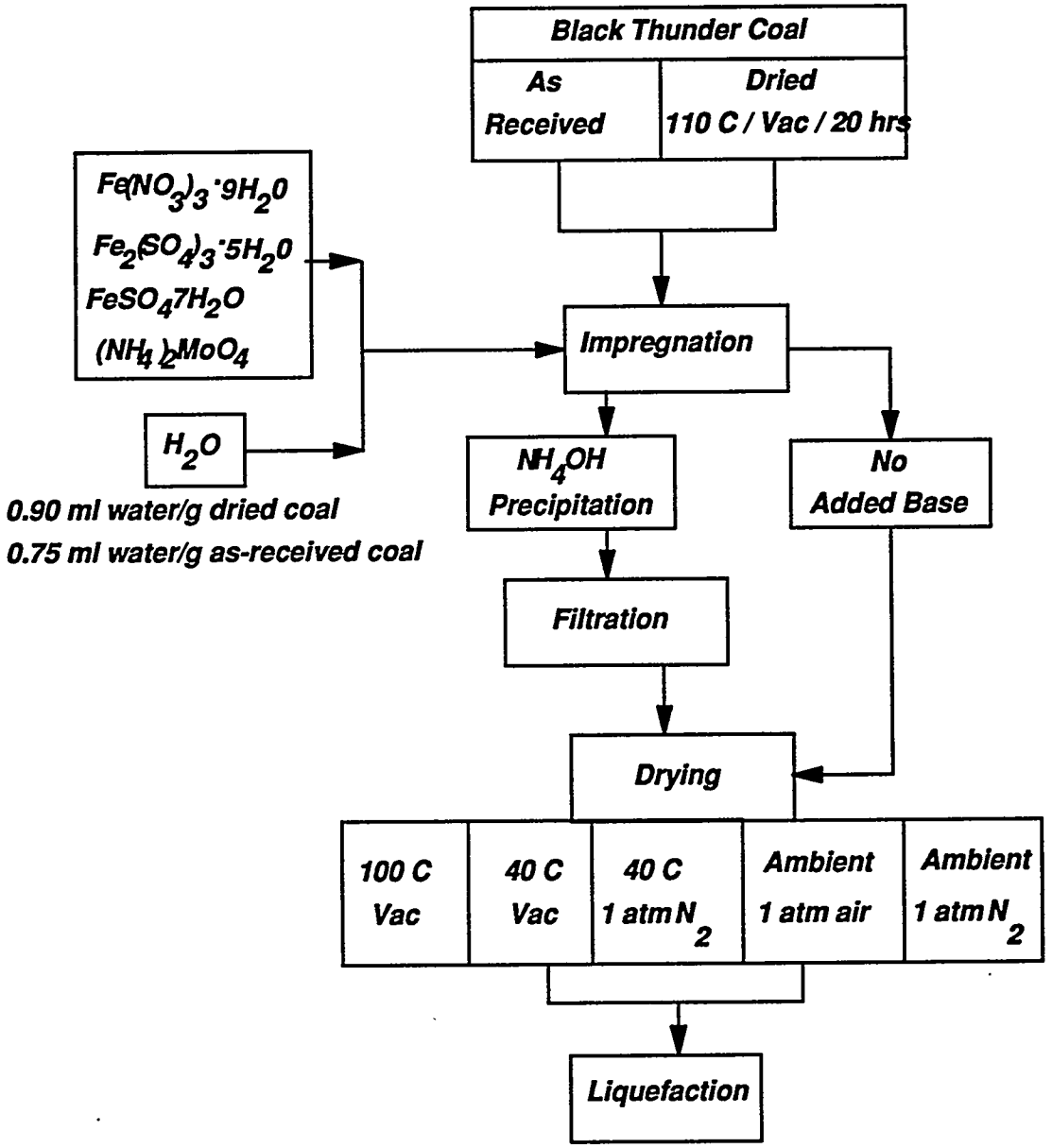


Figure 2-1. Preparation of Metal IW-Impregnated Coal

Table 2-2. Moisture Content of Starting Coal Plus IW[a]		
	"As Received"	Predried[b]
Starting Coal, wt % moisture	21	2-3
IW Water, ml/gram	0.75	0.90
IW water, wt % dry coal	55	48
a. IW = Incipient wetness water b. Predried at 100 °C, 1 Torr, 20 hours.		

mixing will probably be a major problem if performance is significantly affected by dispersion.

Selection of the particular salt to serve as impregnating carrier of the metal is an important factor in applying the IW method. This may be important for attaining high dispersion of the metal onto the coal without adversely affecting the coal itself. For iron, the first requirement in selecting a salt is finding ones that are soluble in water at the level necessary to attain the desired concentration in the defined volume of water. At a 1 wt % iron level on dry coal, this is equivalent to an iron oxide loading of 1.4 wt %. The concentration of the iron nitrate and sulfate salts in the IW-water determined for as-received coal and coal predried at 100 °C, 1 torr, 20 hrs is shown in Table 2-3.

Table 2-3. Concentration of Impregnating Salt in IW Water for 1 wt% Fe Loading		
	Dried Coal	"As Received" Coal
$Fe(NO_3)_3 \circ 9H_2O$	7.52 wt%	8.76 wt%
$Fe_2(SO_4)_3 \circ 5H_2O$	8.1 wt%	10.43 wt%

Solubility of the nitrate salt is not limiting since it can easily be increased, whereas for ferric sulfate, solubility is far more limiting. At lower metal loadings, the ferric sulfate will be less limiting. These concentration values suggest that using volumes of water far below the IW values will be feasible only when the loading on the coal will be at lower levels. This assumes,

of course, that using smaller volumes would provide some benefit, such as if intraparticle penetration or more even surface wetting occurs in preference to uneven liquid surface accumulation.

The sequential impregnation procedure was used in the preparation of Mo and Fe co-impregnated coals. The affect of pH on stability of the soluble metal compounds in the impregnating solution and the potential for metal removal during the precipitation process were considered. The co-impregnated samples were prepared by first adding to as-received coal on a per gram of dry coal basis, 0.25 mL ammonium molybdate solution followed by 0.5 mL of aqueous Fe salt solution.

Base addition was used in some of the preparations, especially for the early preparations in which ferric nitrate was used. As it became evident that adding base had a significant effect on catalyst cost, the direction turned toward eliminating the use of base. Base addition is used, as already discussed above, to convert the soluble Fe salt to FeOOH, which is a precipitated form of iron oxide. Ammonium hydroxide is typically used in order to keep the coal free of added metal ions. Although recipes for preparing FeOOH are well documented, the ratio of Fe^{+3} to NH_4^+ that will be effective in a coal particle has not been investigated. Likewise, the impact of ion exchange upon base addition to the coal matrix must be considered. All of the ferric nitrate and several of the ferric sulfate impregnated coals were treated by addition of ammonium hydroxide after which the samples were separated from the filtrate and dried. The concentration of iron, calcium and nitrate that was removed from the coal during the base washing step was determined by examining the NH_4OH filtrate from base-washed coals (Table 2-4). Analysis of the basic filtrates showed that deposition of Fe onto the coal was quantitative. Analysis of filtrates from subsequent water washes also indicated negligible Ca exchange and loss of Fe. Only 0.5 wt % of the Ca originally in the coal and less than 0.1 wt % of the Fe added to the coal were found in the filtrates. The recovery of NO_3^- in the basic filtrates appeared to be quantitative although the accuracy is poor due to the low concentrations, i.e., $\pm$20%. Absence of nitrate and sulfate ions in the filtrates from the washing step confirmed their complete removal in the basic filtrate suggested that water washing was not necessary since it provided

no additional ion removal from the treated coals. The absence of sulfate remaining on the base washed coals suggested that it could be substituted for nitrate without contaminating the resulting coal samples. Substituting sulfate for nitrate would decrease overall catalyst cost because of the much lower cost of the sulfate salts versus the nitrate salts.

Table 2-4. Filtrate Analysis[a]

	CH-45		CH-51	
Impregnating salt	Ferric nitrate		Ferric sulfate	
Fe Added, wt% dry coal	1.0		2.04	
Filtrate	Base	Water Wash	Base	Water Wash
Ca, wt % dry coal	1.0	-	1.0	-
Calcium Recovery, wt % Ca in dry coal	0.11	0.10	0.39	0.07
Fe Recovery, wt % Added Fe	0.002	0.0099	0.004	0.0033
NO_3^- Recovery, wt %[b]	85	[c]	108	[c]

[a] Direct Current Plasma Emission Spectrometry (DCP). [b] Measured using ion specific electrode. [c] Nitrate ion was not detected.

Under basic conditions, many of the carboxylic acid groups will presumably exchange with the base resulting in the formation of the corresponding ammonium carboxylates. The extent to which this occurs has not been accurately determined. Whether this impacted on the performance of the coal will be discussed separately.

The N_{1s} peaks in the XPS spectra of the base-treated nitrate impregnated coals, which will be discussed below, were consistent with organic nitrogen indicating the absence of nitrate or ammonium ions.[23] For those Fe sulfate impregnated coals which were not treated with base, the sulfate ions remained in the sample.

The level of drying of the impregnated coals were of particular concern relative to its effect on the structural features of a coal and its impact on the coal's performance in liquefaction. Vorres

had found that drying proceeds through two stages.[24] For a low rank North Dakota lignite, the first stage accounts for about 85% of the moisture while the second stage accounts for the remaining 15%. Miknis et al., observed a similar pattern using a microwave drying technique for a Powder River Basin subbituminous coal. They reported that in this technique approximately 75% of the moisture was removed at coal temperatures of approximately 100 °C. Additional moisture was removed only after the coal reached higher temperatures.[25] The earlier work of Silver and Frazee had shown that removing more than 75% of the moisture actually had a detrimental effect on liquefaction resulting in a decrease in both conversion and 850 °F distillate yield.[26] Miknis et al. speculated that moisture removed at temperatures above 100 °C is "an integral part of the gel or pore structure of the coal.....(that).....results in possible disruption of part of the coal matrix enabling some retrograde reactions to take place that diminish the reactivity toward liquefaction."

Coals containing varying amounts of moisture were obtained by drying under different conditions. Drying conditions at near ambient under high vacuum at 40 °C at 10 Torr, at 40 °C at ambient pressure in flowing nitrogen and at 100 °C at 125 torr were examined. Drying in flowing nitrogen gave a product that contained 9 wt % moisture which was essentially the same moisture level as obtained by Lee et al. after drying a similarly prepared Fe-impregnated Black Thunder coal in flowing nitrogen, i.e., 5 to 12 wt %.[27] Air drying, which previously had been shown by Silver and Frazee to have no detrimental effect on subsequent liquefaction, was also evaluated.

XPS Analysis - The surface composition and chemical state of various elements were studied using XPS. The XPS of the various samples of Fe impregnated coal was carried out with the LHS-10 Leybold-Heraeus Spectroscope using Mg K_α radiation with 15 kV, 20 mA and pass energy of 100 eV. The powdered samples were mounted on the XPS sample probe with Double-Stick Scotch tape. The sample powders were gently pressed and covered all of the Scotch tape attached on the stainless steel foil. The constituents of the tape did not contribute to the signals generated by the samples. The analysis chamber vacuum was about 5×10^{-9} torr. The C_{1s}, O_{1s}, Fe_{2p}, Fe_{3p}, N_{1s}, Ca_{2p}, Al_{2p}, Si_{2p}, and S_{2p} elemental spectra and the survey spectra of the coal

samples were obtained under the above working conditions and corrected with the hydrocarbon C_{1s} binding energy of 284.6 eV. The elemental concentrations were calculated and the peak deconvoluted with a computer aided program of damped non-linear least squares curve fitting, using mixed Gaussian/Lorentzian profiles.[28] The quantification of elemental concentrations was performed using background subtraction and element sensitivity factors. Depth profiling was carried out using Ar sputtering at 3.5 kV, 10 mA and pressure of 5×10^{-5} torr. Molybdenum measurements were complicated by overlap of the S_{2s} peak with the Mo_{3d} peak. Reference samples containing iron and $SO_4^{=}$ were used to correct the position of S_{2s} peak and the peak area ratio of S_{2s}/S_{2p} were obtained. Based on the S_{2s}/S_{2p} ratio, subtraction of the S_{2s} peak area from the Mo_{3d} peak area provided an accurate measurement of the Mo concentration. A depth profile of the different elements was also attempted using Ar^+ sputtering in conjunction with XPS measurements. Based upon rates of 13.5 angstroms/min for Cu and 8 angstroms/min for Au, the impregnated coal sputtering rate was estimated to be 20 angstroms/min. Samples were sputtered for up to 160 min.

Results and Discussion

Surface Composition of Impregnated Coals - XPS analysis was used to determine the surface concentration of the Fe and Mo on the impregnated coals and the chemical structure of the catalyst precursor. Since hydrogen cannot be detected in XPS, the surface concentrations, as determined by this technique, is normalized on a hydrogen-free basis and reported on a weight basis. The concentration of Fe in the starting Wyodak coal, calculated on a hydrogen-free basis, was 0.20 wt% with the surface concentration being slightly higher at 0.33 wt%. Higher surface concentrations were also observed for Al and Si indicating that the surface became enriched in these metals during grinding, which was probably due to preferential fracturing of the coal at the maceral-mineral interface (Table 2-5). The metal enrichment on the surface resulted in a slight decrease for all the other elements. The impact on coal composition of impregnating with 1.0 wt% Fe was to increase the Fe concentration in the bulk from 0.19 wt% to 1.17 wt% while also increasing oxygen in the bulk by a small amount from 20.9 wt% to 21.4 wt%. The final oxygen concentration is based on the assumption that FeOOH is the chemical form of the added Fe species. The other elements decreased slightly, with the largest change being in carbon.

Although Fe(III) salts form FeOOH upon treatment with base, the reaction of the Fe(II) ion, under conditions in which exposure to air is limited, is less clear.[29] Surface analysis of coals impregnated with 0.15 to 1.0 wt% Fe that was added as ferric nitrate showed that Fe concentration on the surface increased as the amount of added Fe increased (see Table 2-6). For the nitrate impregnated coals the change is greater at the higher addition levels, as shown in Figure 2-2.

Table 2-5. Element Concentrations in Wyodak Coal

	Bulk, wt%[a]	Surface, wt%[b]
Iron	0.20	0.33
Carbon	73.5	71.1
Oxygen	22.0	20.6
Nitrogen	1.5	1.3
Sulfur	0.6	0.2
Calcium	0.8	0.5
Aluminum	0.4	2.0
Silicon	0.8	4.0

a. Excludes 4.68 wt% hydrogen from calculation.
b. Hydrogen is not detected in XPS.

Much of our screening work on impregnated coals was limited to Fe addition levels of 0.77 wt% on dry coal (Table 2-6), which is equivalent to iron oxide addition levels of slightly more than 1 wt %, which was set as a target level based upon economic considerations. The surface Fe concentrations on all the sulfate-impregnated coals were less than the corresponding 0.77 wt % nitrate-impregnated coal. Treatment with base or impregnating with either Fe(II) or Fe(III) salts appeared to have no effect on surface concentration of Fe. In fact, the Fe concentration on the surface of a coal impregnated with ferric sulfate to a 2.0 wt % added Fe level was only marginally higher than a coal impregnated with ferric nitrate to a 1.0 wt % added Fe

concentration (see Figure 2-2). In both cases the sulfate ion had been removed in the base-treatment step. It appears, then, that the sulfate salts penetrate into the coal particle more easily than the corresponding nitrate salts resulting in lower surface Fe concentrations. In both cases, higher impregnation does not impair the effectiveness of removing the sulfate during the base treatment step and depositing the Fe within the interstitial structure of the coal as FeOOH.

Molybdenum surface concentrations for base-treated coals impregnated with 500 and 1000 ppmw Mo, and containing 0.77 wt% added Fe, were 1100 and 1400 ppmw, respectively. By comparison, two samples of non-base washed coals, to which 1000 ppmw Mo had been added, had Mo surface concentrations of 3000 and 5100 ppmw. This suggests that base treatment may have resolubilized some of the molybdenum salt added in the first step, although the amount was not quantified. Overall, the surface Fe concentrations on the Mo-impregnated coals were intermediate between the Mo-free sulfate-impregnated coals, which were lower, and the nitrate Mo-free coals, which were higher, as shown in Figure 2-2. In all cases, the surface concentrations were greater than the corresponding bulk concentrations, which was somewhat less than the level to which Mo was added to the samples, indicating that Mo did not distribute uniformly within the particles.

Sulfur concentrations on the surface of the base-treated coals were $< 0.6\%$, which is in the range observed for the starting coal. For the sulfate-impregnated coals, which had not been base treated, the sulfur concentrations on the surface were > 1.1 wt%. Both the bulk and surface oxygen concentrations for the Fe-impregnated coals were higher than for the starting coal. For all of these 0.77 wt% Fe-impregnated samples, the surface oxygen levels fell within a rather narrow range well above the level of the starting coal. This indicates that oxygen concentration is strongly influenced by the surface iron concentration although only 3% of oxygen in the coal can be associated with the added Fe. Impregnation did not change the surface concentrations of Al and Si, both of which remained higher than the bulk concentrations in the parent coal (see Table 2-5). There also didn't appear to be any significant differences in the surface concentrations of coals impregnated with Fe(II) or Fe(III)-salts, even though the instability of the ferrous salt solution was obvious during preparation. The original blue-green color of the

Table 2-6. Surface Concentrations of Impregnated Samples

Sample No.	Salt[a]	Base Treated[b]	Drying[c]	Added Fe	Bulk Fe[d]	Surface Concentrations, wt%								
						Fe	Mo	C	O	N	Ca	Al	Si	S
AR Coal[e]	none	N	Vac	0	0.20	0.33		71.1	20.6	1.3	0.5	2.0	4.0	0.2
CH-10	FN	Y	Vac	0.15	0.36	1.0		62.3	25.5	1.4	1.0	3.4	3.5	n.a.[f]
CH-11	FN	Y	Vac	0.28	0.49	1.4		66.2	23.5	1.7	1.0	2.4	3.5	0.3
CH-20	FN	Y	Vac	0.55	0.77	2.4		63.5	25.2	1.5	1.0	2.9	3.3	0.2
CH-31	FN	Y	Vac	0.77	1.0	4.2		62.4	24.8	1.2	1.0	2.5	3.3	0.6
CH-41	FN	Y	Vac	1.0	1.23	6.3		59.6	24.4	1.6	1.0	3.8	3.4	0.3
CH-51	Fe(III)	Y[g]	Vac	2.0	2.22	7.9		50.9	30.6	1.0	0.9	4.3	4.2	0.2
CH-53	Fe(III)	Y[g]	Vac	0.77	1.00	1.5		67.9	23.1	1.1	0.8	2.6	2.5	0.4
CH-503	Fe(III)	N	N2	0.77	1.00	1.6		63.3	23.2	1.0	1.2	3.4	4.3	1.9
CH-504	Fe(III)	N	Air	0.77	1.00	1.9		57.1	26.6	1.0	1.5	4.6	5.0	2.4
CH-52	Fe(II)	Y[g]	Vac	0.77	1.00	1.2		66.3	23.2	1.3	0.8	2.6	4.1	0.4
CH-502	Fe(II)	N	N2	0.77	1.00	1.9		57.1	26.6	1.0	1.5	4.6	5.0	2.4
CH-501	Fe(II)	N	Air	0.77	1.00	0.8		60.9	25.6	1.0	0.8	4.1	5.7	1.2
CH-6	FN-AM	Y	Vac	0.77	1.00	2.5	0.14	62.8	24.4	1.5	1.3	3.5	3.8	0.03
CH-61	FN-AM	Y	Vac	0.71	0.94	3.0	0.11	63.9	24.4	1.4	0.9	3.4	2.8	0.03
CH-604	Fe(III)-AM	N	Air	0.77	1.00	2.3	0.51	56.3	25.5	1.5	1.0	5.5	5.9	1.4
CH-601	Fe(II)-AM	N	Air	0.77	1.00	2.5	0.30	58.7	25.3	1.2	0.8	4.9	5.3	1.1

[a] FN = $Fe(NO_3)_3 \cdot 9H_2O$; Fe(III) = $Fe_2(SO_4)_3 \cdot 5H_2O$; Fe(II) = $FeSO_4 \cdot 7H_2O$; AM = Ammonium molybdate. [b] Y = Sample treated with 1.54 M NH_4OH. N = sample impregnated without washing. [c] Vac = 20 hrs at 40 °C/10 torr; N2 = Dried at 40 °C/1 atm/flowing N_2/20 hrs.; Air = 3 days at 40 °C/1 atm/flowing air. [d] Bulk analysis on SO_3-free ash, hydrogen-free, dry basis. [e] AR = as-received coal. [f] n.a., not available. [g] Sample washed with water following base treatment.

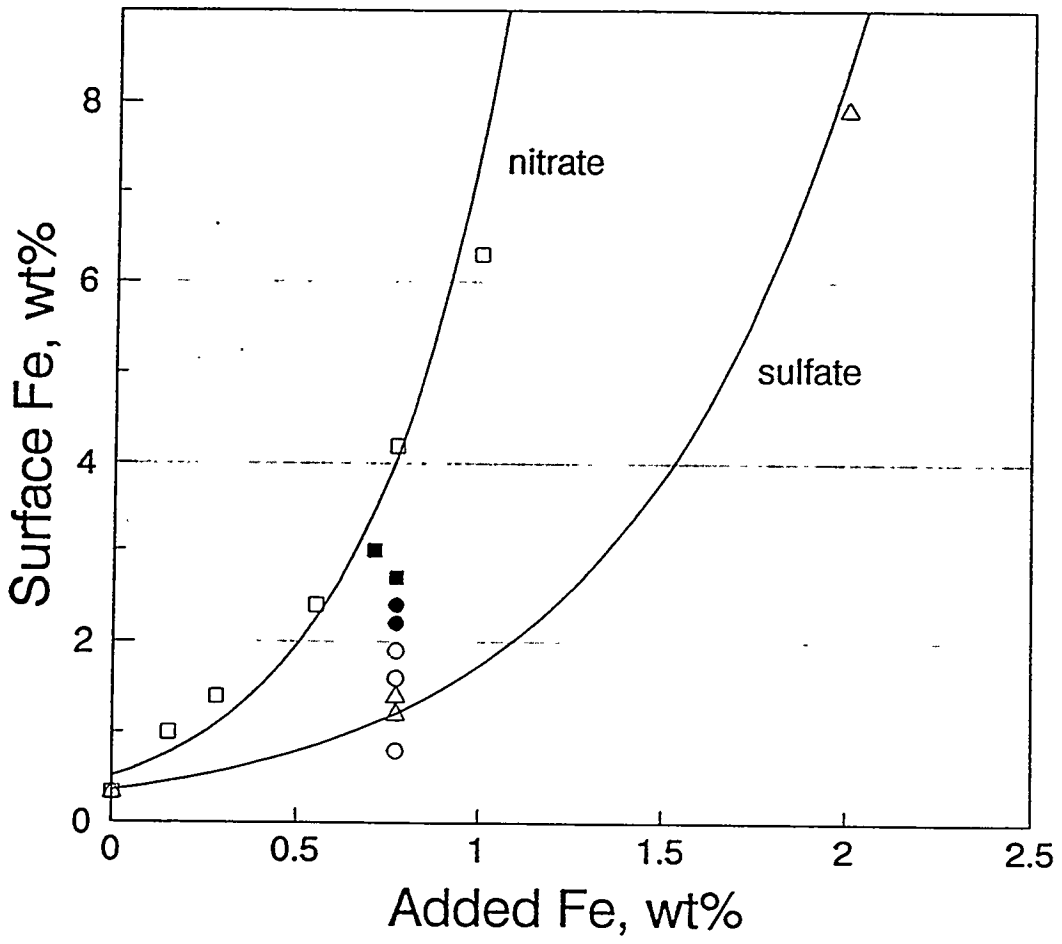


Figure 2-2. Concentration of Fe on the surface versus added Fe. (□ ferric nitrate, base treated; ■ ferric nitrate-Mo, base treated; Δ iron sulfate, base treated; ○ iron sulfate; ● iron sulfate-Mo)

$FeSO_4$ solution rapidly changed to yellow upon exposure to air during the application step and a slight deposit was found in the beaker.

A number of possible variations in the method of impregnating and drying these coals were found not to affect the concentration of the Fe on the surface. One of the variables that was evaluated was the effect of predrying the coal, which could possibly increase access to the interstitial pore structure by allowing greater penetration of the salt solution. XPS showed, however, that the Fe concentration on the surface of these predried coals actually increased by approximately 1 wt % indicating even less penetration by the nitrate salt during impregnation. Other variables that were evaluated were the effect of the quantity of base used in the base-treatment step, washing the coal after base treatment, the method of drying and level of moisture in the final samples. For the nitrate-impregnated coals, varying the amount of base used in the treatment step or washing the impregnated samples following base treatment had no effect on the XPS spectra. Also, varying the method of drying the impregnated samples prior to testing, whether under vacuum, in flowing nitrogen or in air, had no effect on surface concentrations.

Surface Bonding - Base treatment significantly influenced the chemical bonding of Fe, oxygen and sulfur on the surface of the impregnated coals, with distinct differences being found for the Fe_{2p} and Fe_{3p} peaks. In base-treated coals, the multiplet splitting of the Fe_{2p} peaks was consistently less than for the non-base-treated samples, as shown in Table 2-7. Similar splitting values and peak positions were observed for Fe_2O_3 and FeOOH.[20] However, the Fe_{3p} peak positions shifted to higher binding energies agree more closely with the FeOOH structure.

The larger Fe_{2p} splitting values for the non-base-treated, sulfate-impregnated coals indicate different bonding between the Fe and oxygen on the surface of these materials that may be related to the presence of sulfate ions on these materials. The oxidation state of the Fe in the impregnating salts had a small affect on the Fe peaks. The $Fe_{2p\,3/2}$ and Fe_{3p} peaks in the spectra for the non-base treated Fe(III)-impregnated coals appeared at the upper end of the ranges for known iron oxides, while the peaks for the corresponding Fe(II)-impregnated coals appeared at slightly lower energy levels.[30] Reference peaks are shown in Table 2-8. The peaks for both the

Table 2-7. Binding Energies (eV)[a]

Sample No.	Salt	Base Treated	Fe				O_{1s}	$Ca_{2p\ 3/2}$	S_{2p}	Mo_{3d}	
			$Fe_{2p\ 3/2}$	$Fe_{2p\ 1/2}$	Fe_{3p}	Δ^b				$Mo_{3d\ 5/2}$	$Mo_{3d\ 3/2}$
AR			709.3	722.3	52.3	13.0	532.7	347.2	-	-	-
CH-10	FN	Y	711.6	725.5	56.7	13.9	532.6	347.3	-	-	-
CH-11	FN	Y	711.5	725.2	56.7	13.7	532.4	347.5	-	-	-
CH-20	FN	Y	711.4	725.5	56.8	14.1	532.4	347.8	-	-	-
CH-31	FN	Y	711.1	725.1	56.6	14.0	531.7	346.2	-	-	-
CH-41	FN	Y	711.2	725.1	56.2	13.9	531.3	346.6	-	-	-
CH-51	Fe(III)	Y	711.3	725.1	56.6	13.8	531.7	n.a.	-	-	-
CH-53	Fe(III)	Y	711.5	725.6	56.2	14.1	532.4	347.2	-	-	-
CH-503	Fe(III)	N	710.9	725.9	55.9	15.0	532.9	349.8	171.3	-	-
CH-504	Fe(III)	N	711.4	726.6	56.4	15.2	532.7	350.1	171.5	-	-
CH-52	Fe(II)	Y	711.7	725.4	56.3	13.7	532.5	347.4	-	-	-
CH-502	Fe(II)	N	710.3	n.d.	55.6	n.d.	532.6	349.8	171.1	-	-
CH-501	Fe(II)	N	710.5	725.9	55.6	15.4	532.9	349.9	171.2	-	-
CH-6	FN-AM	Y	711.3	724.8	56.1	13.5	532.2	n.a.	-	232.4	235.9
CH-61	FN-AM	Y	711.3	725.1	56.0	13.8	532.0	347.5	-	232.5	235.6
CH-604	Fe(III)-AM	N	710.5	727.6	55.4	17.1	532.6	n.a.	170.9	232.3	235.4
CH-601	Fe(II)-AM	N	709.8	727.4	53.5	17.6	532.6	349.9	171.2	232.5	235.4

[a] For notations see **Table 2-6.** [b] $\Delta = Fe_{2p\ 1/2}-Fe_{2p\ 3/2}$

Fe(II) and Fe(III) Mo-containing non-base-treated-impregnated coals appear at slightly lower energy levels than the corresponding Mo-free coals. The $Fe_{2p\ 3/2}$ and Fe_{3p} peaks for ferric sulfate, which were found at 711.5 and 56.7 eV, respectively, are also found at the same positions in the spectra of the Fe(III)-impregnated coals. Although these same peaks agree with Fe oxyhydroxide, this structure would not likely form in any significant amount in the absence of added base. The slightly lower energy levels for the Fe(II)-impregnated coals is consistent with the observed lower position for Fe(II) sulfate versus the corresponding Fe(III) salt. This suggests the absence of any significant oxidation of Fe(II) on these samples during or after impregnation. Sputtering experiments failed to provide any additional information regarding the oxidation state of the iron in the bulk phase due to significant structural modifications that occurred as material was removed by the argon ion beam.

The addition of Fe to the coal tends to shift the position of the O_{1s} peak to lower energy. For the Mo-free nitrate-impregnated coals, the binding energies decreased linearly as the added Fe loadings increased, as shown in Figure 2-3. The peak positions in the spectra of the Mo-containing nitrate-impregnated coals were only slightly higher than predicted from this correlation. However, the sulfate-impregnated coals all depart quite significantly from this line. A better correlation is obtained by plotting O_{1s} peak positions against surface Fe concentrations, as shown in Figure 2-4. Only the non-base-treated impregnated coals depart significantly from this correlation with their O_{1s} peaks falling at higher energies than predicted from the correlation. This higher energy shift is probably related to the higher binding energy of the sulfate groups remaining on the surface of these samples. This relationship for the base-treated coals demonstrates that the added Fe not only influences the oxygen concentration, but also strongly influences the oxygen bonding. In the spectra of the starting coal, Fe appears to have little impact on the position of this peak since it is higher than any of the known iron-oxygen structures. The position of the O_{1s} peak is more influenced by the Al_2O_3 and SiO_2 structures, both of which have higher energy O_{1s} peaks.

Intense S_{2p} peaks observed in the spectra of non-base treated samples are related to the abundance of sulfate ions on the surface. In base-treated samples, these were broad peaks

Table 2-8. Reference Binding Energies

Compound	$Fe_{2p\ 3/2}$	Fe_{3p}	O_{1s}	S_{2p}	Other	Reference[a]
Fe	707.0					Wagner, 79
	706.7					Lebugle, 81
	706.8					Asam, 76
	707.0					McIntyre, 77
Fe_2O_3	710.9					Wagner, 79
	710.8		530.2			Nefedov, 75
			529.6			Limo, 80; Haber, 76
Fe_2O_3 (α)	710.9	55.7	529.6			McIntyre, 77
Fe_2O_3 (γ)	710.9	55.7	529.8			McIntyre, 77
	711.2					Allen, 74
FeO	709.4	54.9	529.8			McIntyre, 77
	710.3					Allen, 74
Fe_3O_4	708.2	53.9	530.0			McIntyre, 77
	710.4					Okui, 76
	711.2					Allen, 74
FeOOH (α)	711.8	56.6	530.3 531.4			McIntyre, 77
FeOOH (γ)	711.3					Konno, 80
	710.8					Allen, 74
$Fe_2(SO_4)_3$	711.5	56.6		170.6		Ni, this study
$FeSO_4$			532.0	169.4		Limouzin-Maire, 81
FeS_2	706.7			169.2		Binder, 73
$Fe_{1-x}S$	710.3 712.2			169.2		Carver, 72
Al_2O_3					Al_{2p} 74.7 eV	Wagner, 79
SiO_2					Si_{2p} 103.6 eV	Wagner, 79
CaO					$Ca_{2p\ 3/2}$ 346-347 eV	Wagner, 79
$CaSO_4$				170	$Ca_{2p\ 3/2}$ 347-348	Wagner, 79

a. See Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. "Handbook of X-ray Photoelectron Spectroscopy", Perkin-Elmer Corp., Eden Prairie, MN, 1992.

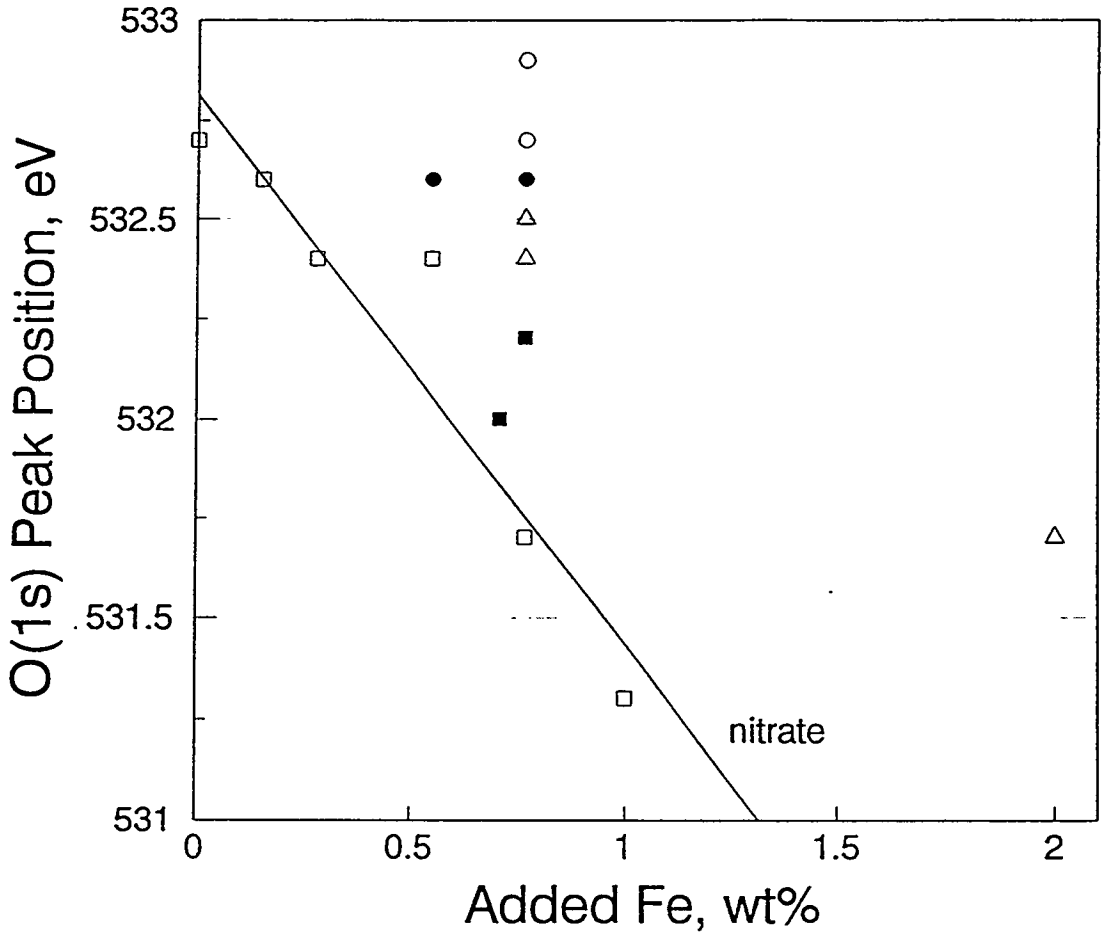


Figure 2-3. Position of O_{1s} peak as function of added Fe. (□ ferric nitrate, base treated; ■ ferric nitrate-Mo, base treated; Δ iron sulfate, base treated; ○ iron sulfate; ● iron sulfate-Mo)

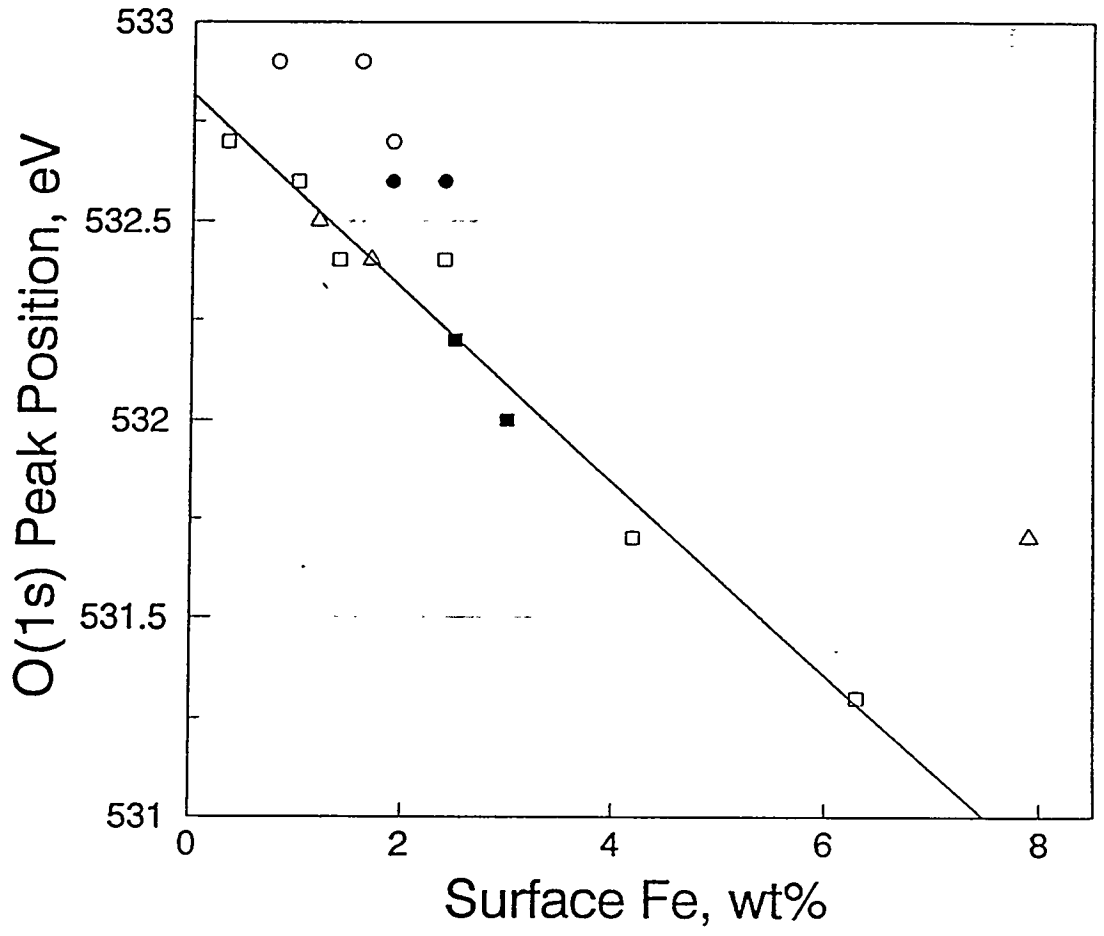


Figure 2-4. Position of O_{1s} peak as function of surface Fe concentration. (□ ferric nitrate, base treated; ■ ferric nitrate-Mo, base treated; Δ iron sulfate, base treated; ○ iron sulfate; ● iron sulfate-Mo)

having low intensity that appear to be related to the background mineral sulfur in the coal. $Ca_{2p\ 3/2}$ binding energies in non-base-treated impregnated coals indicates the presence of $CaSO_4$ while base-treated samples had binding energies which are consistent with Ca-O structures.

Molybdenum Analysis - Mo in the 500-1000 ppmw range approaches the detection limit of XPS making quantification and characterization difficult, even though the surface concentration is typically higher than the bulk concentration. This analysis is further complicated by the overlap of the S_{2s} peak which broadens the Mo_{3d} doublet making measurement especially troublesome in samples having low concentrations of Mo and high concentrations of sulfur. A peak subtraction method was used to resolve this problem.[14] Peak deconvolution was performed based upon the relative positions and intensities of the S_{2s} and S_{2p} peaks, as well as the positions of the two Mo_{3d} peaks in external standards. The external standards were Mo, Ni and W impregnated sulfated iron oxide samples having S_{2s} and S_{2p} peaks for $SO_4^=$ at 232.6 eV and 169.5 eV, respectively, with a S_{2s}/S_{2p} peak intensity ratio of 0.45-0.52. The averaged $Mo_{3d\ 5/2}$ and $Mo_{3d\ 3/2}$ peak positions at 232.3 and 235.4 eV, respectively, agree with the corresponding peaks for the Fe-Mo-impregnated coals (see Table 2-7). Mo concentrations were determined by subtracting the S_{2s} peak areas from the measured Mo_{3d} peak areas. This assumes the relative intensities and photoionization cross section of S_{2s} and S_{2p} of the standard samples and the impregnated coals are equivalent,[31] especially for similar sample compositions and instrument conditions. The measured S_{2s}/S_{2p} intensity ratios agree with the S_{2s}/S_{2p} photoionization cross section ratios reported by Siegbahn[32] and Scofield.[33] The spectra of the base-treated Mo-impregnated samples, which contained only the residual sulfur from the original coal, showed the fine structure of separated Mo_{3d} peaks. At these very low concentrations Mo had no effect on the oxygen O_{1s} peak.

Thickness of Surface Layer - An argon sputtering technique was used to explore the chemistry of the sub-surface of the metal impregnated coals. Argon sputtering at 3.5 kV, 10 mA and a pressure of 5×10^{-5} torr was performed for periods of up to 2 hrs. The sputtering rate was calibrated with standard Au and Cu films at these same sputtering conditions. Based on the composition of the impregnated coal samples, a sputtering rate of 15 angstroms/min was

presumed. The thickness of the layer that would be sputtered from the coal then would be 0.1 μm for 75 min and 0.2 mμ for 120 minutes. Generally, at these levels of intensity, sputtering for 1 minute will remove approximately 30 angstroms of surface. Several of the samples of Fe and Fe-Mo-impregnated coals were examined by this technique.

The element concentrations for ferric sulfate-impregnated coal (CH-504) was determined after 45 and 75 minute sputtering exposures (Table 2-9). The metals and carbon concentrations all increased with increased sputtering time. Oxygen, however, dropped quite dramatically from 26.6% to 8.2%, while sulfur decreased from 2.4% to 1.5%. With the drop in oxygen peak intensity, the relative position of the 533 eV peak did not shift, although other peaks began to appear at 524 and 540 eV, as shown in Table 2-10. Thus, the type of oxygen bonding did not appear to change. Likewise, for the iron, the peak at 710-711 eV also did not noticeably change, suggesting no significant change in the Fe bonding.

Sputtering of a Mo-Fe-impregnated coal sample CH-604 over a period of 2 hours showed an increase in iron concentration on the surface similar to the Mo-free sample as shown in Table 2−11. As previously noted, however, the iron concentration on the Fe-Mo sample was higher than the Fe-only sample. Unlike the Fe-only sample, the Mo-Fe sample showed a slight loss in Si, a somewhat greater loss in Al, and no significant change in Ca, versus sizable gains for all three in the Fe-only sample. The changes in oxygen and sulfur, however, were similar to the Fe-only sample dropping quite sharply. The oxygen went from 25.5% in the unsputtered sample to 12.2% after 120 minutes. The Mo concentration that was loaded at 1000 ppm started at 0.50 wt % on the surface in the unsputtered sample decreasing to 0.12 wt % after 120 minutes, suggesting that the deposition of the Mo was primarily on the outer most surface of the coal. The peak positions shown in Table 2-12 indicate that no significant change in the bonding occurred even after 120 minutes, unlike the Fe-only sample.

It appears, therefore, that at 0.2 mμ below the outer surface of the coal, the concentration of Fe is still quite high, while the Mo concentration drops off indicating that the Mo is located primarily in a thin layer of 0.02 μm thickness. Most of SO_4^{-2} ion is contained in the 0.2 μm

thick layer. The oxygen concentration drops below the bulk level of the coal which is a result of the Ar+ sputtering effect. During sputtering, the lighter elements are more easily removed. However, for some reason, the nitrogen does not seem to be overly affected by sputtering. With the removal of oxygen atoms, a change in the oxidation state on the surface of the coal likely occurs, which for iron appears as broadening toward lower energy. This results in a deconvoluted peak at 703-704 eV, which could be a lower oxidation state of Fe such as an FeO structure or free Fe.

Table 2-9 . Surface Composition of Sputtered Fe-impregnated Wyodak Coal, wt%

	Coal (dry)	0.77 wt% Fe^{+++} CH-504		
		Not Sputtered	Sputtered 45 min	Sputtered 75 min
Impregnating Salt	None	$Fe_2(SO_4)_3 \cdot 5H_2O$	$Fe_2(SO_4)_3 \cdot 5H_2O$	$Fe_2(SO_4)_3 \cdot 5H_2O$
Fe	0.33	1.89	2.14	2.26
Carbon	71.1	57.1	62.2	64.6
Oxygen	20.6	26.6	11.4	8.2
Nitrogen	1.3	1.0	1.3	1.6
Silicon	4.0	5.0	6.8	6.8
Aluminum	2.0	4.6	5.0	5.1
Calcium	0.5	1.5	9.1	10.1
Sulfur	0.2	2.39	2.09	1.52

Conclusions from XPS Study - The Fe concentration on the surface of coals impregnated with ferric nitrate was higher than for coals impregnated with either ferric or ferrous sulfate, while the concentration on the Fe-Mo co-impregnated coals were intermediate between the two groups. Ammonium hydroxide treatment of these impregnated coals converted the Fe on the surface to FeOOH but had no impact on the relative surface concentration of the Fe. During base treatment the anion of the impregnating salt, whether sulfate or nitrate, was removed in the basic filtrate and the position and splitting of the Fe_{2p} peaks along with the position of the Fe_{3p} peaks confirmed the presence of FeOOH. The sulfur concentration on the surface of non-base treated

Table 2-10. Binding Energies for Fe-Impregnated Coal CH-504			
	Unsputtered	Sputtered 45 min†	Sputtered 75 min†
$Fe_{2p\ 3/2}$	710.9 711.4 711.9	710.6 703.4	710.2 704.2
$Fe_{2p\ 1/2}$	726.6	724.7 716.8	725.5 717.7
Fe_{3p}	56.4	56.6	56.9
O_{1s} eV	532.7	533.1 523.9 539.5	532.8 524.3 540.0
N_{1s} eV	400.7	399.3	400.9
Si_{2p} eV	104.1	104.1	103.8
Al_{2p} eV	75.4	72.1	72.7
$Ca_{2p\ 3/2}$	350.1	345.9	346.9
$Ca_{2p\ 1/2}$	353.9		
S_{2p} eV	163.6 171.5 185.6	164 171	171.3 164
*CH-501 Fe_{3s}=93.8 and 96.0 eV †Sp60m = Sample Ar sputtered 60 min.			

Table 2-11. Surface Composition of sputtered Fe-Mo-impregnated Wyodak Coal, wt%					
	0.77 wt% Fe^{+++} CH-604				
	Unsputtered	Sputtered 15 min	Sputtered 30 min	Sputtered 60 min	Sputtered 120 min
Salt	$Fe_2(SO_4)_3 \cdot 5H_2O$	$Fe_2(SO_4)_3 \cdot 5H_2O$	$Fe_2(SO_4)_3 \cdot 5H_2O$	$Fe_2(SO_4)_3 \cdot 5H_2O$	$Fe_2(SO_4)_3 \cdot 5H_2O$
Fe	2.34	2.8	3.0	3.4	3.6
Mo	0.51	0.20	0.12	0.12	0.12
Carbon	56.3	64.3	66.9	68.7	71.1
Oxygen	25.5	17.6	15.0	14.4	12.2
Nitrogen	1.5	1.4	1.6	1.4	1.4
Silicon	5.9	6.2	5.9	5.5	5.5
Aluminum	5.5	5.3	5.1	4.6	4.1
Calcium	1.0	1.1	1.2	0.9	1.1
Sulfur	1.4	1.3	1.2	1.1	0.9

Table 2-12. Binding Energies for Fe-Mo Impregnated Coals

	Fe eV			C_{1s}eV	O_{1s} eV	N_{1s} eV	Si_{2p} eV	Al_{2p} eV	Ca_{2p} eV		S_{2p} eV	Mo_{3d} eV	
	$Fe_{2p\ 3/2}$	$Fe_{2p\ 1/2}$	Fe_{3p}						$Ca_{2p\ 3/2}$	$Ca_{2p\ 1/2}$		$Mo_{3d\ 5/2}$	$Mo_{3d\ 3/2}$
CH-604	710.5	727.6	55.4	299.0- 14.4	532.6	399.5 394.1	104.1	73.7			163.0 170.9	232.3	235.4
CH-604 Sp15m†	710.2	728.4	55.4	298.2- 13.6	533	399.8	103.7	74.6	349.9	353.4	163.0 171.3	233.0	235.9
CH-604 Sp30m†	710.8 715.6	727.3 729.1	56.6	297.9- 13.3	533.3	400.1	104.0	74.9	350.7	354.4	163.0 171.8	234.9	237.4
CH-604 Sp60m†	710.8 715.0	724.0 729.7	56.4	297.9- 13.3	532.8	398.3 394.7	104.0	74.9	350.7	353.1	163.2 172.1	235.9	237.7
CH-604 Sp120m†	710.6	729.8	56.3	297.5- 12.9	533.1	399.4	104.3	75.4	350.7	353.3	163.5 171.1	234.3	236.1

†Sp60m = Sample Ar sputtered 60 min.

sulfate-impregnated coals was significantly higher than for the base treated coals indicating deposition of the sulfate ion. The splitting of the Fe_{2p} peaks and the position of the $Fe_{2p\ 3/2}$ and Fe_{3p} peaks confirmed the presence of iron sulfates. These results support greater penetration of the sulfates into the coal particle relative to the nitrate salts. Mo was present on the surface as MoO_3 and its concentration was higher than in the bulk. Oxygen concentrations on the surface were strongly influence by the presence of Fe being significantly greater than for the as-received coal and always exceeding the bulk concentration.

Liquefaction Performance

A screening test was used to evaluate the effect of the variables involved in the preparation method on the liquefaction of the impregnated coals. The tests were run at 415 °C in tetralin at a solvent to coal weight ratio of 1.8 to 1 for 60 min with an initial hydrogen pressure of 1000 psig. These experiments were performed following our standard method in 50 ml microautoclaves to which were added coal, tetralin, and dimethyl disulfide (1.2 mol/mole added Fe). In these runs the condensed products were analyzed by solvent separation in which they were separated into THF insoluble, THF soluble-pentane insoluble (PA+A), and pentane soluble (oils+water) fractions. The product distributions were calculated on a SO_3-free ash basis assuming complete recovery of ash and conversion of catalyst to pyrrhotite ($Fe_{0.9}S$). The logic for applying this correction to low rank coals is discussed elsewhere.[34,35,36] The total of the net products equals the amount of moisture and ash-free coal in the feed and reflects the net make of each of the solubility fractions; coal conversion equals 100 minus the yield of IOM. In calculating the product distribution from liquefaction of the sulfate-impregnated coals that had not been treated with base, a stoichiometric amount of sulfate equivalent to that added during the impregnation step was assumed to form H_2S and water.[37] This subject is treated below.

Coal that had been dried to a moisture level of 2 wt % had a 2% lower THF conversion and 4% lower oil yield than as-received coal with 21 wt % moisture (see Table 2-13). Surprisingly, drying of the Fe-nitrate impregnated coals seemed to have no affect on their liquefaction performance. The liquefaction results were similar for impregnated samples that were prepared from either predried or as-received coals. All of these coals, whether they were predried or not,

were final dried to less than 10% remaining moisture. Similar reduction in oil yields upon drying of Wyodak coals had previously been observed.[38] However, why the impregnated samples behaved differently is unknown.

Other variables in the method of preparation that were found to have little affect on liquefaction includes the quantity of base used in the base-treatment step, washing of the coal after base treatment, and the method of drying the final samples. Either varying the amount of base solution used in the treatment up to an ammonium ion to Fe ratio of 138 or washing the impregnated samples following base treatment had no effect on liquefaction results. Also, varying the method of drying the impregnated samples prior to testing, whether under vacuum, in flowing nitrogen, or in air, did not affect the liquefaction results.

Addition of Fe, however, affected both oil yield and THF conversion, as shown in Table 2-13. The THF conversion increased steadily from 82%, observed for the non-impregnated coal that had been dried to a similar low moisture level, to 88 to 90% observed for coals with 0.77 to 1.0 wt% added-Fe, as shown in Figure 2-5. Three of the four Fe-Mo-impregnated samples gave higher conversion than the corresponding 0.77 wt% Fe-impregnated samples indicating a positive influence of the presence of Mo.

The oil yield increased steadily over this range from 39 wt% for the dried non-impregnated sample to 46 to 49 wt% for the 0.77 to 1 wt % added Fe samples, as shown in Figure 2-6. Co-impregnation of 500 to 1000 ppmw Mo gave the highest oil yields. There appears to be no particular preference of the sulfate over the nitrate samples, other than one of the sulfate Fe-only samples (sample 16, Table 2-14) approached the Fe-Mo samples in performance. However, the scatter of the Fe-only samples shows that the average performance of these sulfate preparations fall about 3 wt % lower. The results with the base treated Mo-Fe-impregnated samples suggest that most of the Mo had remained on the coal and was not removed during base treatment.

From these results, the key parameters in the preparation of these coals that influences the resulting liquefaction performance is the concentration of Fe and the presence of Mo. Treatment

Table 2-13. Effect of Fe Concentration on Liquefaction of Fe-Impregnated Coal[a]									
Sample No.	AR Coal	Dried AR Coal	3	4	5	6	13	14	1
Added Fe, wt% dry coal	0	0	0.15	0.28	0.55	0.77	0.77	0.71	1.0
Added Mo, ppmw dry coal							1000	500	
Final moisture in coal	21	2	1	2	nil	1	1	1	4
Products, wt% maf coal									
HC Gases	1	1	1	1	1	1	1	1	1
CO_2+CO	5	4	5	4	4	4	4	4	4
Oils	43	39	39	43	44	44	50	50	46
PA + A	35	38	37	37	37	38	32	35	37
IOM	16	18	18	15	14	13	13	10	12
THF Conv	84	82	82	85	86	87	87	90	88
mg H_2 Consumed/g maf coal	30[b]	20	19	29	30	32	32	33	35

a. For notation see Table 2-6. [b] Corresponds to 23 wt% conversion of total H_2 in feed and 8.4 mg H_2 consumed/g total maf feed.

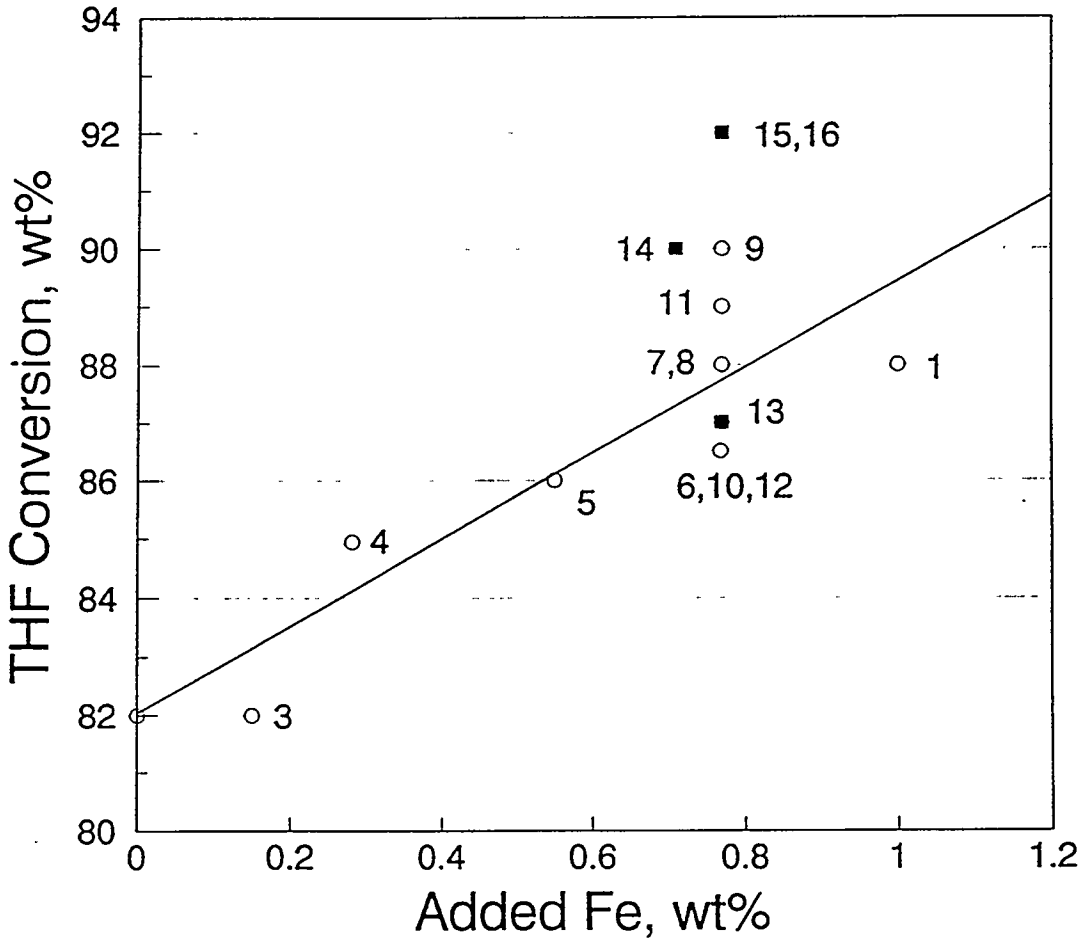


Figure 2-5. THF conversion of impregnated coals. (Sample Number; ○ Fe-samples; ■ Fe-Mo-samples)

with base to form FeOOH apparently had no affect on promoting better conversions or higher oil yields. Also, the Fe(II) and Fe(III) impregnated coals gave the same liquefaction results indicating the oxidation state of the iron in the impregnating salt does not appear to influence liquefaction. Since satisfactory yields were obtained from both nitrate and sulfate-impregnated coals, sulfate remaining on the coal after impregnation is not detrimental to either the liquefaction of the coal or the catalytic action of the metal. Also the greater penetration of Fe into the bulk coal by the sulfate salts during impregnation does not appear to provide an advantage in liquefaction. Since added Mo improved coal conversions and oil yields for these coals, its catalytic action is independent of the form of the Fe in the starting coal.

Mossbauer analysis of the residue from a 15 minute liquefaction run of IW Fe impregnated coal indicates that the 60-70% of the Fe was present as super-paramagnetic oxide/oxyhydroxide and 30-40% pyrrhotite. The size of the residual oxide/oxyhydroxide suggests that the iron is dispersed as very small particles on the surface of the coal. The dominant factor thus far appears to be the concentration of Fe on the coal.

Fate of Impregnated Sulfate During Liquefaction

It has been assumed that sulfate ion remaining on the coal after impregnation would decompose in H_2 to H_2S and water while the final form of the Fe in the residual product was assumed to form pyrrhotite in the presence of the excess of sulfur. Recently Artok et al.,[39] reported the decomposition of ferrous sulfate after 1 hour at 425 °C in H_2, as well as in H_2 containing 5% H_2S. The product obtained in H_2 was determined to be a mixture of troilite and pyrrhotite while the product obtained in a mixture of H_2 and H_2S was entirely pyrrhotite. The decomposition of $FeSO_4 \cdot 7H_2O$ in a mixture of 1.5% H_2S, 48.5% H_2 and 50% He was studied by TGA. Although both the H_2S and H_2 partial pressures in the TGA were less than exist in a liquefaction reactor, this data provides an indication of the fate of sulfate under these conditions. Measurements were made with a Seiko TG/DTA320, coupled to a VG Micromass quadrapole mass spectrometer via a heated, fused silica capillary transfer line. Ferrous sulfate was treated in a 1:1 mixture of H_2 and He, as well as with helium alone. In these studies, 50 mg samples were used at a gas flow rate of 200 ml/ min. The samples were first treated at 120 °C after which the temperature was

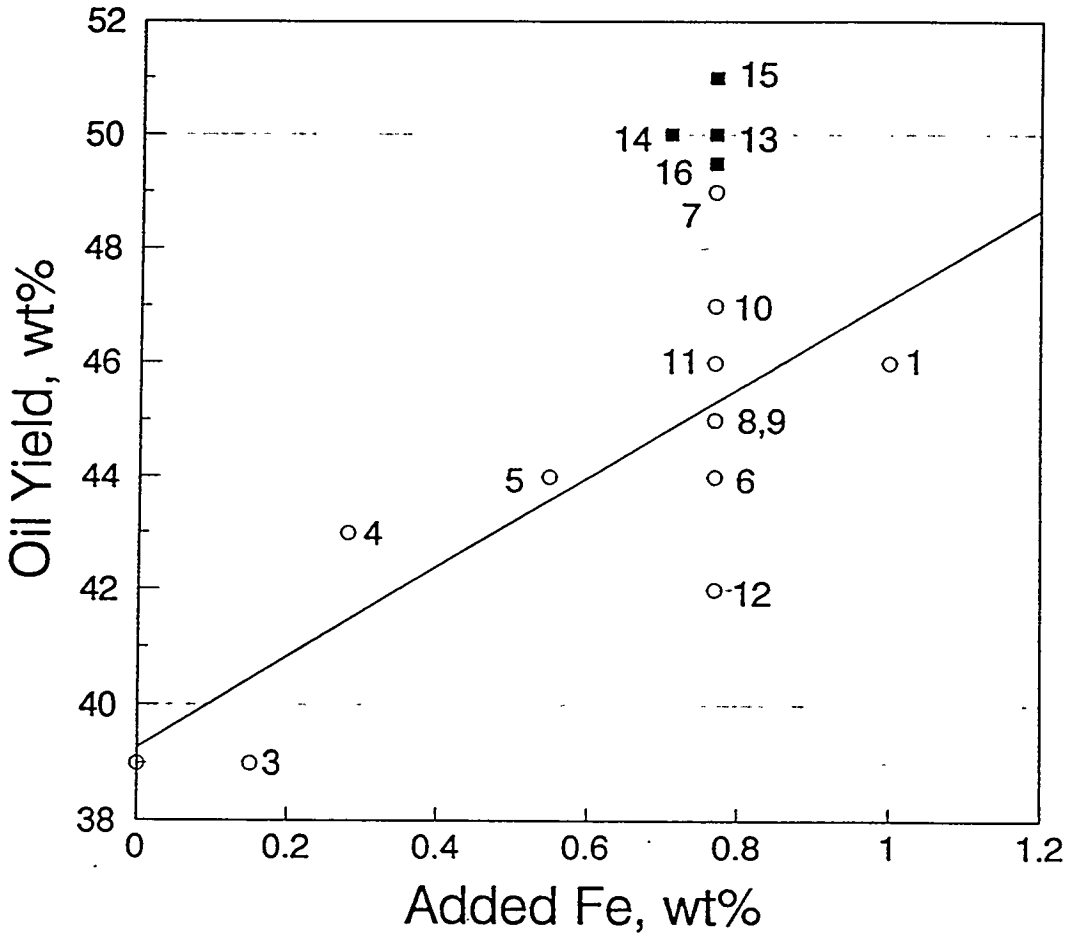


Figure 2-6. Oil yield of impregnated coals. (Sample Number; O Fe-samples; ■ Fe-Mo-samples)

Table 2-14. Liquefaction of Sulfate Impregnated Coals Containing 0.77 wt% Added-Fe [a]								
Sample No.	7	8	9	15	10	11	12	16
Impregnating Fe Salt	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(II)	Fe(II)	Fe(II)	Fe(II)
Mo Added, ppmw dry coal	0	0	0	1000	0	0	0	1000
Treated with NH_4OH	Y	N	N	N	Y	N	N	N
Drying	Vac	N2	Air	Air	Vac	N2	Air	Air
Moisture, wt%	nil	6.2	7.0	9.7	nil	7.3	7.6	7.6
Products, wt% maf coal								
HC Gases	1	1	2	1	1	1	1	1
CO2+CO	4	6	7	5	4	6	6	6
Oils	49	45	45	51	47	46	42	49
PA + A	34	36	36	35	35	36	38	36
IOM	12	12	10	8	13	11	13	8
THF Conv	88	88	90	92	87	89	87	92
mg H2/g maf coal	29	31	39	31	28	24	25	31
[a] For notations see Table 2-6.								

increased at a uniform rate to 900 °C.

The TGA pattern in flowing He along with the mass spec analysis of the effluent gas stream is shown in Figure 2-7. The thermal scan indicates a two-step loss of water, the second being complete at 270 °C. Since the weight loss was only 33% versus a theoretical value of 45% for the decahydrate, presumably some of the water chemically combines with the substrate during the thermal treatment. A major transition occurred between 540 °C and 660 °C that was associated with the evolution of SO_2. A blip in the H_2S plot indicates its presence in the effluent gas. During this transition no water was observed. The absence of any further weight change in the product up to 900 °C is consistent with hematite, which was reported by Artok et al.[39]

The thermal decomposition of ferrous sulfate in a H_2 and He gas mixture is shown in Figure 2−8. The loss of water is essentially the same as in He alone being complete at 270 °C. The next transition occurred between 480 °C and 530 °C and is associated with evolution of SO_2, water and H_2S. In the presence of hydrogen, this transition starts at a lower temperature than in He alone and occurs over a more narrow temperature window. Unlike in He alone, water is evolved in the presence of H_2 at this higher temperature. A subsequent slower transition then appears to occur starting at approximately 600 °C. This appears related to reduction of the sample to elemental Fe, as suggested by the final weight of 23%, versus 20 wt% Fe in the original ferrous sulfate sample. Since H_2S was being evolved during this latter transition, this suggests that Fe mono-sulfides are the products from the initial reduction of the ferrous sulfate in H_2 that occurs between 480 °C and 530 °C, as reported by Artok et al.[39]

The thermal behavior of ferrous sulfate in 1.5% H_2S in 50:50 H_2/He is shown in Figure 2-9. The loss in weight due to removal of H_2O, which ends at a slightly higher temperature than in the previous two cases, i.e., 300 °C, is equivalent to essentially all of the hydration water. The next transition that begins at ~380 °C occurs at a lower temperature than for the above two cases. The mass spec shows evolution of SO_2 and water; H_2S is obscured by its high concentration in the flowing gas. This transition terminates below 500 °C, and well below the temperatures required for evolution of sulfur species in the previous experiments. The lineout

of the baseline above this temperature indicates the absence of any further transitions. The final weight is consistent with troilite or pyrrhotite being the final phase as identified by Artok et al.[39]

The transitions for each of these cases above 200 °C are shown in Figure 2-10. The transitions in H_2 occurs at a lower temperature than in an inert gas while H_2S further decreases this temperature. In contrast to the results of Artok et al., the decomposition of anhydrous ferrous sulfate actually commences at a much lower temperature than 425 °C when H_2S is present, suggesting that in our microautoclave liquefaction runs that decomposition of the ferrous sulfate giving pyrrhotite is a valid assumption.

Assuming that the sulfate is removed from coals that were impregnated with ferrous sulfate, both coal conversion and oil or 1050 °F$^-$ distillate yields are reduced by about 2.1%. When the anion was assumed to remain unaltered on the coal residue, the Fe portion of the salt was assumed to combine with hydrogen sulfide producing a product having the stoichiometry of $Fe_{0.9}S$. Sulfur was derived from the added dimethyldisulfide. In this case, for a known weight of THF insoluble residue from a liquefaction run, the weights of SO_3-free coal ash, SO_3-free process recycle oil ash, process recycle oil IOM, pyrrhotite, and sulfate were subtracted from the THF insolubles to determine the IOM attributable to coal, and thus the coal conversion.

When sulfate is assumed to decompose and not be present in the THF insoluble residue, a higher weight of IOM attributable to coal is calculated. Both coal conversion and oil or distillate yield decreases accordingly. Table 2-15 shows an example of the liquefaction yield that was calculated based upon including sulfate in the IOM and assuming it was removed. This example is for liquefaction of an IW-1 coal preparation in solvent from R-258K V-131B. As shown in the table, the coal conversion decreases by 2.1% and resid conversion decreases by 1% when sulfate was assumed to be removed during liquefaction.

Conclusions - Liquefaction for Fe-Mo co-impregnated coals was greater than for Fe-only impregnated coals. Both the nitrate and sulfate-impregnated coals performed similarly with coal conversion and oil yield being related to the concentration of added Fe but unaffected by the form of Fe on the surface of the starting impregnated coal.

Figure 2-7

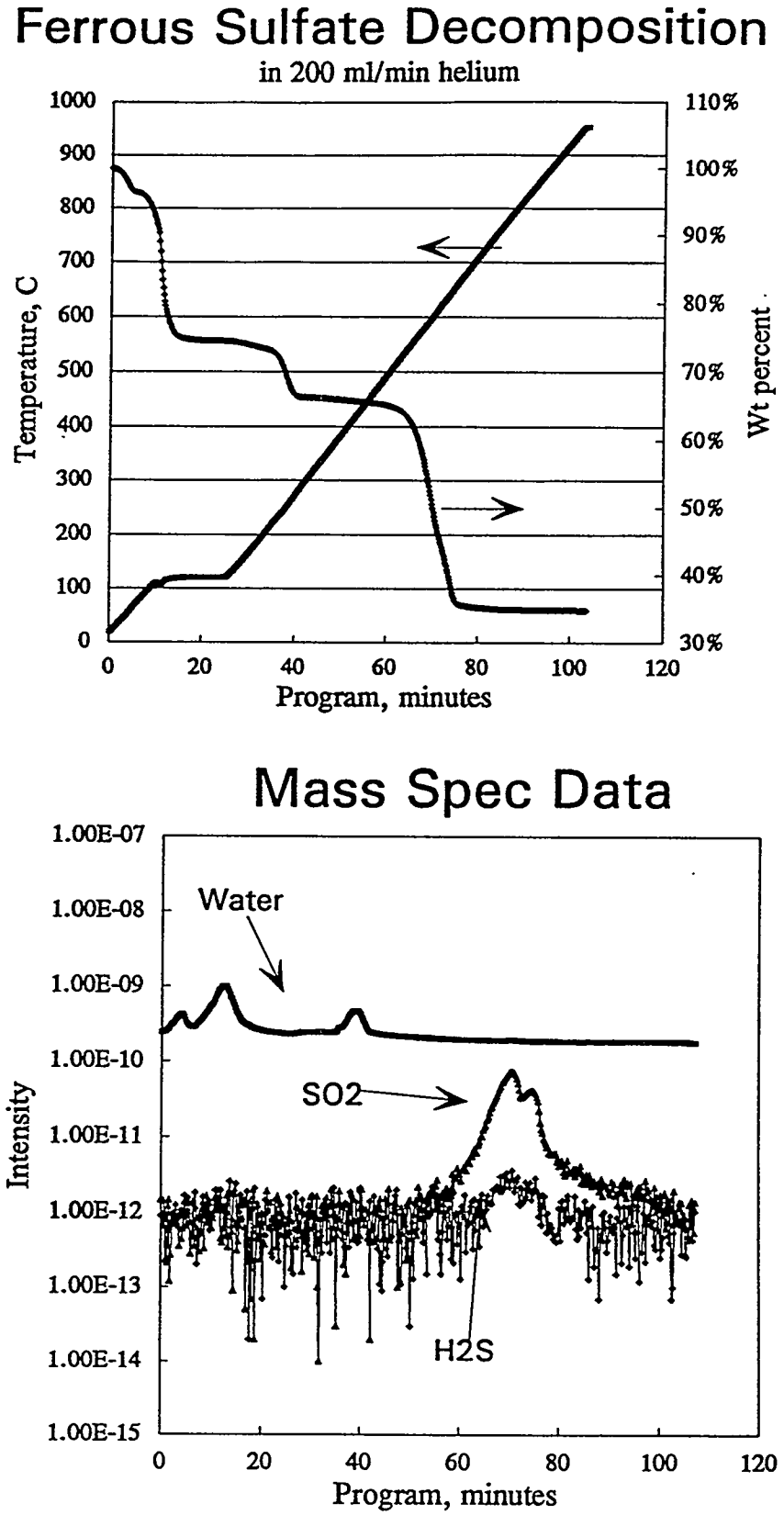
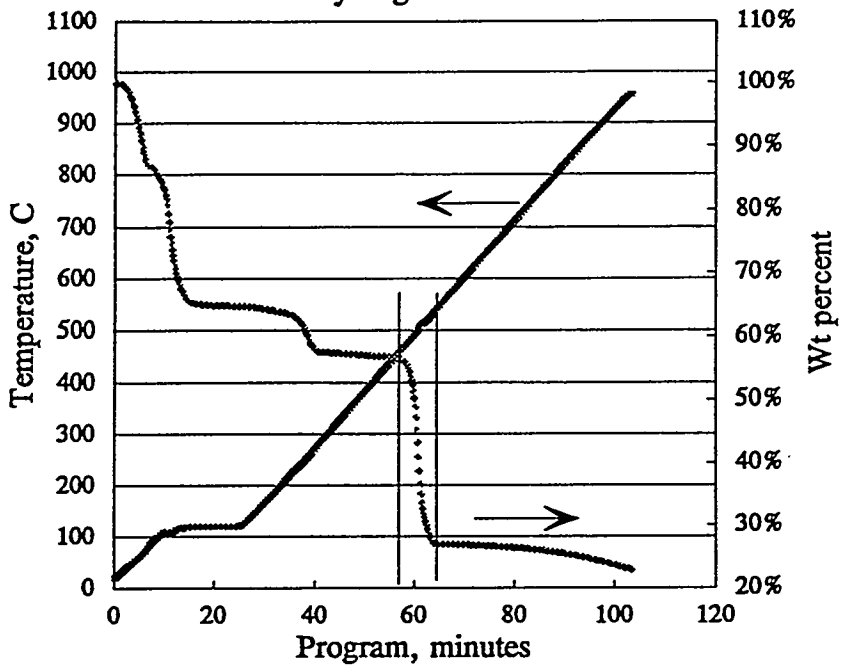

Ferrous Sulfate Decomposition
in 200 ml/min helium
Temperature, C
Wt percent
Program, minutes
Mass Spec Data
Water
SO2
H2S
Intensity
Program, minutes

Figure 2-8

Ferrous Sulfate Decomposition

in 50% hydrogen/ 50% helium



200 ml/ min total gas flow

Mass Spec Data

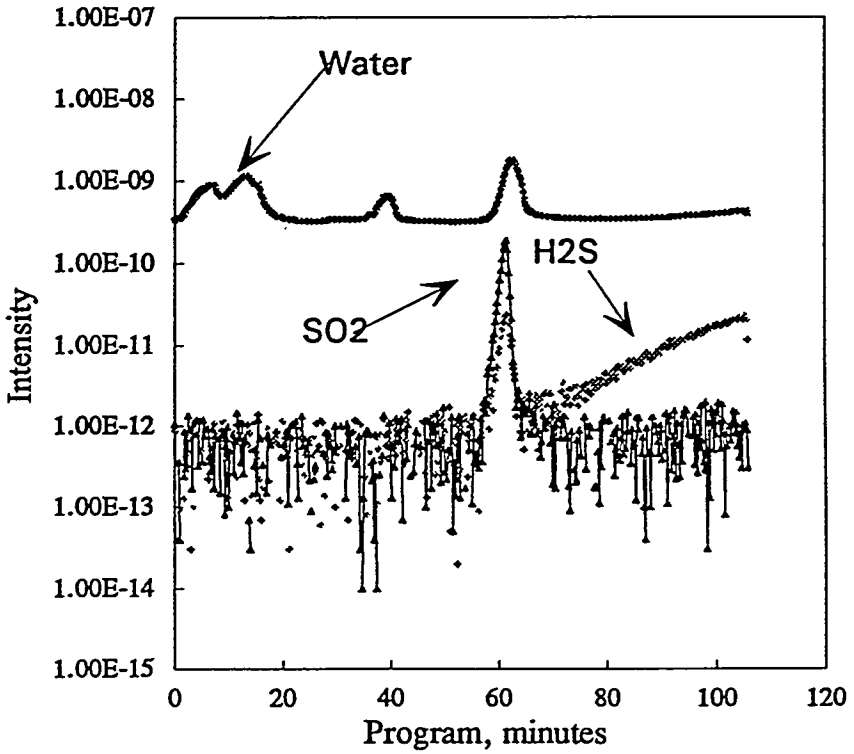
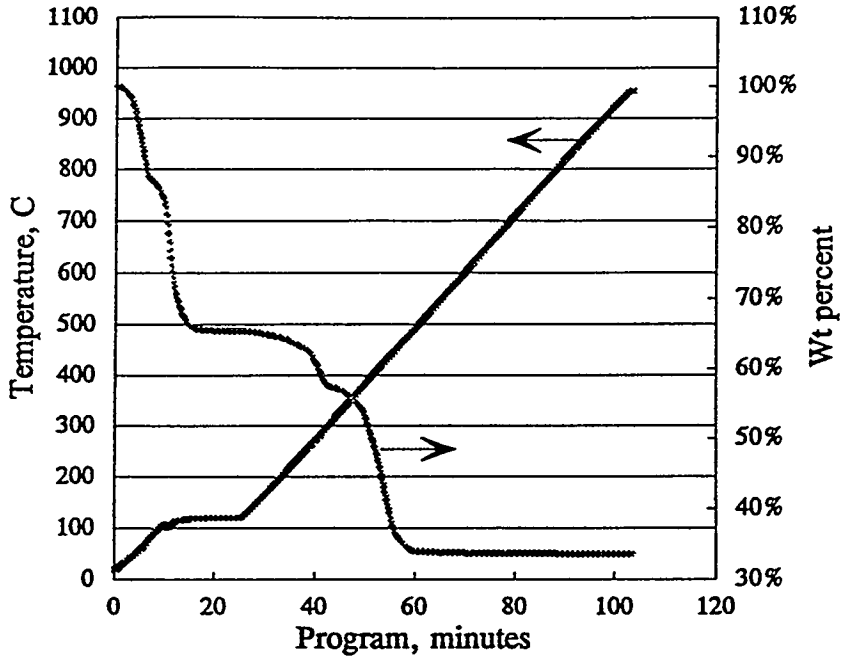


Figure 2-9

Ferrous Sulfate Decomposition

in 1.5%H2S/ 48.5% H2/ 50% He



200 ml/ min total gas flow

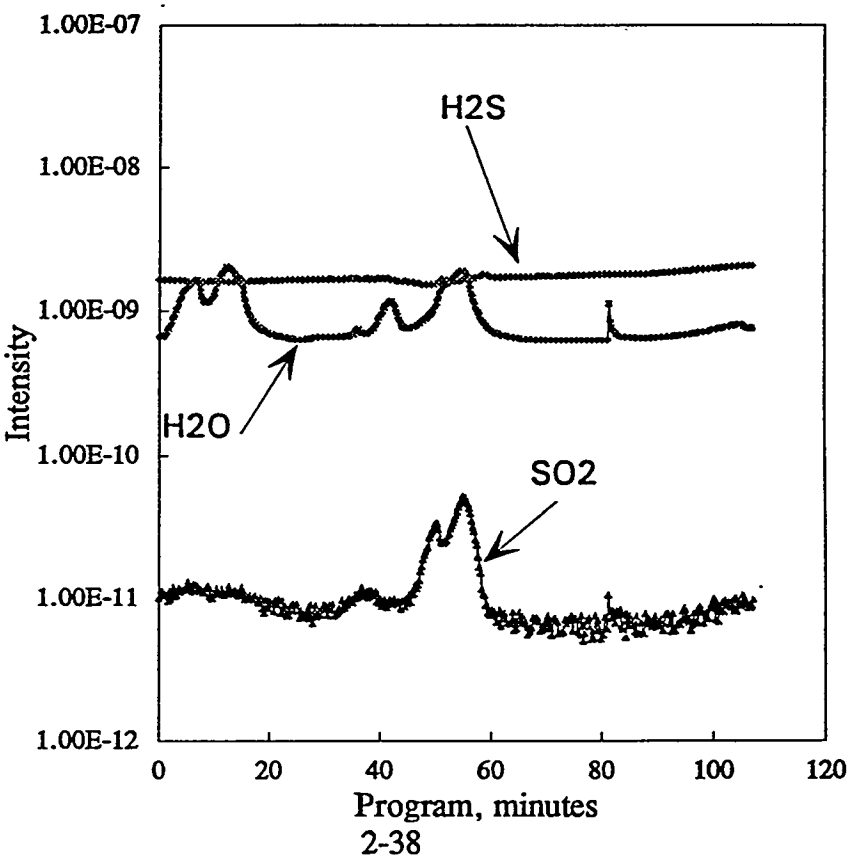


Figure 2-10

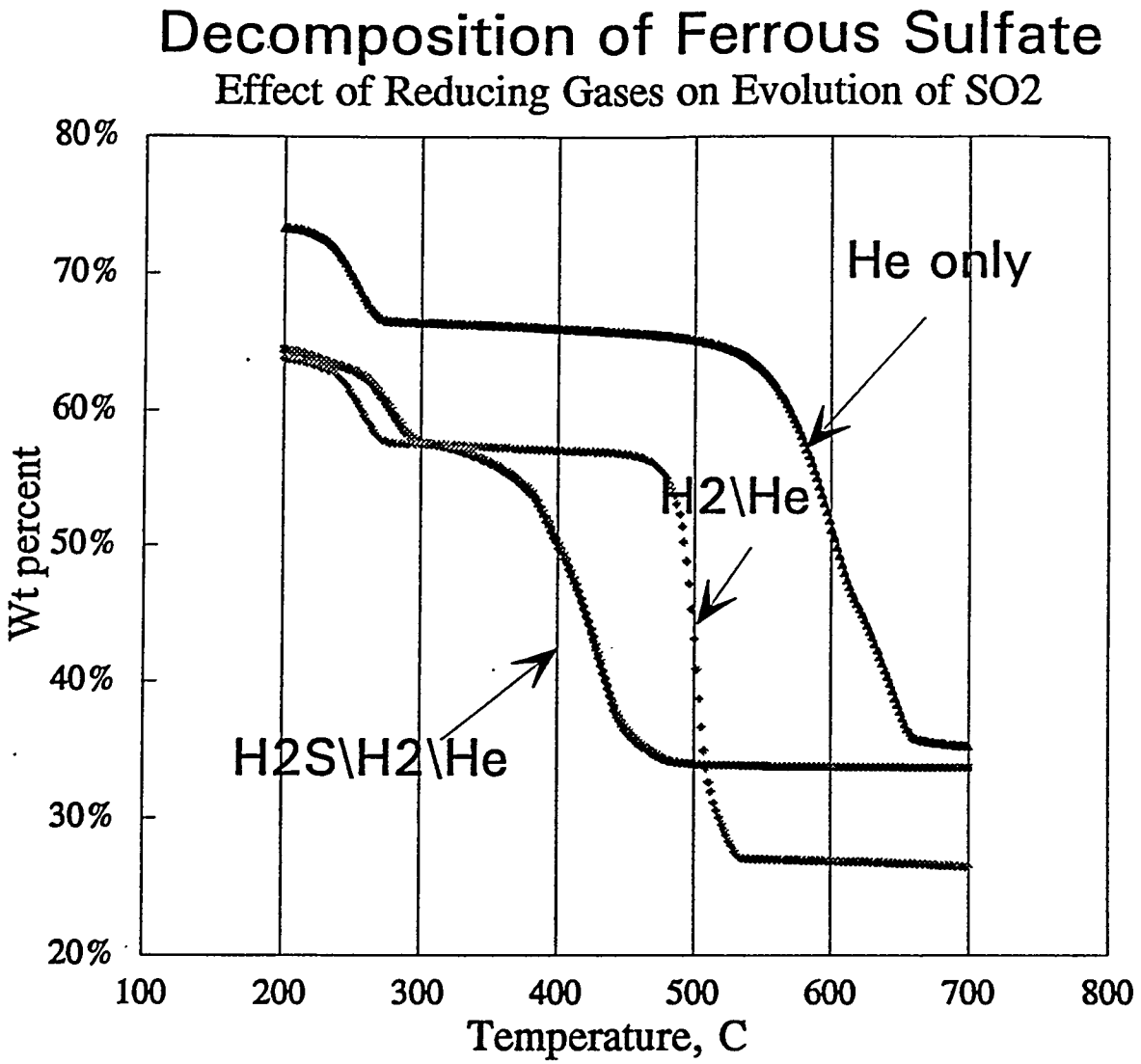

Decomposition of Ferrous Sulfate
Effect of Reducing Gases on Evolution of SO2
80%
70%
60%
50%
40%
30%
20%
Wt percent
He only
H2\He
H2S\H2\He
100
200
300
400
500
600
700
800
Temperature, C

Table 2-15. Effect of Sulfate Treatment on Conversion Calculations.[a]			
	SO_4^{-2} in ash	SO_4^{-2} free ash	Δ
maf Coal charge, g	2.6143	2.6143	-
THF insol liquefaction residue, g	1.4317	1.4317	-
less coal ash, g	-0.1533	-0.1533	-
less V-131B ash, g	-0.4467	-0.4467	-
less V-131B IOM, g	-0.8308	-0.8308	-
less final Fe weight (as $Fe_{0.9}S$), g	-0.0349	-0.0349	-
less sulfate added with Fe, g	-0.0550	-0-	0.0550
less inerts in ferric sulfate salt, g	-0.0029	-0.0029	-
less final Mo weight (as MoS_2), g	-0.0023	-0.0023	-
Net coal IOM, g	-0.0942	-0.0392	0.0550
Coal conversion, wt% maf coal	103.6	101.5	-2.1
1050 °F⁻ distillate, wt% maf coal	40.4	38.3	-2.1
Resid conversion, % maf resid	25.4	24.4	-1.0
a. Based on run number 4039-4, which used 3.0007 g salt impregnated coal feed (IW-1), with 5.4877 g R-258K V-131B process recycle oil. Metal loadings were 0.77 wt% Fe and 500 ppmw Mo (mf coal basis).			

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Chapter 3

Catalyst Impregnated Vector Coals

Introduction

Introducing the catalysts into the reaction system by impregnating onto the feed coal has been found to be a suitable alternative to adding it in a form that is soluble in the organic phase. Implementing the impregnated catalyst approach could involve a considerable materials handling problem which would impact on overall process costs. Therefore, there is incentive to simplify the catalyst impregnation technique. Several studies have suggested that complete dispersion of the catalyst precursor onto the coal may not be essential for satisfactory results. Cugini et al.[1] recognized the need to reduce the solids handling problem in preparing catalyst impregnated coal by concentrating the metal catalyst precursor on a portion of the coal. They reported "spiking" as little as 10% of the feed coal to an added Fe concentration level of 5 wt % in order to give a final Fe concentration of 5000 ppmw. In a related type application, Bockrath et al.[2] reported better results by spiking 20,000 ppm Mo onto 5% of a coal feed, reacting it at liquefaction conditions, and then mixing the reacted product with the remaining 95% of the coal followed by reacting the mix at the same reaction conditions.

Our earlier results had shown that liquefaction performance was not related to the method of impregnating the catalyst onto the coal. The next step was to determine whether the catalyst placed onto only a portion of the coal would be as effective for liquefaction as catalyst that was distributed over all of the coal. From a process standpoint, depositing the catalyst uniformly onto all or any significant portion of the coal would be cumbersome. Not having to uniformly deposit the catalyst onto all the coal might, as an alternative, allow the impregnating solution to be merely sprayed onto the coal without much concern for maintaining intimate contact with all of the coal particles. By reducing the need for mixing, major equipment and operating costs would likely be avoided.

Earlier we found that liquefaction of Fe-impregnated coals that were not treated with base

performed as well as base-treated coals.[3] Since performance was most strongly related to Fe concentration and appeared to be unaffected by other factors associated with dispersing the metal, experiments were performed to determine if depositing the catalyst precursor onto only a portion of the feed coal would affect results. This overall approach appears to offer opportunity for reducing the cost associated with catalyst addition. It also offers the possibility that other more robust and/or active substrates might be considered as the catalyst carrier.

The term "vector" has been applied to that portion of the coal that acts as carrier for the metal. In some cases a number accompanying the vector term denotes the amount of carrier contained in the total feed coal.

Results and Discussion

Scoping Studies in Tetralin

Vector coal samples were prepared by the following method: $FeSO_4 \cdot 7H_2O$ equivalent to 0.78 wt % Fe on total feed coal (dry basis) was dissolved in a volume of water equivalent to 0.76 g H_20 per gram of dry coal. This solution was added dropwise while stirring the dry coal. Following complete addition of the aqueous Fe solution, the coal was allowed to stand for ¼ hour. Then an ammonium hydroxide solution, which had been prepared from concentrated ammonium hydroxide that had been diluted 10:1 with distilled water, was added at a mole ratio of 138 mol NH_3/mol Fe. The resulting coal slurry was vacuum filtered to removed the base solution and washed with distilled water (25 cc/g coal) until the odor of ammonia was absent. The sample was then dried to approximately 20% moisture in flowing N_2 at 25 °C for 20 hours.

The ammonium hydroxide filtrate and the wash water were combined and analyzed for iron content. The efficiency of iron deposition onto the coal was calculated based upon the Fe found in the filtrates as shown in the following equation and presented in Table 3-1.

$$\text{Efficiency} = (1 - Fe_{lost} / Fe_{original}) * 100$$

Recovery of Fe in the impregnation step was high, ranging from a low of 97.8 up to 99.8 wt %. The lower number was observed when deposition was made from the most

concentrated Fe solution onto the smallest amount of coal. When impregnating larger amounts of coal with solutions having lower concentrations of Fe, the recovery increased to 99.8 wt %.

Also shown in Table 3-1 is the range of salt (as wt % FeOOH) on the vector coal, which is of interest when considering the physical character of the vector coal. This value ranged from a high of 10.3% for the 10% laden fraction (CB-24), to a low of 0.8% for the sample where all the coal was loaded with iron (CB-16).

Table 3-1. Fe Recovery on Impregnated-Base Treated Coals

Vector fraction of total feed coal, wt %	10	50	90	100
Amount of vector prepared, g AR coal	4	20	20	22
Combined base filtrate and wash water soln, mL	487	887	729	775
Fe concentration in combined solution, ppmw	11.1	0.73	0.35	0.29
Fe recovered in vector, wt %	97.8	99.7	99.8	99.8
Added Fe, wt % dry vector	7.59	1.55	0.87	0.78
Added Fe as FeOOH, wt % wet vector	10.3	2.0	1.1	0.8
Vector sample number	CB-24	CB-22	CB-15	CB-16

These coals were evaluated in liquefaction experiments using the following procedure. A total of 3.0 g of a mixture of vector coal and the appropriate amount of as-received coal was placed, along with 5.4 g of tetralin, into 50 ml microautoclaves. The reactors were pressurized to 6.89 MPa with hydrogen, sealed, and shaken in an air-fluidized sand bath at 415 °C for 30 minutes. Whenever iron was added to the reaction mixture, sulfur as DMDS, was added in excess at a minimum ratio of 1.5 mol S/mol Fe. The products of the reaction were removed from the reactor and extracted in a Soxhlet apparatus with THF. The soluble material was separated into pentane soluble (oil) and pentane insoluble (PA+A) fractions.

The liquefaction results using these base-treated impregnated vector coals are shown in Table 3−2. The THF conversions of these coals containing various amounts of the vector coal

are very similar ranging from a low of 82.7% for the 90% vector case to a high of 85.1% for the 10% vector case. Statistically, these conversions are essentially the same. The oil yields also appeared to be about the same with a slight advantage for the 10% case. A corresponding relationship was observed for PA+A with the 10% case being somewhat lower. Overall, the results using the vector coals and the 100% impregnated coal are very similar, suggesting that impregnation of the iron onto a portion of the coal does not hinder the performance of the coal. Not only does this impact on the overall understanding of the mechanism operating in this case but it also suggests the possibility of using this technique for injecting the catalyst into the reactor.

Multi-Metal Addition

Previous synthesis of impregnated coals containing both Fe and Mo were performed by stepwise addition of the Mo salt followed by addition of the Fe salt. When base treatment was used, there was some concern regarding the loss of Mo from the coal, although XPS and liquefaction performance measurements suggested that it was, at most, quite minor. As the impregnation technique evolved toward eliminating the base treatment step in order to reduce catalyst cost, the loss of co-impregnated metals would not be a problem. At the same time, it became apparent from a cost standpoint that substitution of other metals, especially ones that were significantly less expensive than Mo, could also contribute toward reducing catalyst cost. Based on these factors, an approach toward adding multiple metals to the reaction mixture through use of multiple vectors was evaluated.

Separate vectors were prepared by the incipient wetness technique, each of which contained one or more metals. Ferrous sulfate, ammonium molybdate or nickel ammonium sulfate solutions were added to the coals in the manner described above except that the base-treatment and water-washing steps were omitted. These coals were subsequently dried to moisture levels that were significantly greater than 10% in every case. The specific methods for preparing the vectors that were then evaluated in full-range process solvents are shown in Tables 3-3 and 3-4.

Table 3-2. Effect of Vector Coals on Liquefaction of Black Thunder Coal in Tetralin										
Vector Coal/total coal, wt%	10		50		90		100		none	
		±σ		±σ		±σ		±σ		±σ
Coal moisture, wt% total Coal	20.6	0.0	21.0	0.5	19.2	0.0	35.2	5.1	20.7	1.6
Added Fe, wt% mf total Coal	0.81	0.00	0.78	0.00	0.78	0.00	0.78	0.00	none	0.0
S/Added Fe mol/mol	2.1	0.4	2.0	0.3	1.7	0.3	2.7	0.2	0	-
Products, wt% maf total Coal										
HC Gases	1.0	0.1	1.0	0.0	0.8	0.0	1.1	0.1	0.7	0.0
CO+CO2	4.8	0.1	4.9	0.1	4.7	0.4	5.8	0.7	4.7	0.6
Oils	38.2	0.4	33.3	0.4	32.6	1.5	34.3	3.3	33.2	5.0
PA+A	41.1	0.6	44.0	1.1	44.6	1.5	43.6	0.4	37.9	4.7
IOM	14.9	0.4	16.8	0.8	17.4	0.5	15.3	2.1	23.6	0.6
THF Conv	85.1	0.4	83.2	0.8	82.7	0.5	84.7	2.1	76.4	0.6
Run numbers	3322-1 3322-2		3316-2 3320-1		3246-3 3258-1		3267-1 3253-1		2154-1 3291-3 3341-1	

Fe-Impregnated Coals in Full-Range Process Solvents

A comparison of the liquefaction of a 10% Fe-vector with a completely impregnated coal was obtained in Run 258 V-131B. The completely impregnated IW coal, CH-504, was prepared by impregnating with ferric sulfate and drying to final moisture level of 7%. The Fe-vector CB-39/41 (see Tables 3-3 & 3-4) was prepared from ferrous sulfate and dried to a moisture level of 19%, which is close to the moisture level of the as-received coal. The results with these two coals are shown in Table 3-5 along with comparable data for the liquefaction in the absence of any added Fe.

Both of the Fe-impregnated coals had better conversion than the coal in the absence of Fe. The vector coal was also substantially better than CH-504 which could be the result of overdrying. Previous results in tetralin had shown no significant difference in the FeII and FeIII impregnated coals. It seems unlikely that this difference can be attributed to any difference in oxidation state of the Fe. In any case, the added fresh Fe was only ~20% of the total Fe present in the reaction mixture, but resulted in a 4.5 to 12.1 wt % increase in 565 °C$^-$ distillate. This suggests that a significant effect can be attributed to some form of Fe other than pyrrhotite. The corresponding performance values of THF conversion also increased. Hydrocarbon gas and $CO+CO_2$ gas make as well as H_2 consumption were very nearly the same.

Although the vector coal performed somewhat better than the coal that had been entirely impregnated with Fe, this result, we believe, merely substantiates that using the vector approach is not detrimental to the performance of the Fe in the system. Coupled with our earlier results that the method of impregnation does not appear to affect the ultimate performance of the Fe catalyst, dispersion of the Fe onto only 10% of the coal also does not appear to be detrimental to the performance of the Fe. The next area of investigation was to determine whether deposition of multiple metals onto different fractions of the coal would be detrimental to its performance.

Table 3-3. Vector Preparations.

	CB-26 (for Mo)	CB-31 (for Fe)	CB-32 (for Mo/Ni)	CB-39 (for Fe)	CB-40 (for Mo)
Coal sample, g	4.0028	4.0014	4.0000	4.0009	3.9994
Salts impregnated, (g used)	$(NH_4)_2MoO_4$ (0.0664)	$FeSO_4 \cdot 7H_2O$ (1.8702)	$(NH_4)_2MoO_4$ (0.0661) $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ (0.0498)	$FeSO_4 \cdot 7H_2O$ (1.8870)	$(NH_4)_2MoO_4$ (0.0665)
Wt% metal/ dry coal	1.03 % Mo	11.72 % Fe	1.03 % Mo 0.23 % Ni	11.94 % Fe	1.06 % Mo
Approximate wt % vector/total coal feed	5% produces 500 ppmw Mo	10% produces 0.77% Fe	5% produces 500 ppmw Mo and 113 ppmw Ni	10% produces 0.77% Fe	5% produces 500 ppmw Mo
Impregnation water (deionized, distilled), g	2.4	2.42[a]	1.65 (Mo, ⅔ water) followed by 0.83 (Ni, ⅓ water)	2.35[a]	2.0
Base precipitated or water washed?	No	No	No	No	No
Drying conditions	40 °C, no vacuum for 1 hour	40 °C, 22" vacuum for 1¼ hours	40 °C, 22" vacuum for 1¼ hours	40 °C, no vacuum for 1¼ hour	40 °C, 22" vacuum for 1½ hours
Moisture content, wt % laden mixture	13.2	16.6	11.3	19.0	13.0

a. Water is warmed to dissolve the ferrous sulfate.

Table 3-4. Vector Preparations (continued)

	CB-41 (for Fe)	CB-43 (for Fe/Mo)	CB-44 (for Mo)	CB-45 (for Ni)	CB-46 (for Fe)
Coal sample, g	4.0115	20.0013	4.0007	4.0021	3.9982
Salts impregnated, (g used)	$FeSO_4 \cdot 7H_2O$ (1.8862)	$FeSO_4 \cdot 7H_2O$ (.6089) $(NH_4)_2MoO_4$ (0.0165)	$(NH_4)_2MoO_4$ (0.0659)	$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ (0.2210)	$FeSO_4 \cdot 7H_2O$ (1.8836)
Wt % metal/ dry coal	12.01 % Fe	0.78% Fe 526 ppmw Mo	1.03 % Mo	1.03 % Ni	11.95 % Fe
Approximate wt % vector/total coal feed	10% produces 0.77% Fe	Non-vector, 0.77% Fe and 500 ppmw Mo	5% produces 500 ppmw Mo	5% produces 500 ppmw Ni	10% produces 0.77% Fe
Impregnation water (deionized, distilled), g	2.0[a]	6.48 (Fe, ⅔ water) followed by 2.71 (Mo, ⅓ water)	2.0	2.0	2.00[a]
Base precipitated or water washed?	No	No	No	No	No
Drying conditions	40 °C, 22" vacuum for 1⅓ hours	40 °C, 22" vacuum for 2⅓ hours	40 °C, 22" vacuum for 1½ hours	40 °C, 22" vacuum for 1½ hours	40 °C, 22" vacuum for 1¼ hours
Moisture content, wt % laden mixture	18.6	25.5	14.7	11.9	16.6

a. Water is warmed to facilitate solubility of the ferrous sulfate.

Performance of Multiple-Metal Impregnated Coals

Among the vectors that were prepared containing other metals besides Fe were three different 1 wt % Mo-vectors, which were prepared by adding ammonium molybdate, and one Ni-vector, which was prepared by adding 1 wt % Ni as nickel ammonium sulfate. In addition, a combined Ni/Mo-vector was also prepared that contained 1 wt % Mo and 0.23 wt % Ni. The amounts of these individual vectors that were added in the liquefaction experiments is shown along with other information regarding these preparations in Tables 3-3 and 3-4.

In order to provide comparable data with 100% impregnated coals, a sample containing 0.77 wt % Fe as ferrous sulfate and 526 ppmw Mo (CB-43) was prepared in the same manner as used previously when the Mo salt was added first followed by addition of the Fe salt. The composition of this coal is essentially the same as that prepared from ferric sulfate (IW-1) with the same concentrations of Fe and Mo (discussed in Chapter 2). Liquefaction results from these two coals along with the Mo-vectors are shown in Table 3-6. In all these runs a nominal 500 ppmw Mo and 0.8 wt % Fe was present in the coal mix. All these coals, except for the IW-1 coal, contained moisture levels that were comparable to as-received coals.

The completely impregnated coal, labelled IW-1 and Non-vector in Table 3-6, gave the same total THF conversion although H_2 consumption was higher for the "non-vector" coal . The effect of adding the Fe as ferrous sulfate and Mo as ammonium molybdate on separate coal vectors is shown in the column labeled "Vector". THF conversion and hydrogen consumption for the vector case is similar to the Non-vector case. However, distillate yield improved markedly, suggesting a benefit to processing mostly as-received coal. Although these runs suggest an advantage of the vector approach, without additional information this conclusion is somewhat uncertain at the present time. The result does suggest that addition of the metal catalyst by this method does not adversely affect performance, which agrees with the tetralin results discussed above.

Distillate yields from liquefaction of a combination Fe/Mo/Ni vectors appear to be intermediate between the completely dispersed non-vector case and the Fe/Mo-vector case, as shown in

Table 3-6. The corresponding THF conversions and gas yields appear to be the same while the H_2 consumption numbers appear to vary, being especially low for the Fe/Mo/Ni case. In IW-3, there appears to be no special advantage for adding the Ni since overall product distribution appears to be changed very little.

Table 3-5. Liquefaction Fe-impregnate and Fe-vector Coals in Run 258K V-131B Process Solvent[a,b]

	Thermal		CH-504		Fe Vector	
Fe added, wt% mf Coal	0	0	0.77	n.a.	0.82	0.01
Mo added, ppmw mf Coal	0	0	0	n.a.	0	0
Ni added, ppmw mf Coal	0	0	0	n.a.	0	0
S added, mol S/mol Fe	0	0	1.7	n.a.	1.3	0.2
Products, wt% maf Coal		σ		σ		σ
HC Gases	3.0	0.3	2.6	n.a.	3.1	0.1
$CO+CO_2$	6.4	0.4	7.1	n.a.	6.7	0.4
1050 °F-	26.1	5.5	30.6	n.a.	38.2	4.1
1050 °F+	64.5	5.2	59.7	n.a.	52.0	4.1
Total	100.0	0	100.0	n.a.	100.0	0
THF Conv	98.1	1.8	101.9[c]	n.a.	102.3	0.1
Resid Conversion, wt% maf resid	16.7	2.5	20.6	n.a.	22.2	1.9
Hydrogen consumed, mg/g maf coal	30	5	31	n.a.	30	3
Coal moisture, wt % Coal	23.4	0.4	7.2	n.a.	23.1	0.5
Run number and coal preparation	4251-1 4208-1 4173-1	-	3287-1	-	4220-3 4223-2 4283-1	CB-39/41 CB-41 CB-46

a. Liquefaction at 440 °C for 22 minutes, using 6.89 MPa hydrogen (cold). Analysis by distillation.
b. Distillation calculations updated for allocated head weight: ⅔ resid and ⅓ distillate, and a forced N_2 gas composition to account for incomplete mixing in the gas sample system.
c. THF conversion is from Run 3286-2 (solvent separated), since it was not determined in 3287-1.

Table 3-6. Liquefaction of Coals Impregnated with 0.8% Fe and 500 ppmw Mo in Run 258K V-131B Process Recycle Oil.[a,b]

	IW-1		Non-vector		Vector		IW-3 (vector Fe/Mo/Ni)	
Fe added, wt% mf Coal	0.77	0	0.78	0	0.81	0.0	0.80	0.00
Mo added, ppmw mf Coal	500	0	526	0	563	45	580	2
Ni added, ppmw mf Coal	0	0	0	0	0	0	130	0
S added, mol S/mol Fe	1.3	0	1.6	0.2	1.3	0.1	1.3	0.2
Products, wt% maf Coal		σ		σ		σ		σ
HC Gases	3.0	0.2	3.3	0.6	2.9	0.2	2.8	0.2
$CO+CO_2$	6.4	0.3	7.2	0.8	6.1	0.2	6.2	0.4
1050°F-	41.1	3.1	41.2	4.5	47.9	7.5	43.9	0.8
1050°F+	49.5	2.7	48.3	5.5	43.1	7.7	47.1	0.2
Total	100.0	0	100.0	0	100.0	0	100.0	0
THF Conv	102.3	1.2	107.5	1.7	106.2	0.7	106.7	0.5
Resid Conversion, wt% maf resid	25.9	1.4	23.7	2.7	26.4	3.6	24.6	0.1
H_2 consumed, mg/g maf Coal	36	0	40	2	39	1	34	0
Coal moisture, wt % Coal	4.9	0.3	24.4	2.1	22.8	0.3	21.4	0.9
Run number and coal preparation (CB-#)	4039-4 4041-1 4041-2	-	4221-3 4255-2 4286-2	-43 -43 -43	4203-2 4206-2 4220-1 4221-1	26/39 26/39 40/39 40/41	4097-2 4201-1	31/32 32/39

a. Liquefaction at 440°C for 22 minutes, using 6.89 MPa hydrogen (cold). Analysis by distillation.
b. Distillation calculations updated for allocated head weight: ⅔ resid and ⅓ distillate, and a forced N_2 gas composition to account for incomplete mixing in the gas sample system.

Molybdenum Activity

Resid conversion has consistently been less in the Mo-free Run 258K V-131B solvent relative to the corresponding Run 262E V-131B solvent. This suggests that the recycled Mo contained in the Run 262E solvent is very active. This observation was observed during the PST series when very high distillate yields (60.9%) and resid conversions (31.7%) were obtained with the

Run 262E solvent, as shown in Table 3-7. The added catalyst in this run was 0.64 wt % Fe as Wilsonville iron oxide and 100 ppmw Mo as Molyvan L to give total metals concentrations of 4.4 wt % Fe and 440 ppmw Mo on maf coal. In other runs made in the Run 262 V-131B, similar conversions were obtained regardless of the amount of additional Mo that was added. Comparative runs with 0.64 wt % Fe as Wilsonville iron oxide and 100 ppmw Mo as Molyvan L in the Mo-free Run 258K V-131B solvent gave significantly less distillate yield and resid conversion suggesting that the recycled-Mo activity was responsible for this increase in conversion.

Increasing the Mo concentration in the Mo-free Run 258 V-131B solvent increased distillate yield but failed to attain the same level of conversion as attained in the Run 262E V-131B. Addition of 500 or 1000 ppmw Mo impregnated onto coal indicated a stepwise increase in distillate yield which was still well below the level observed for the Run 262E V-131B solvent (see Table 3-7). At the 500 ppmw Mo addition level, results from coals prepared by the vector approach gave somewhat higher yields than the 100% impregnated coals, as illustrated by Fe/Mo Vector and IW-1 data. Data at Mo-addition levels of 1000 ppmw were reversed in that CH-605, which was prepared by impregnating all of the coal, was somewhat better than results with coals using the vector approach. At both Mo levels the distillate yields were significantly lower than observed for the solvent containing recycled Mo.

Addition of more sulfur to the system to promote better activation of the Mo was tested. The DMDS addition to a coal containing 500 ppmw Mo was doubled to a sulfur to Fe molar ratio of 2.5 as shown in Table 3-8. Using vector coals, in the higher sulfur case, distillate yields increased by about 4 wt %, indicating that incomplete sulfiding of the catalyst precursor may be responsible for the lower activity. In each of these cases, although the atomic ratio of added sulfur to added Fe was at least 1.2, the added sulfur to Mo atomic ratio at the 500 ppmw level was 19. If in this environment the Mo became only partially sulfided at this level of excess sulfur addition, the possibility exists that Mo cannot effectively compete with the Fe for the available sulfur. Although there was an excess of sulfur relative to the stoichiometric requirement for converting the Fe oxide to the pyrrhotite form, the sulfur that was actually

available could be altered by an undefined additional sulfur requirement of the Fe species contained in the recycle solvent. If any of the added sulfur is consumed by the Fe-S species, this would diminish the sulfur available to react with the added metals.

The effect of preactivating the Mo was examined by treating the Mo vector in hydrogen at reaction conditions prior to running the liquefaction experiment. In this experiment the Mo vector (CB-44) was first reacted in hydrogen alone at 440 °C for 22 minutes in the presence of a large excess of DMDS which was added at a ratio of ~40 mol S/mol Mo. The reactor was cooled, the reactor opened and the remaining vectors, CB-41 and CB-46, and as-received coal were added along with recycle solvent and additional sulfur as DMDS in the ratio of 1.2 mol S/mol Fe. The reactor was re-pressurized with H_2 and the mixture was heated at 440 °C for an additional 22 minutes. The product was analyzed in the usual manner and the yields were calculated as though the reaction was a single-step experiment. Preactivating the Mo resulted in a further increase in distillate yield and a slight increase in THF conversion, as shown in the Table 3-8. This agrees directionally with the results of Bockrath et al. who found that a prereacted enriched Mo-impregnated coal, when added to the liquefaction mixture, provided increased conversion relative to liquefaction without Mo enrichment.[4]

Added Fe was present in all of the experiments up to this point except for the preactivation experiment just mentioned. The effect of freshly added Fe on the activation of the Mo was explored in a run in the Mo-free Run 258K V-131B solvent to which only Molyvan L was added. At a nominal 500 ppmw Mo addition level, the distillate yield that was obtained was quite high being equal to the Mo-pretreated case. This began to suggest that freshly added Fe may be having an effect on the activity of the added Mo catalyst. A comparison run was made in which the Fe vector from the Fe/Mo vector run made previously, as shown in Table 3-7, was omitted. In this Mo-only vector run, the distillate yield increased dramatically to 55.1 wt % versus 47.9 wt % in the presence of the Fe vector (compare Tables 3-8 with 3-7). The corresponding THF conversion, which increased by 1%, gas yields, and H_2 consumption did not significantly change. A comparable result was also observed in the Ni/Mo system. The distillate yield from a feed coal containing a Ni/Mo vector was also higher by a similar amount

Table 3-7. Liquefaction Experiments Comparing Coals using Nickel Catalysts in Run 258K V-131B Process Recycle Oil.[a,b]

	Base case Run 262E V-131B		IW-1		Fe/MoVector		CH-604		Fe/ Hi Mo Vector	
Fe added, wt% mf Coal	0.64	0.00	0.77	0	0.81	0.0	0.77	n.a.	0.80	0.01
Mo added, ppmw mf Coal[c]	440	-	500	0	563	45	1000	n.a.	1,138	72
Ni added, ppmw mf Coal	0	0	0	0	0	0	0	n.a.	0	0
S added, mol S/mol metals	1.2	0.0	1.3	0	1.3	0.1	1.9	n.a.	1.6	0.1
Products, wt% maf Coal		σ		σ		σ		σ		σ
HC Gases	2.3	0.2	3.0	0.2	2.9	0.2	3.3	n.a.	2.6	0.1
$CO+CO_2$	5.5	0.0	6.4	0.3	6.1	0.2	6.6	n.a.	6.0	0.1
1050°F- distillate	60.9	0.4	41.1	3.1	47.9	7.5	53.3	n.a.	48.5	9.4
1050°F+ resid	31.4	0.6	49.5	2.7	43.1	7.7	36.8	n.a.	42.9	9.3
Total	100.0	0	100.0	0	100.0	0	100.0	n.a.	100.0	0
THF Conv	n/a	n/a	102.3	1.2	106.2	0.7	105.8[c]	n.a.	107.3	0.5
Resid Conv, wt% maf resid	31.7	0.2	25.9	1.4	26.4	3.6	31.6	n.a.	26.5	4.5
H_2 consumed, mg/g maf Coal	49	1.5	36	0	39	1	38.5	n.a.	37	3
Coal moisture, wt % Coal	21.5	0.0	4.9	0.3	22.8	0.3	10.5	n.a.	22.4	0.9
Run number and coal preparation (CB-#)	4014-1 4014-2	-	4039-4 4041-1 4041-2	-	4203-2 4206-2 4220-1 4221-1	26/39 26/39 40/39 40/41	3293-1	-	4215-1 4227-2 4230-1	-26/39 -40/41 -40/41

a. Liquefaction at 440°C for 22 minutes, using 6.89 MPa hydrogen (cold). Analysis by distillation.
b. Distillation calculations updated for allocated head weight: ⅔ resid and ⅓ distillate, and a forced N_2 gas composition to account for incomplete mixing in the gas sample system.
c. Includes Mo present in solvent equivalent to 332 ppmw.

Table 3-8. Liquefaction Experiments Comparing Coals using Nickel Catalysts in Run 258K V-131B Process Recycle Oil.[a,b]

	Vector, Hi Sulfur		Vector, Pretreat Mo		Molyvan L alone		Vector Mo alone		Vector Mo/Ni only	
Fe added, wt% mf Coal	0.83	0.01	0.82	0.01	0	n.a.	0	0	0	0
Mo added, ppmw mf Coal	576	6	577	5	540	n.a.	565	5	558	3
Ni added, ppmw mf Coal	0	0	0	0	0	n.a.	0	0	125	1
S added, mol S/mol metals	2.5	0.1	1.4	0.2	40.5	n.a.	38.6	1.5	(40.2)	0.5
Products, wt% maf Coal		σ		σ		σ		σ		σ
HC Gases	3.5	0.2	3.4	0.1	3.6	n.a.	2.9	0.3	3.2	0.1
$CO+CO_2$	6.9	0.6	5.8	0.2	6.3	n.a.	5.9	0.2	6.0	0.3
1050°F- distillate	51.2	6.6	54.2	2.9	54.6	n.a.	55.1	3.8	57.8	3.0
1050°F+ resid	38.5	5.8	36.6	2.8	35.5	n.a.	36.1	3.4	33.0	3.0
Total	100.0	0	100.0	0	100.0	n.a.	100.0	0	100.0	0
THF Conv	107.0	0.1	108.4	0.8	107.4	n.a.	107.3	0.4	108.4	0.6
Resid Conv, wt% maf resid	28.5	2.5	29.3	1.3	30.4	n.a.	30.3	1.6	31.7	1.4
H_2 consumed, mg/g maf Coal	41	0	37+	0	41	n.a.	38	2	37	5
Coal moisture, wt % Coal	21.9	0.3	22.8	0.2	22.6	n.a.	21.7	0.7	21.6	0.3
Run number and coal preparation (CB-#)	4290-1 4290-2	44/46 44/46	4249-1 4265-2	41/44 46/44	4270-1	-	4230-2 4234-1 4241-1 4284-1	-40 -40 -40 -44	4243-2 4255-1 4286-1	-32 -32 -32

a. Liquefaction at 440°C for 22 minutes, using 6.89 MPa hydrogen (cold). Analysis by distillation.
b. Distillation calculations updated for allocated head weight: ⅔ resid and ⅓ distillate, and a forced N_2 gas composition to account for incomplete mixing in the gas sample system.

relative to a Fe/Ni/Mo vector feed. The Fe-free coal gave 57.8 wt % distillate while the Fe/Ni/Mo feed gave 43.9 wt % (compare Table 3-8 with IW-3 in Table 3-6).

Catalyst Activity in Solids-Free Recycle Solvent

Measuring catalyst activity in ashy-resid containing recycle solvents is complicated by the presence of metals accumulated during recycle. To measure catalyst activity without this complication requires that these solids be removed. Solids were removed from a sample of Run 258K V-131B by filtration. Filtration reduced the ash content from 8.1 wt % to 0.25 wt %. The IOM content of the sample was reduced from 15.6 wt % to 7.1 wt %, as shown in Table 3−9.

Table 3-9. Characterization of Hot-Filtered Run 258K V-131B

Solvent Fractions	
Oils, wt % af	60.5
PA+A, wt % af	32.4
IOM, wt % af	7.1
Total	100.0
Ash, wt %	0.25
Fe, wt %	0.009
1050 °F⁻ Distillate, wt %	52.3

Liquefaction of Fe, Mo and Ni-vector coals in this solvent provided an indication of the activity of these metals in the absence of background metals since the ash had essentially been completely removed. Mo was added at the nominal 500 ppmw level in each of the runs while the Ni was added at a level of 125 ppmw. Distillate yields were significantly higher in the absence of Fe for both the Mo and Mo/Ni runs as shown in Table 3-10. THF conversion for Fe/Mo and Mo were essentially the same while a higher conversion was indicated for Ni/Mo. Hydrocarbon and CO_x gas yields and H_2 consumption were unchanged. These results are further evidence that higher activity is observed for Mo catalysts in the absence of added Fe oxide.

Table 3-10. Liquefaction of Coals in Hot-Filtered Run 258K V-131B Process Recycle Solvent.[a]						
	Fe/Mo-Vector		Mo Vector		Mo/Ni Vector	
Fe added, wt% mf Coal	0.83	0.0	0.0	0.0	0.0	0.0
Mo added, ppmw mf Coal	594	30	562	10	563	0
Ni added, ppmw mf Coal	0	0	0	0	125	0
S added, mol S/mol Fe	1.7	0.1	39.2	1.9	37.2	2.0
Products, wt% maf Coal		σ		σ		σ
HC Gases	3.4	0.6	3.5	0.1	3.4	0.3
$CO+CO_2$	6.8	0.9	6.6	0.3	6.4	0.3
1050°F-	39.1	1.4	45.8	4.2	45.2	0.6
1050°F+	50.7	2.3	44.1	3.8	45.0	1.1
Total	100.0	0	100.0	0	100.0	0
THF Conv	86.3	1.8	87.0	4.5	90.2	1.6
Resid Conversion, wt% maf resid	24.6	1.2	28.2	1.8	27.7	0.5
H_2 consumed, mg/g maf Coal	27	3	30	2	29	3
Coal moisture, wt % Coal	22.9	1.1	23.3	1.0	22.1	2.3
Run number and coal preparation (CB-#)	4292-3 44/46 4299-2 44/46 4326-1 44/46		4292-1 44 4304-1 44		4303-2 44/45 4310-1 44/45	
a. Liquefaction at 440°C for 22 minutes, using 6.89 MPa hydrogen (cold). Analysis by distillation.						

Nickel as Catalyst

Nickel as a component of the multimetallic catalyst systems in some cases showed an improvement while in others the level of conversion was comparable to runs made in its absence. Liquefaction of the Mo/Mi vector coal gave higher distillate yields than with Mo vector, both in the absence of any added Fe (see Table 3-8). Runs with a coal feed incorporating 1000 ppm Ni in a Ni vector gave the same level of distillate yield as with 500 ppm Mo as Mo vector, both in the absence of fresh Fe. Because of the significantly lower cost of Ni relative to Mo, this may afford an opportunity to reduce catalyst cost. Further investigation is necessary to decide whether an advantage can be gained by using nickel catalysts.

Conversion Correlations

An extensive amount of liquefaction data has been collected in the Run 258K V-131B solvent at 440 °C, 1000 psig H_2 (cold) for 22 min reaction times. In all these runs, distillate yield, THF conversion, H_2 consumption, and gas yields (C_1-C_3, CO, CO_2) were measured. A plot of distillate yield versus THF conversion for these runs, as shown in Figure 3-1, shows a relationship between these two parameters. An unweighted regression analysis gives a correlation coefficient of 0.71 between these two parameters, which is remarkably good considering the range of catalyst systems included in these data. In Figure 3-2, a plot of H_2 consumption and total THF conversion gives a correlation coefficient of 0.728. Also shown in this figure is the 95% prediction interval which describes the range where the data values will fall 95% of the time for repeated measurements. Because of the strong interaction between THF conversion and distillate yield, H_2 consumption can also be assumed to relate to distillate yield. These relationships provide a good check on experimental data providing multiple parameters for identifying inconsistent run data.

Conclusions

Various methods have been investigated for introducing the metallic catalyst precursors into the reaction system. Comparable results have been obtained by either impregnating the metals onto all of the coal feed or placing the metal onto only a portion of the coal. In the latter case, that portion of the coal carrying the metal component, the vector, varied 20 fold in concentration relative to the fully impregnated coal. Although THF conversions and H_2 consumptions for the vector cases often exceeded the Non-vector cases, it appears that addition of the catalyst using the vector approach does not adversely affect performance.

Significant experimental work was directed toward understanding the lower activity of freshly added Mo versus Mo contained in the recycle solvent. Adding additional sulfur to the feed promoted additional activity. Preactivating the catalyst by prereacting the Mo-Vector resulted in an increase in THF conversion and distillate yield. This suggested that the activation of the fresh Mo was either kinetically limiting or that the presence of freshly added Fe oxide was, in some way, retarding the activation of the Mo. Using the Vector approach, Mo in the absence

Figure 3-1

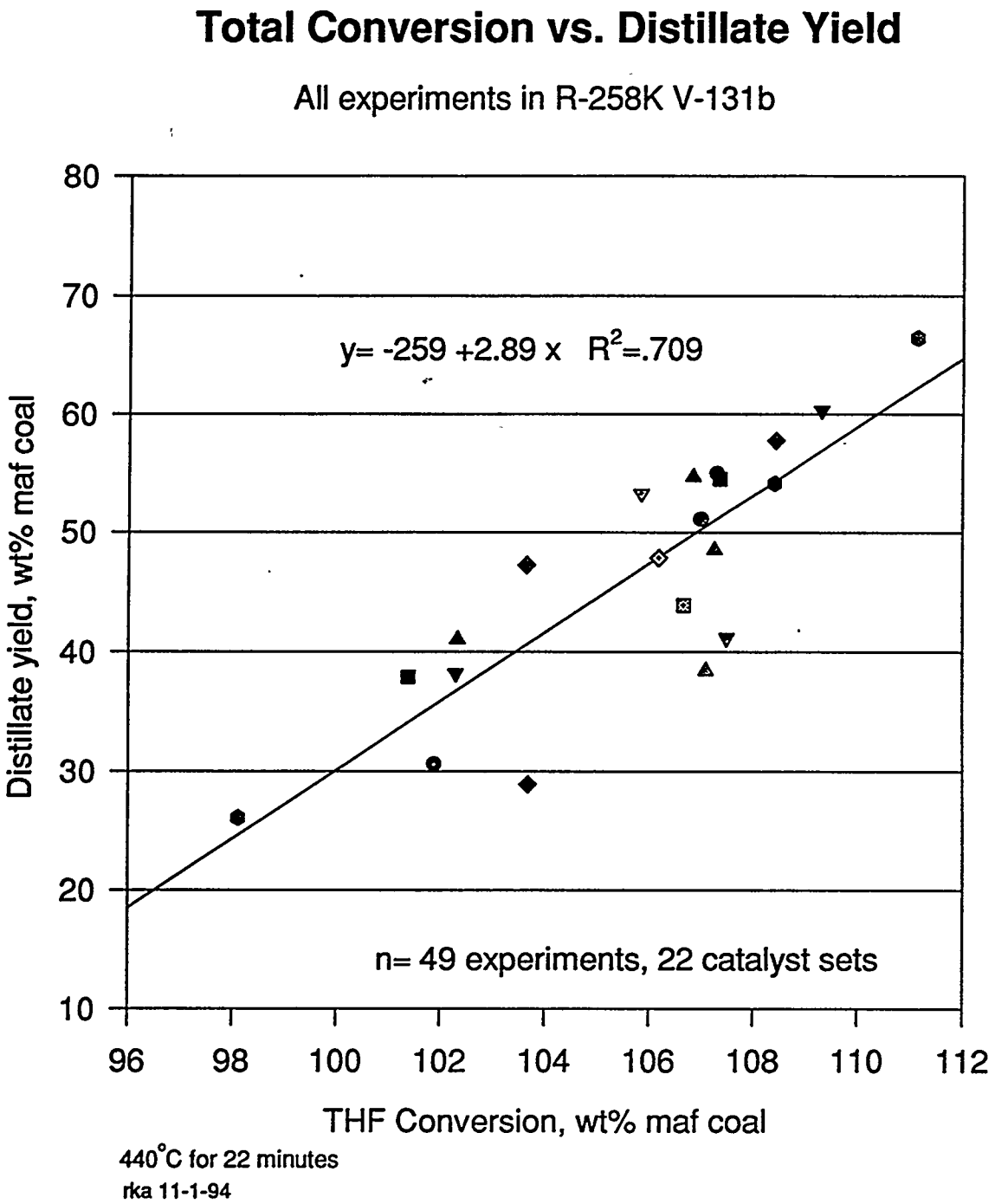
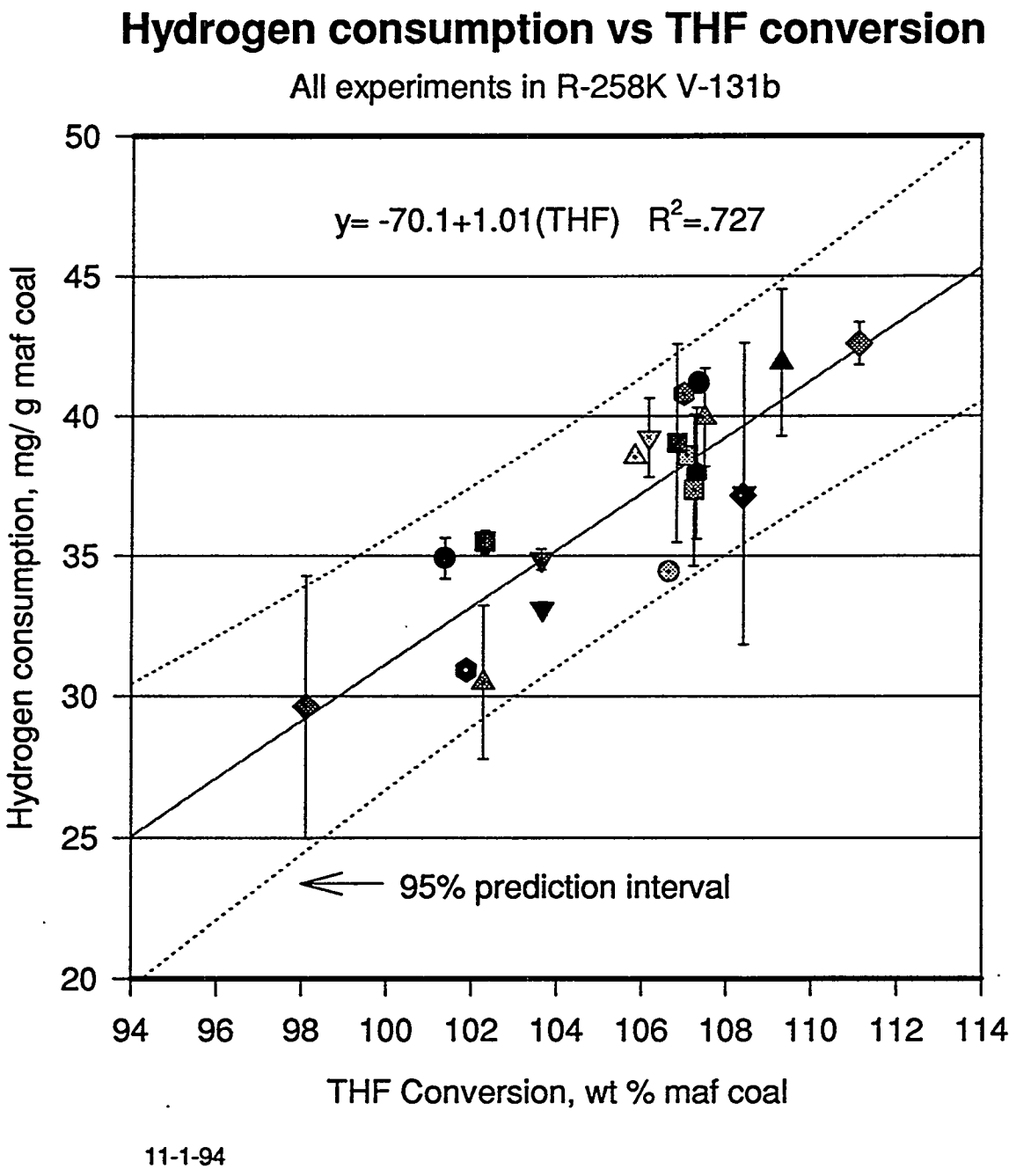

Total Conversion vs. Distillate Yield
All experiments in R-258K V-131b
y= -259 +2.89 x R2=.709
n= 49 experiments, 22 catalyst sets
Distillate yield, wt% maf coal
THF Conversion, wt% maf coal
80
70
60
50
40
30
20
10
96
98
100
102
104
106
108
110
112
440°C for 22 minutes
rka 11-1-94

Figure 3-2


Hydrogen consumption vs THF conversion
All experiments in R-258K V-131b
y= -70.1+1.01(THF) R^2=.727
95% prediction interval
Hydrogen consumption, mg/ g maf coal
THF Conversion, wt % maf coal
50
45
40
35
30
25
20
94
96
98
100
102
104
106
108
110
112
114
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of any fresh Fe, produced significantly greater distillate yield (55%) than when fresh Fe was present (48-51%). A comparative run with Molyvan L in the absence of any fresh Fe gave nearly identical results. This response of Mo in the absence of added Fe suggests that fresh Fe is inhibiting the complete activation of the Mo.

Adding Ni either alone or in combination with Mo indicates promise as a catalyst in these systems. Nearly equal performance was observed with Ni at 1000 ppmw, Mo at 500 ppmw or Mo/Ni at 500 and 125 ppmw, respectively. Although definitive data are not yet available, Ni has promise because of its much lower cost than Mo. The strongest benefit may be a possible increase in THF conversion at the same distillate yield and H_2 consumption level.

Data analysis of all this data collected for a variety of different catalyst systems in Run 258K V-131B showed a good correlation between THF conversion and distillate yield. There is also a very good correlation between calculated hydrogen consumption and total THF conversion for these combinations. Regression analyses for both sets of data provided correlation coefficient of approximately 0.7.

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Chapter 4
Nanoscale Iron Catalysts

Introduction

Historically, finely divided iron oxide catalysts were first used in the coal liquefaction developments in Germany during WWII to increase the conversion of bituminous and subbituminous coals[1,2]. Since that time, great efforts have been made to increase the efficiency of the liquefaction process while reducing the severity of the reaction conditions. To this end a wide variety of techniques have been utilized including the use of multiple processing stages, pretreatment of the coal, and the addition of catalysts. Due to their inexpensive nature, the use of highly dispersed iron-based catalysts shows promise for enhancing the process economics, despite their having only moderate activity. Efforts to improve the activity of these catalysts are focussed on increasing and maintaining high dispersion during the liquefaction process, and on rapidly establishing the presence of an active phase.

As already observed, the application of dispersed iron based catalysts to direct coal liquefaction has been practiced for some time[3] and considerable research has also been applied to determining the active phase of the catalyst. It is generally accepted that the sulfided form of the catalyst exhibits a higher activity than the oxide phase[4]. While the addition of pyrite is known to result in higher conversions and selectivity to oils, studies have shown that, under liquefaction conditions, pyrite decomposes to form pyrrhotite with the evolution of hydrogen sulfide[5,6]. Some researchers have proposed that pyrrhotite is the active

phase of the catalyst [4-6] while others have suggested that the hydrogen sulfide evolved during the decomposition of pyrite is responsible for the catalytic activity [7,8]. Subsequent studies have concluded that both hydrogen sulfide and pyrrhotite are necessary for high catalytic activity [9,10].

Still other research has suggested that the active phase of the catalyst is a reduced form of α-Fe which exists as a short-lived intermediate on the surface which is subsequently resulfided [11,12]. Another report identifies a γ-Fe phase formed during the liquefaction process as being the active catalytic species, having a higher activity for the liquefaction of a brown coal than pyrrhotite [13]. The active form of the iron based catalysts is still a matter of considerable debate.

Several studies have shown that, for several different forms of the iron precursor, in the presence of sufficient sulfur the iron will transform to pyrrhotite under liquefaction conditions. Similarly, in the presence of sulfur, most molybdenum compounds also tend to sulfide to MoS_2. However, recent work has shown that the carbides and nitrides of molybdenum and tungsten possess high catalytic activity while resisting the transformation to the sulfide phase [14-16]. This indicates that the sulfide is not the only phase of molybdenum which is catalytically active. The purpose of this research was to compare the catalytic activity of three nanoscale iron catalyst precursors, and also to determine if iron carbide would exhibit high activity while remaining in the carbide phase. A laser pyrolysis technique was used to synthesize two of the iron-based particles.

Catalyst Preparation

Three nanoscale iron-based catalysts were utilized in this study. Iron carbide and iron sulfide were synthesized using a laser pyrolysis technique first developed by Haggerty and co-workers [17] for the production of nanoscale ceramic particles. The uniqueness of this technique lies in its rapid heating and cooling rates (~100,000 °C/sec), allowing the non-equilibrium production of nanoscale particles. The technique involves the intersection of a tunable CO_2 laser with a gas stream carrying a combination of reactant gases. The energy of the laser is coupled to a strong rotational-vibrational mode in at least one of the reactant gases which in turn creates a small (~1mm^3) pyrolysis zone at the intersection. The particles produced by this method have been reported to have a narrower size distribution and be less contaminated than those produced by conventional oven-based methods[17].

Iron carbide particles were generated in the laser pyrolysis apparatus shown in Figure 1[18]. The ethylene gas (Air Products, CP grade) flowed, at ambient temperature, through a sintered Pyrex bubbler at the bottom of a container of iron pentacarbonyl (Aldrich) and the flow rate was regulated by a mass flow controller (AGA Gas, Inc.). The reactant gases flowed vertically through the reaction nozzle into the reaction chamber and intersected the laser beam (Laser Photonics Model 150) forming a pyrolysis zone. The pressure in the reaction chamber was maintained at ~ 300-500 torr by a vacuum pump located downstream of the reaction chamber. A coaxial flow of argon contained the reactant gases in a well collimated stream forming a "wall-less" reactor. The energy of the laser was coupled to the rotational-vibrational absorption line of ethylene at 950 cm^{-1} by tuning the laser frequency to the P20

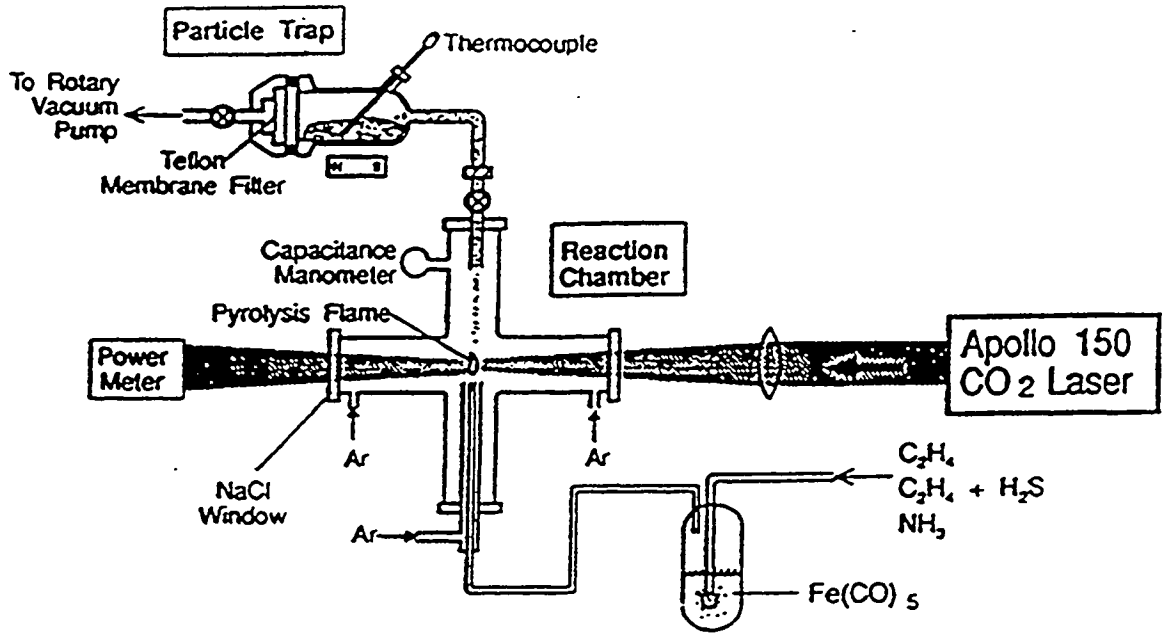

Figure 1. Schematic Diagram of Laser Pyrolysis Apparatus

line (945 cm^{-1}).

The particles formed in the pyrolysis zone were carried out of the reaction chamber and into a Pyrex particle trap where they were separated from the gas stream by a large ferrite magnet placed under the trap. Separation was possible due to the ferromagnetic properties of the iron carbide particles. A 0.2 μm pore Teflon membrane filter was placed at the trap outlet to prevent stray particles from entering the vacuum pump.

The as-formed particles are pyrophoric and were passivated prior to exposure to air. The passivation process involved the slow introduction of a 4-10 % oxygen in helium gas mixture to the particle trap while carefully monitoring the temperature to detect uncontrolled oxidation. This process required several hours, and when complete it allowed the safe handling of the particles in air.

The mechanism for the formation of the particles has been reported in detail elsewhere [18]. It has been proposed that iron carbides are formed by the catalytic decomposition of ethylene on the iron particles that result from the decomposition of the iron pentacarbonyl. The deposited carbon then diffuses into the particles leading to the formation of carbide phases, provided the particles are sufficiently hot. The departure from the pyrolysis zone causes a rapid quenching of the particles thereby eliminating further particle growth or agglomeration, and arresting the process of carbon diffusion, resulting in the formation of a carbon coating on the surface.

By manipulating the reaction parameters, the phase and size of the particles can be controlled. Typical reaction parameters for the formation of α-Fe, Fe_3C, and Fe_7C_3 are shown in Table 1. The identity of each of the phases has been confirmed by X-ray diffraction as well as by Mössbauer spectroscopy[18].

Table 1. Typical Reaction Parameters used in Laser Pyrolysis

	α-Fe	Fe_3C	Fe_7C_3	$Fe_{(1-x)}S$
Laser Intensity, W	30	50	54	70
Beam Width, mm	1	1	0.2	1
Nozzle Diameter, mm	1.7	0.8	0.8	1.8
Chamber Pressure, torr	100	300	500	300
Ethylene Flowrate, sccm	9	9	25	25
H_2S Flowrate, sccm	0	0	0	5

The addition of 20 % hydrogen sulfide to the reactant gases allowed the production of iron sulfide. The XRD spectrum of the particles confirmed the production of $Fe_{(1-x)}S$. Table 1 shows the reaction parameters used for the production of the pyrrhotite particles. The iron sulfide particles are paramagnetic, therefore the ferromagnet was removed and the particles were separated from the gas stream by the teflon filter. The as-formed particles were less pyrophoric than the iron carbide phase but still required passivation prior to removing from the trap.

The third catalyst used in this study, a superfine iron oxide (SFIO), was provided by Mach I Inc. and was reported to be a 30 Å diameter α-Fe_2O_3 particle. The properties of the three catalysts used in this study, as determined by XRD and nitrogen BET adsorption measurements, are presented in Table 2.

Table 2. Catalyst Characterization Data

	Phase (XRD)	Diameter (nm) (XRD)	Surface Area (m^2/g)
SFIO	*see text*	3	195
Iron Sulfide	$Fe_{(1-x)}S$	14	42
Iron Carbide	Fe_7C_3	17	92

ExperimentalLiquefaction experiments were carried out in 50 ml horizontal microautoclave reactors, a configuration that reduces mass transfer limitations. The reactors were agitated by vertical oscillation at 400 cycles/minute in a heated fluidized sand bath, allowing the rapid (<2 minutes) attainment of reaction temperature, and minimization of errors associated with long heat-up times. The microautoclaves were loaded with 3 g of a subbituminous Black Thunder coal and 5 g of tetralin, used as a hydrogen donor solvent. An analysis of the coal is shown in Table 3. Catalyst loadings of 0.7 and 1.4 wt % Fe on as-received coal were used, corresponding to 1 and 2 wt % Fe on maf coal respectively, and dimethyldisulfide (DMDS) was added as a catalyst sulfiding agent in these runs. The reactors were sealed, purged and pressurized to 1000 psig (cold) with hydrogen.

Table 3. Analysis of Black Thunder Coal

Proximate	wt%	Ultimate	wt% dry	Sulfur	wt %
Moisture	22.4	Carbon	70.01	Total Sulfur	0.39
Ash	5.46	Hydrogen	4.93	Pyritic Sulfur	0.07
Volatile Matter	34.4	Nitrogen	1.23	Sulfate	0.09
Fixed Carbon	39.8	Sulfur	0.50	Organic Sulfur	0.23
		Oxygen (diff)	16.29		
		Ash	7.04		

Two sets of conditions were used in the liquefaction experiments. A low severity condition of 385°C for 15 minutes and a high severity condition of 415°C for 60 minutes. After reaction, the microautoclaves were quenched in a cool fluidized sand bath. A sample of the gas phase of the reactor was removed for analysis by gas chromatography. The contents of the reactors were removed using tetrahydrofuran (THF) and were analyzed by solubility class. All conversions were determined and reported on a maf coal basis. Total conversion was defined by THF solubility. The ash-free THF-insoluble material was defined as insoluble organic matter (IOM) while the THF-soluble, pentane-insoluble fraction was defined as preasphaltenes + asphaltenes (PA&A). The oil yield, contained in the pentane-soluble fraction, was determined by difference. All liquefaction experiments were done in duplicate to ensure reproducability.

The amount of tetralin dehydrogenation was calculated from the naphthalene/tetralin ratio determined by GC analysis of the pentane soluble fraction. The H/C ratio of the PA&A

fraction was determined by elemental analysis. The phase of the catalyst, as well as the average crystallite diameter, was determined by XRD analysis. Surface area was measured using a nitrogen BET adsorption method.

A set of blank liquefaction experiments were carried out in the absence of coal to determine the effect of sulfur on the iron carbide particles under liquefaction conditions. A microautoclave reactor was loaded with 0.2 g of Fe_7C_3, 5g tetralin, and DMDS at twice the stoichiometric loading needed to form FeS_2. The mixture was reacted at 385 °C for 30 minutes. The solid product from the run was collected and analyzed by XRD.

Results & Discussion

Catalyst Characterization.

Due to the small size of the SFIO particles, which severely limited the use of traditional characterization techniques such as XRD, there is some speculation on the actual iron phase present. A recent study, using Mössbauer and XAFS spectroscopies, reported that the major phase is ferrihydrite [19]. Another study has identified the major phase as γ-Fe_2O_3 based on energy-dispersive X-ray analysis and microdiffraction [20]. The material is also reported to be extremely sensitive to moisture and to tend to form large (~150 Å) particles of α-Fe_2O_3 [21]. For the purposes of this study the SFIO will be considered to consist of Fe_2O_3.

XPS studies of the passivated iron carbide indicated that the surface of the particles becomes oxidized to some extent, while XRD data indicate that the bulk remains as the carbide phase.

Similarly, the iron sulfide particles also were passivated though they were less pyrophoric than the carbide particles.

The results of the nitrogen BET adsorption measurements showed that there was very little porosity associated with any of the materials used in this study. Therefore, unlike supported catalysts, in which much of the surface area is associated with micropores, the active sites are essentially present on the external surface area and therefore accessible to the coal. The results of the catalyst precursor characterization studies, shown in Table 2, indicate that the SFIO consisted of the smallest particles (3 nm diameter) and corresponding to highest surface area (195 m^2/g). A Debye-Scherrer analysis of XRD linewidths indicate that the diameter of the iron sulfide and iron carbide were very similar (14 and 17 nm respectively), although their surface areas differed significantly (42 and 95 m^2/g respectively). The reason for this difference may lie in disorder-induced broadening of the XRD lines for the iron sulfide particles.

While it has been shown that iron oxide, in the presence of sufficient sulfur, will transform to pyrrhotite under liquefaction conditions [10], the behavior of iron carbide has not been reported. The results of the blank runs showed that the latter transforms to pyrrhotite within 30 minutes at 385°C, indicating that the iron carbide does not possess the stability reported to exist for molybdenum and tungsten carbides [14-16]. While the pyrrhotite is not expected to undergo a phase change, although it is possible that their stoichiometry will change as a function of the sulfur concentration in the system [6,10].

Coal Liquefaction.

The results of the coal liquefaction experiments indicate that, at the high severity conditions and a catalyst precursor loading of 0.7 wt % Fe on as-received coal, all three precursors yielded nearly identical catalytic effects, with an increase in the total conversion from 81 wt% for the thermal runs to 87 wt % for the catalytic runs. The increase in conversion, as shown in Figure 2, appears to be due solely to increases in oil yield, while the PA&A and gas yields show no significant change from the thermal baseline. Increasing the iron concentration to 1.4 wt % showed minimal effect on total conversion for each precursor, however a slight increase in selectivity to oils was observed. As shown in Figure 3, in the case of the $Fe_{(1-x)}S$ and the SFIO precursors, slight decreases in the PA&A yield were also observed.

Liquefaction experiments were conducted at the low severity conditions to minimize thermal effects and to show more clearly the influence of the catalyst precursors. Further, since both the carbide and the oxide precursors transform to a sulfide phase under liquefaction conditions in a relatively short time, the longer reaction time used in the high severity experiments may have also obscured the distinctions between the catalyst precursors.

The results, shown in Figure 4, indicate that at the low severity conditions there are only minor differences in catalytic activity with precursor type for an iron loading of 0.7 wt %. The $Fe_{(1-x)}S$ showed the highest activity with a total conversion, 52.6 wt %, followed by SFIO at 52.2 wt %, Fe_7C_3 at 50.3 wt %, compared to a thermal conversion of 46.2 wt %. The increased conversions were mostly due to increases in PA&A, with little change in the oil or

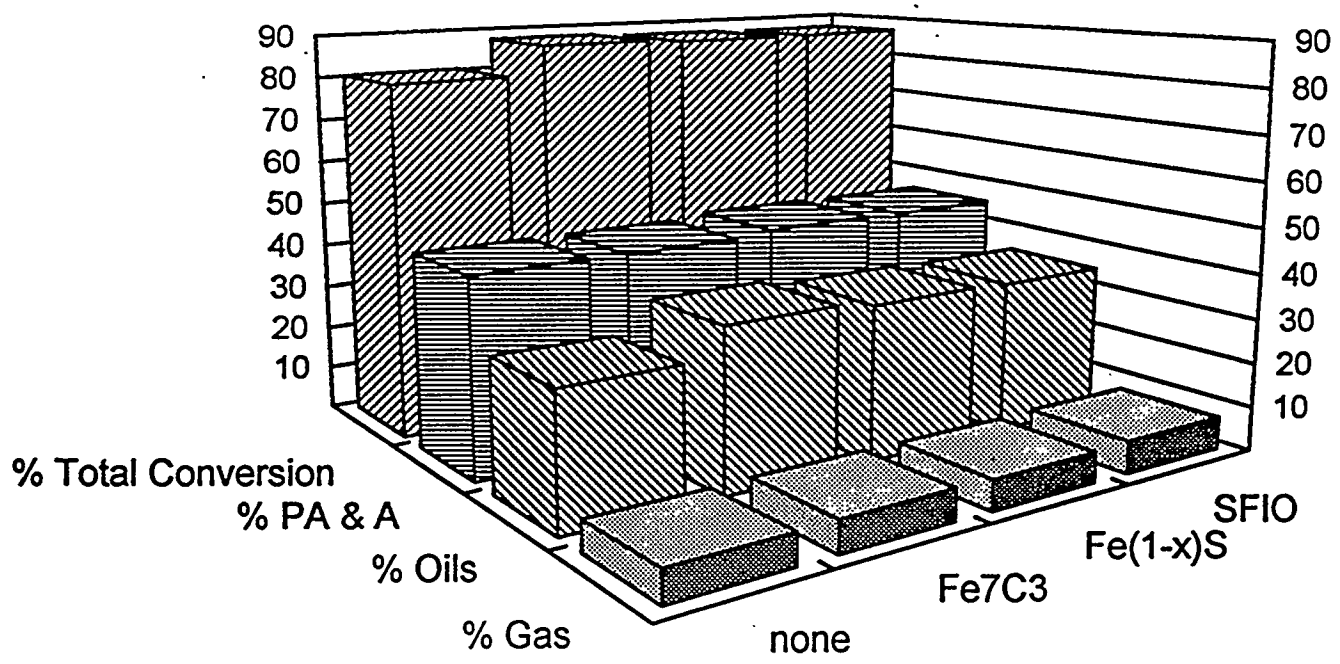

Figure 2. Effect of 0.7 wt% Fe Catalyst on Conversion at 415 C for 60 minutes

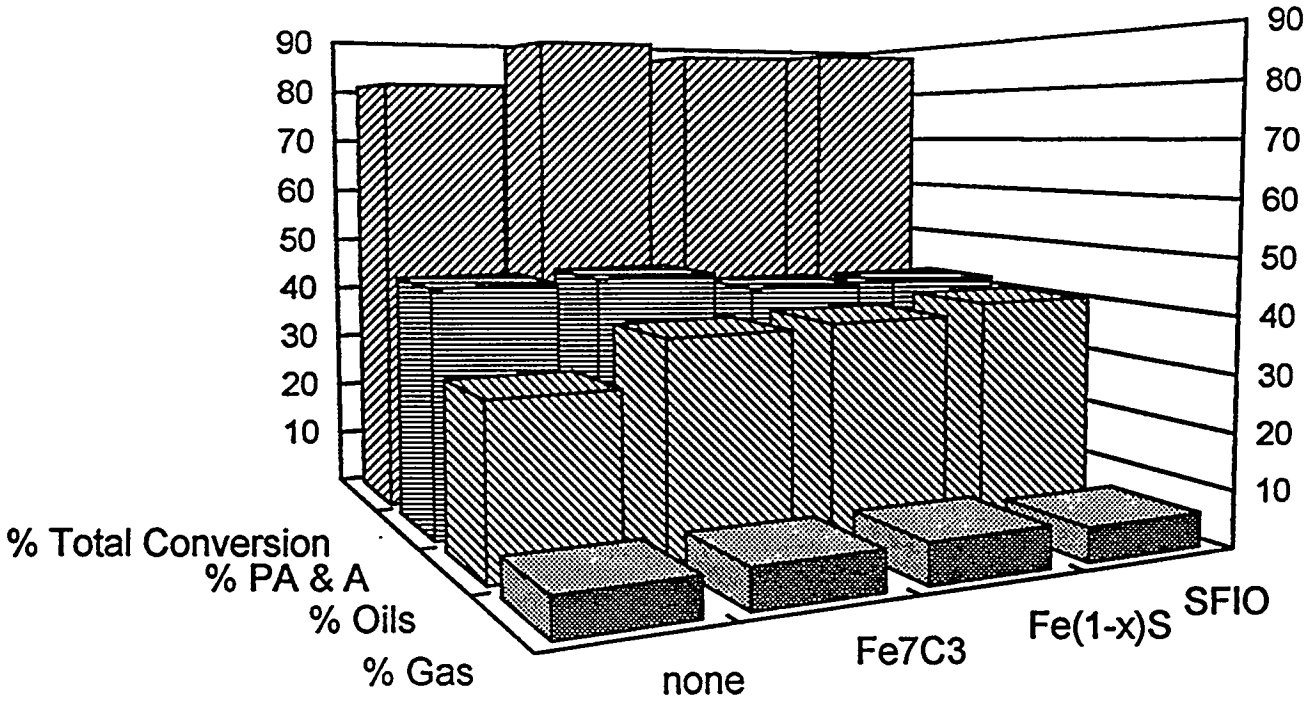

Figure 3. Effect of 1.4 wt% Fe Catalyst on Conversion at 415 C for 60 minutes

gas yields.

As the previous discussion indicate, all three iron-based precursors demonstrated very similar activities and selectivities, particularly at the high severity conditions. In contrast, the amount of hydrogen consumption showed a strong dependence on the phase of the catalyst precursor, particularly at high severity. Under low severity conditions, at a loading of 0.7 wt % Fe, the effect of precursor phase on the amount of total hydrogen uptake is minimal, each iron phase producing a similar increase over the thermal baseline. The total hydrogen consumption is calculated as the sum of the gas phase hydrogen consumption and the hydrogen liberated by tetralin dehydrogenation. Increasing the severity to 415 °C for 60 minutes produced a marked increase in the total hydrogen consumption, as shown in Figure 5. The $Fe_{(1-x)}S$ and Fe_7C_3 precursors showed similar behavior whereas the SFIO caused significantly higher hydrogen uptake.

The hydrogen consumed from the gas phase follows the trend thermal<Fe_7C_3 <$Fe_{(1-x)}S$ << SFIO while the solvent dehydrogenation followed the opposite, though less distinct, trend. The higher gaseous hydrogen consumption and lower solvent dehydrogenation indicates a higher hydrogenation activity for the SFIO. This is particularly interesting since the liquefaction yield data showed the effect of the three catalyst precursors to be nearly identical. It may be that thermal bond cleavage, rather than the availability of labile hydrogen, limited the total conversion, in which case hydrogenation activity would not be a significant factor.

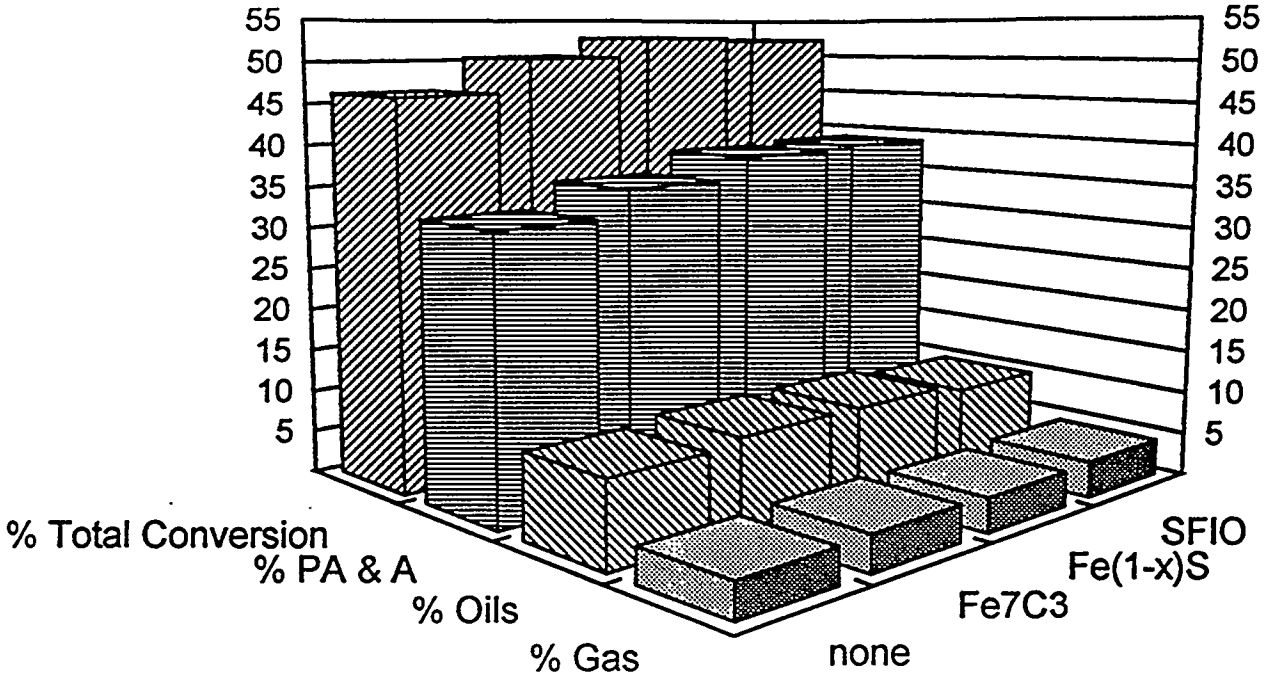

Figure 4. Effect of 0.7 wt % Fe Catalyst on Conversion at 385 C for 15 minutes

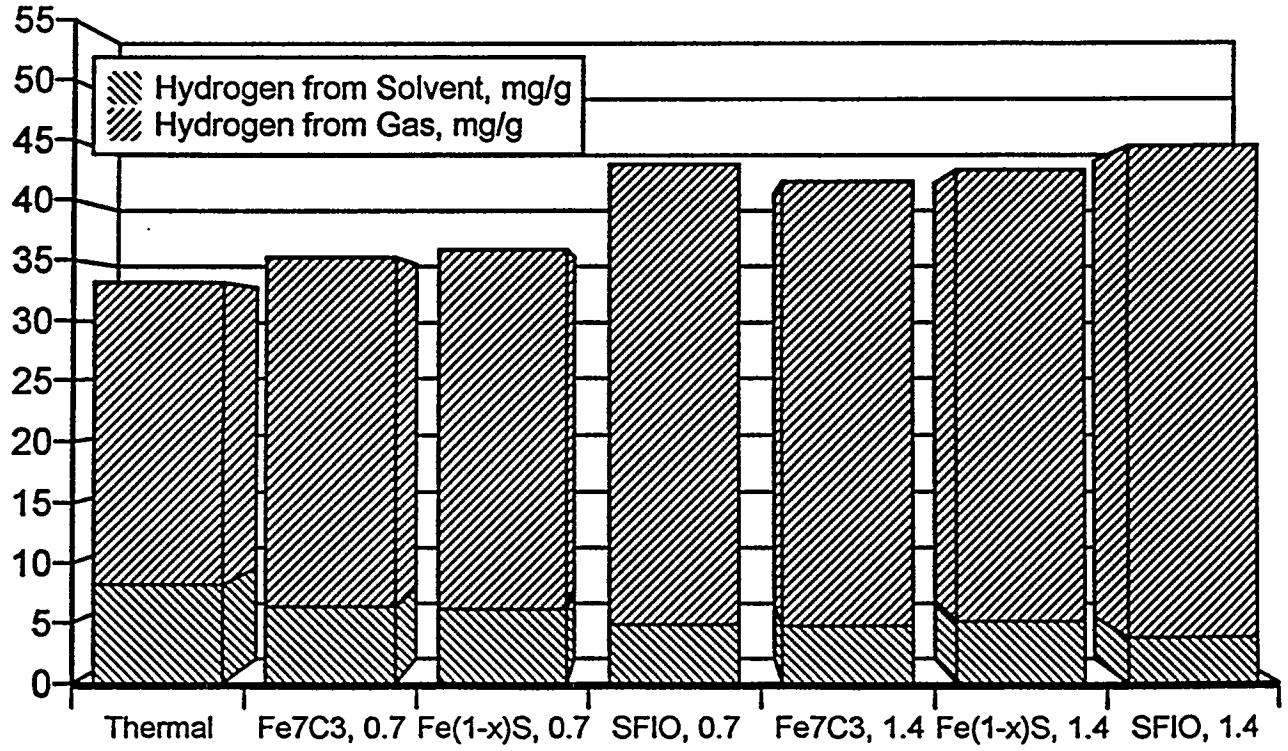

Figure 5. Effect of Catalyst on Hydrogen Consumption at High Severity

Increasing the iron concentration to 1.4 wt % has a significant impact on the total hydrogen consumption for the Fe_7C_3 and the $Fe_{(1-x)}S$ precursors bringing the values closer to that found for the SFIO, although the SFIO still causes significantly less solvent dehydrogenation, as shown in Figure 5.

The H/C atomic ratio for the PA&A fractions showed that the additional uptake of hydrogen with the SFIO precursor can, in part, be accounted for by its incorporation into these products. The increase in the H/C ratio with increasing SFIO concentration followed a trend similar to that of the total hydrogen consumption, as shown in Figures 6 and 7, respectively. A generally similar trend was observed for Fe_7C_3 precursor. This may be indicative of an increase in conversion from preasphaltenes to asphaltenes which was not discernable by the separation methods used in this study. However, the $Fe_{(1-x)}S$ precursor, at a catalyst loading of 1.4 wt % Fe, actually reduced the H/C ratio almost to that for the thermal reaction. Confidence in this data was high due to the fact that the runs were made in duplicate with a standard deviation of less than ±3.5%. Overall, it appears that these catalysts exhibit differences in hydrogenation activity that are not reflected by product yields. It seems reasonable to assume that the effects may then be realized as improvements in the quality of the coal liquids.

The final phase of iron-based catalysts in a coal liquefaction process is usually pyrrhotite, provided that sufficient sulfur is present to allow that transformation. As previously noted,

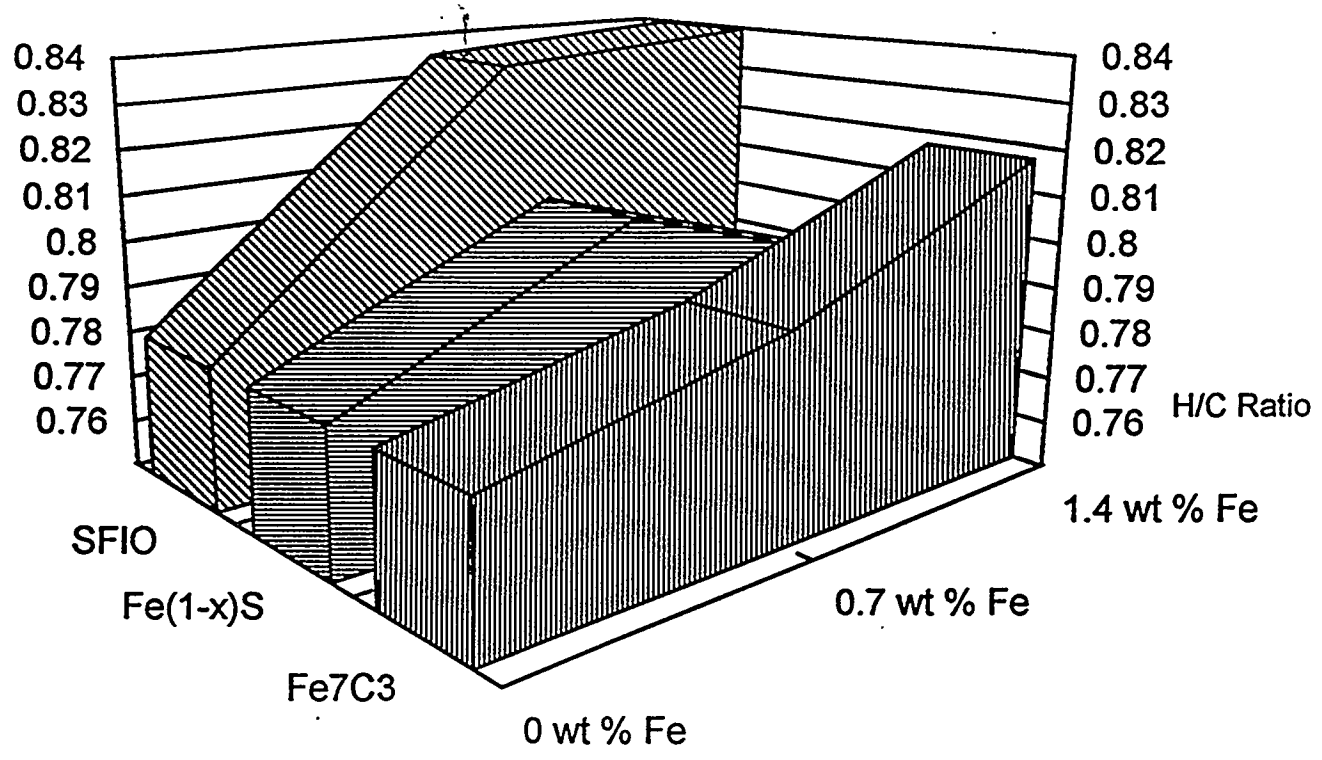

Figure 6. Effect of Catalyst Concentration on H/C ratio of PA&A fraction from high severity liquefaction experiments

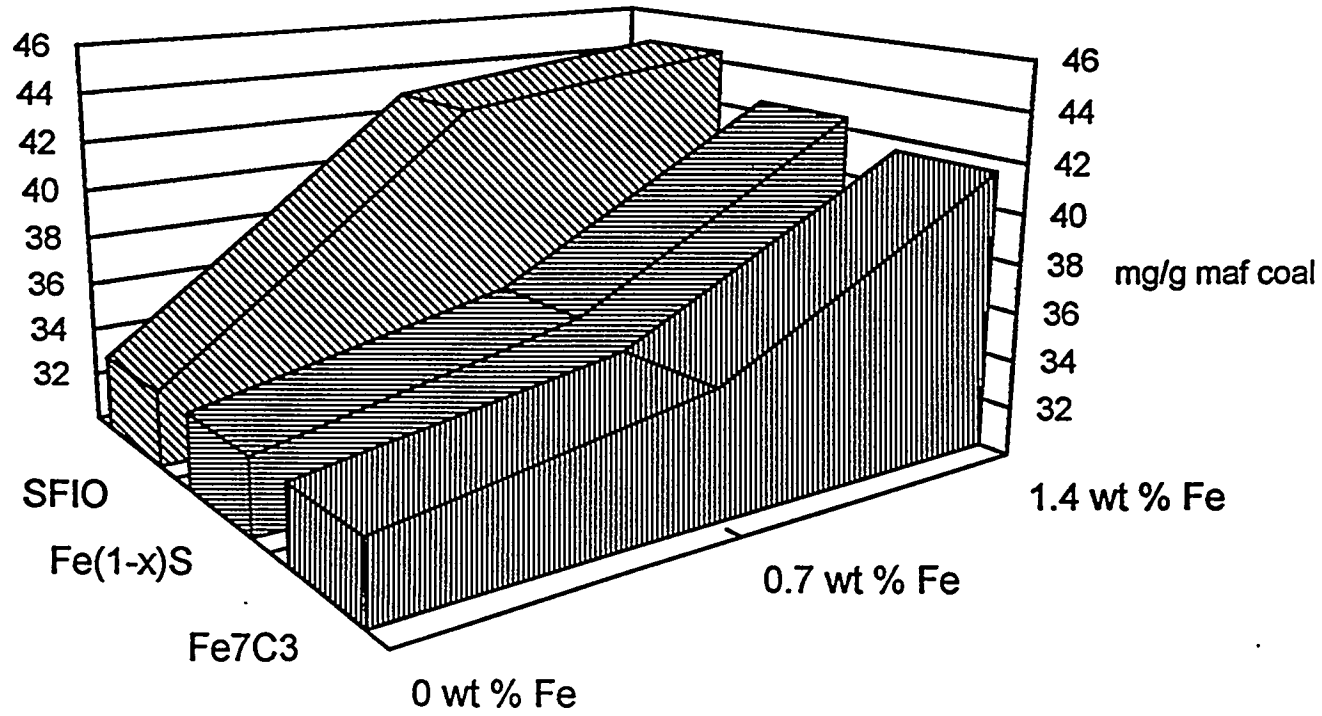

Figure 7. Hydrogen Consumption as a Function of Catalyst Concentration

the conversion of the carbide phase occurs within 30 minutes at 385 °C. The conversion of the catalyst precursor may occur by reduction of the surface oxide or carbide followed by sulfidation of the reduced iron sites [11]. The sulfur could then diffuse into the interior of the particle as the internal oxygen or carbon diffuses to the surface where it reacts with hydrogen. Since the activity of the particles is associated with active sites located on the external surface and the initial formation of a sulfided surface is expected to be very rapid, this may explain why the three precursors produced similar effects and why the sulfide precursor was no more effective than the oxide and carbide. Further, the activity of the SFIO precursor for solvent hydrogenation is significantly higher than the $Fe_{(1-x)}S$ precursor which was in turn slightly higher than Fe_7C_3 precursor. Particularly for the high severity conditions, the difference in hydrogenation activity is probably related to the surface area, rather than the phase, of the precursor.

A study by Stohl [22], which reported that the surface area of the precursor did not correlate with conversion, agrees well with the findings of this study. However, this work suggests that the surface area, or particle diameter, has a significant effect on hydrogenation. The relation between solvent dehydrogenation and surface area, shown in Figure 8, indicates that, particularly at high severity conditions, there is an inverse relationship. Similarly, Figure 9 indicates an inverse correlation between the total hydrogen consumption and the particle diameter with higher hydrogenation activity relating to particle diameter, or surface area. There is either increased utilization of molecular hydrogen, or more effective solvent rehydrogenation, or both.

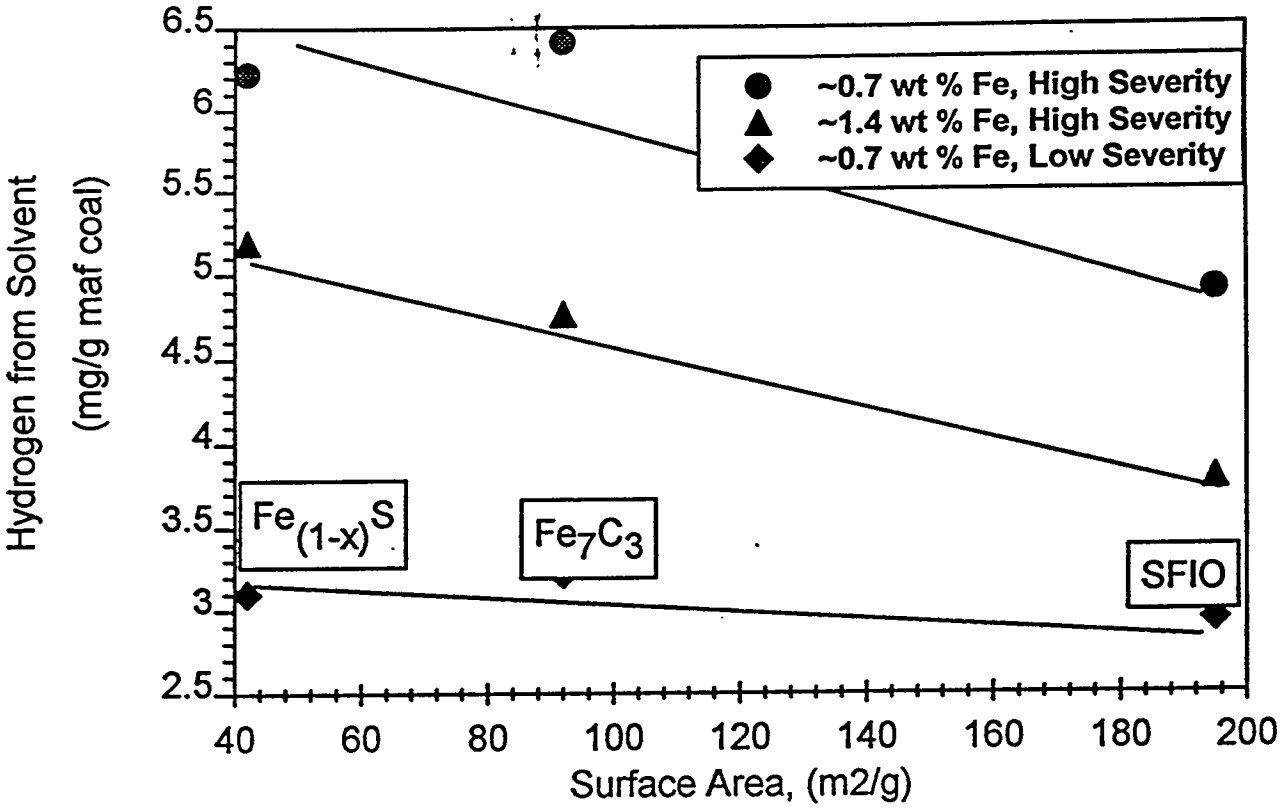

Figure 8. Effect of Surface Area on Solvent Dehydrogenation

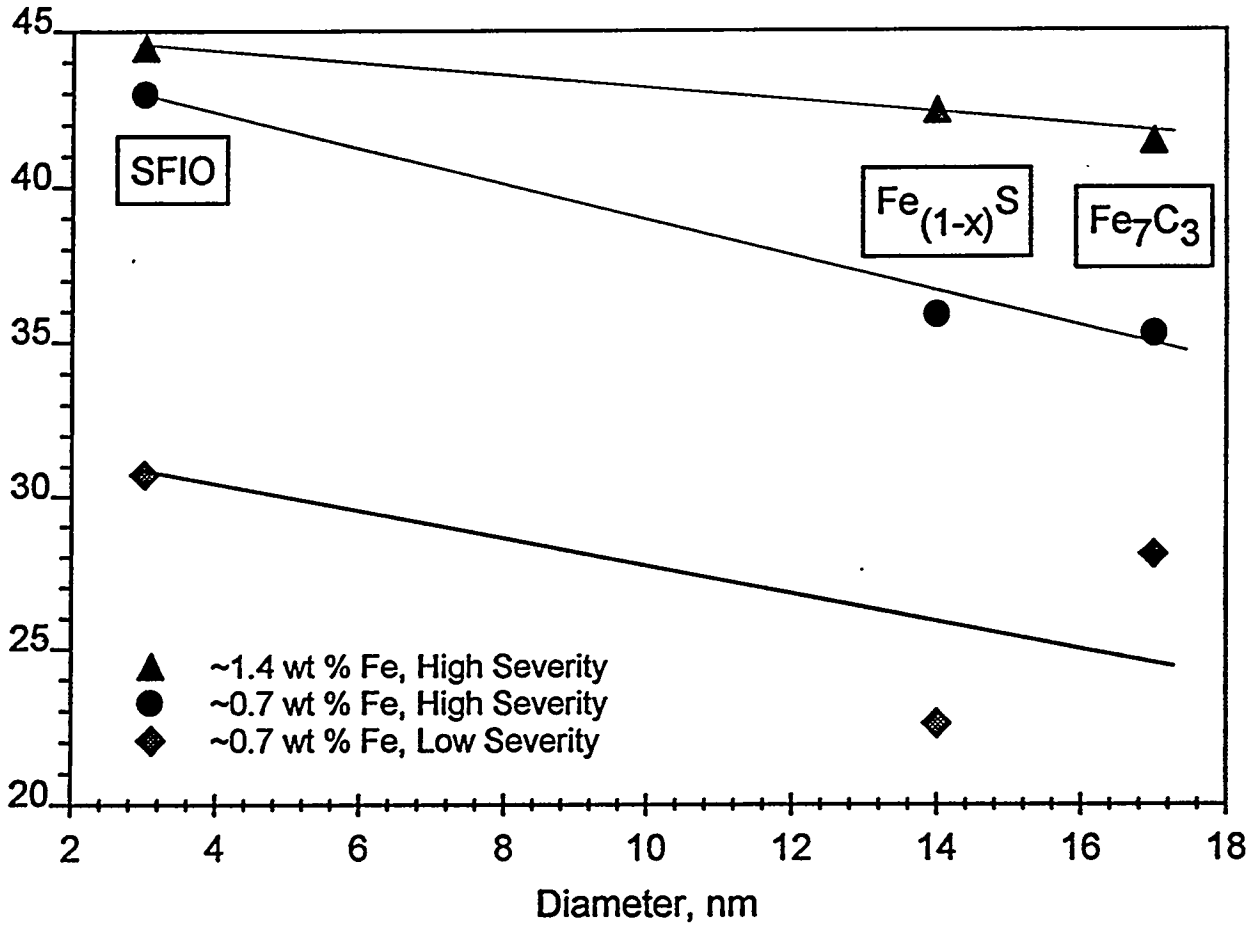

Figure 9. Effect of Particle Diameter on Total Hydrogen Consumption

The specific surface area, defined as the surface area per 100g maf coal, may provide a measure of the catalytic sites available for reaction with the coal. Using this number, a plot for all experiments conducted at high severity was constructed, as shown in Figure 10. The total hydrogen consumption increases rapidly at low specific surface areas followed by a plateau at higher values, suggesting a saturation condition above which increasing the catalyst concentration produces minimal benefit, which could explain the greater effect of increasing the catalyst loading for $Fe_{(1-x)}S$ and Fe_7C_3 compared to SFIO, as shown in Figure 5. The higher specific surface area of the SFIO precursor results in attainment of the saturation level at lower concentrations.

Conclusions

The three catalyst precursors tested in this study, Fe_7C_3, $Fe_{(1-x)}S$, and SFIO, demonstrate very similar activity with respect to the conversion of a subbituminous coal. At low severity the primary effect of 0.7wt % Fe catalyst loading was represented by a slight (4-6 wt %) increase in total conversion, which was mostly related to an increase in the PA&A yield. At high severity, the same catalyst loading resulted in a 6-7 wt % increase in total conversion, associated almost exclusively with an increase in oil yield and showing an improvement in catalyst selectivity, as well as activity for conversion. Doubling the catalyst concentration to 1.4 wt % Fe resulted in only minor changes to conversion, but effected some increase in selectivity to oils, particularly for the SFIO and $Fe_{(1-x)}S$ precursors.

The effects of the different catalyst precursors on hydrogen consumption from the gas phase

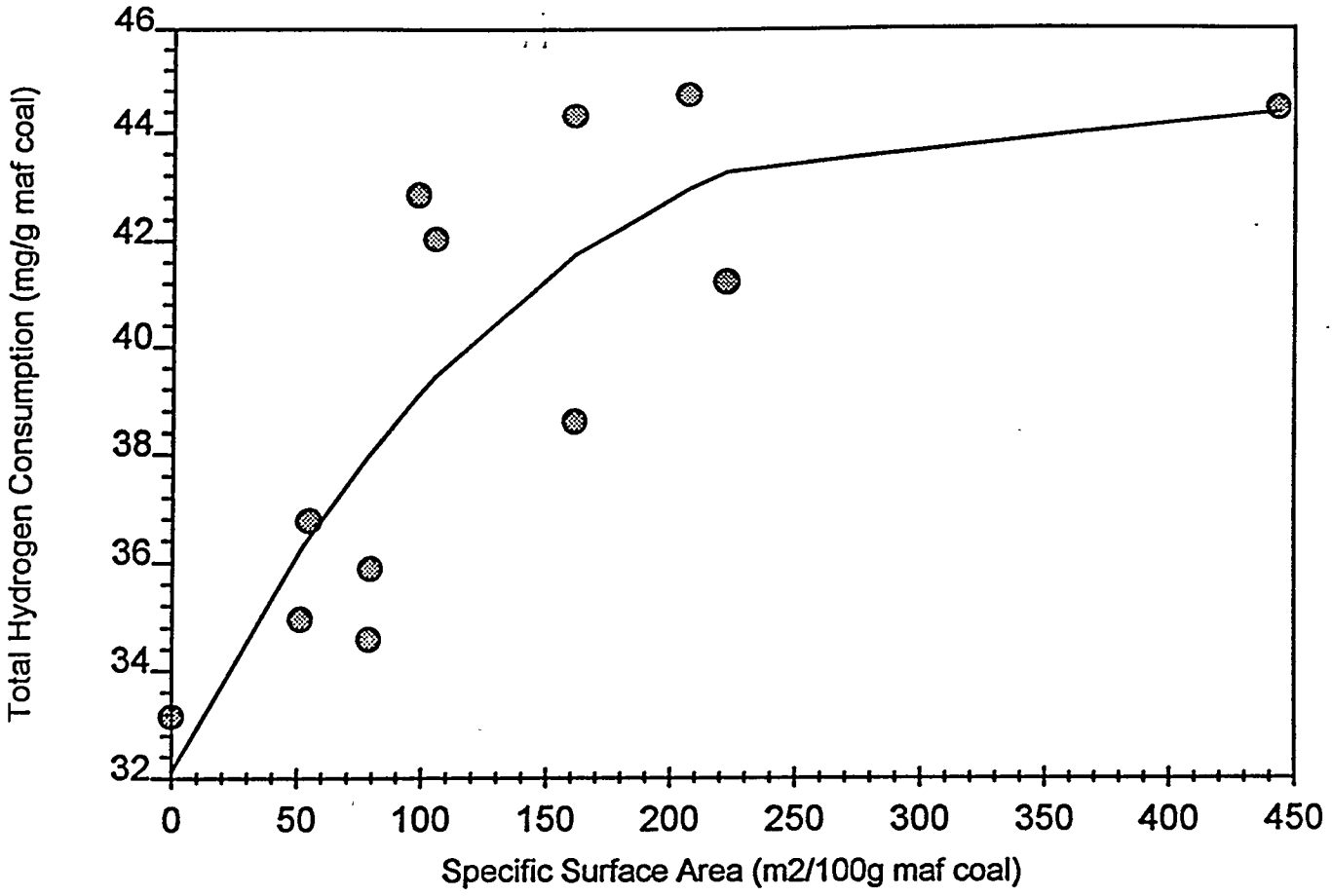

Figure 10. Effect of Specific Surface Area on Hydrogen Consumption

and on the extent of solvent dehydrogenation were more pronounced. Under high severity conditions, at a catalyst loading of 0.7 wt % Fe, the total amount of hydrogen consumed followed the trend thermal<Fe_7C_3<$Fe_{(1-x)}S$<<SFIO. The amount of hydrogen consumed from the gas phase followed a similar trend while the amount of solvent dehydrogenation followed the opposite, though much less distinct, trend. The increase in hydrogenation activity correlates well with precursor particle diameter or surface area suggesting that the differences in activity may be more related to these parameters than to the phase of the catalyst precursor.

An increase in catalyst concentration to 1.4 wt % further increased the total hydrogen consumption but narrowed the gap between the SFIO and the other two precursors. This result may be explained on the basis of an approach to a saturation of the specific surface area of catalyst available for reaction. As this plateau is approached, increasing the catalyst loading realizes minimal additional benefit.

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Chapter 5
Promoted Sulfated Hematites

Background

The utility of iron based particulate catalyst for coal liquefaction has been well known for the better part of this century. These catalysts have been shown to be particularly useful in the processing of low rank coals. Early liquefaction research used molybdenum based dispersed catalysts in the first stage [1]. However, the high cost of molybdenum lead to the development of iron based catalysts. It was found that a low cost iron ore, a byproduct from aluminum production, was very active at concentrations of 2 wt% on coal.

Current research has focussed on ways to improve the activity of the iron based catalysts while maintaining a low cost. Improving the dispersion of the catalyst thereby improving the contact with the coal is one method to improve the catalyst activity. This may be done by reducing the particle size of the dispersed catalyst. It has been proposed that sufficiently small particles may exhibit significantly different properties compared to the bulk phase, particularly with regard to surface energetics. Another technique which has been investigated to improve the activity of the iron based catalysts is the chemical modification of the surface. The sulfated hematite catalyst represents a combination of both approaches.

The first reported use of sulfated hematite catalysts for coal liquefaction was reported by Hattori and co-workers in the late 1980's[2]. The notation Fe_2O_3/SO_4^{2-} does not represent a stoichiometric relationship between the iron oxide and the sulfate group. Rather the catalyst

may be seen as hematite with SO_3 chemisorbed on the surface. The particles, synthesized by a simple aqueous precipitation technique, were reported to have surface areas of ~50 m^2/g and an average diameter of 5 μm. X ray diffraction (XRD) studies of the catalyst revealed an amorphous structure.

Hattori and co-workers reported the activity of the sulfated hematite to be higher than that of a molybdenum on titania catalyst for the liquefaction of a low sulfur bituminous coal. Previous studies had found that the addition of the sulfate group to the hematite increased the dehydration of 2-butanol by a factor of 300 - 2000 compared to the unsulfated hematite[2]. Other reactions also known to be catalyzed by acids responded favorably to the addition of the sulfate group. This led to the conclusion that the high activity of the sulfated hematite for coal liquefaction was due to the acidic nature of the sulfate group on the surface, as shown in Figure 1. This early study already recognized that the sulfate group may change under liquefaction conditions. While the catalyst was very stable in air at 500 °C it was readily reduced in the presence of hydrogen.

Interest in the catalytic properties of the sulfated hematite for coal liquefaction led to further research. Several studies were undertaken which showed the high activity of this catalyst for both lignites and bituminous coals[2 3 4 5]. These studies again related the activity of the sulfated hematite to increased acidity. However, Pradhan and co-workers [6] reported similar high activity but proposed that increased dispersion was more important than increased acidity. An average particle diameter of ~ 20 nm and a surface area of ~ 80 m2/g were reported. The

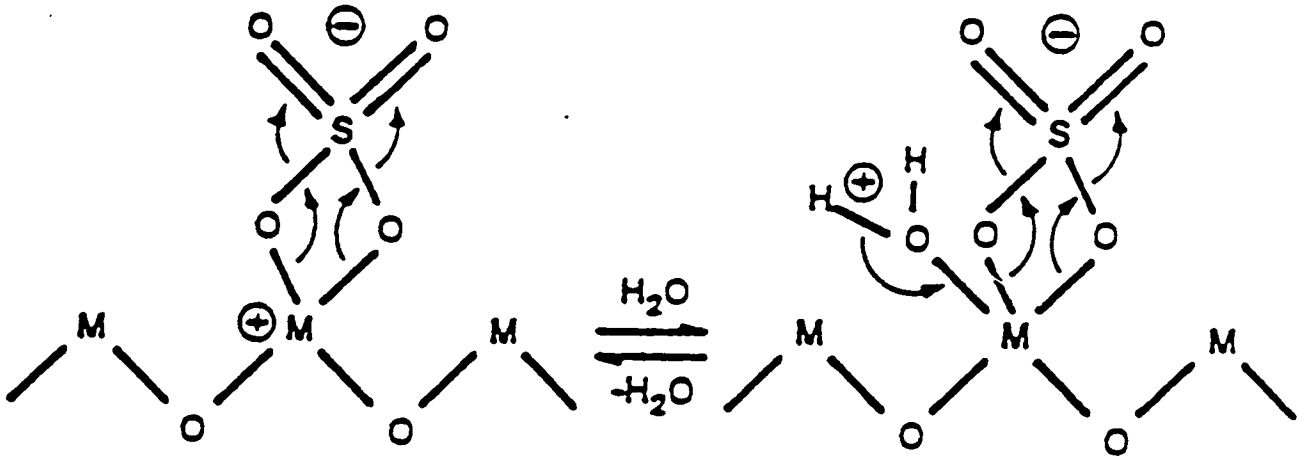


Figure 1. Transformation of Lewis acid site to Bronsted acid site.

larger particle size reported by Hattori and co-workers was probably due the agglomeration of the nanoscale particles into micron size clusters.

The importance of sulfur to the activity of iron oxide catalysts is well known [7]. Pradhan and co-workers [6 8] demonstrated that the sulfated hematite followed a similar trend. It was found that in the presence of additional sulfur both sulfated and unsulfated hematites achieved very high conversions. However, use of the sulfated hematite resulted in substantially higher oil yield compared to the unsulfated catalyst. XRD analysis of the spent catalyst revealed that the sulfated hematite had transformed to pyrrhotite ($Fe_{1-x}S$, $x<0.125$) with trace amounts of FeOOH and Fe_3O_4. It was found that the average particle diameter of the sulfated hematite had increased only slightly to ~30 nm. From this it was concluded that the addition of the sulfate group resulted in a smaller particle size and, consequently a higher dispersion. The role of the acidity was believed to be transient.

The use of promoter metals on the sulfated hematite has also been investigated [9],[6],[10]. The use of molybdenum as a promoter metal was shown to improve the activity of the sulfated hematite for both coal liquefaction and coprocessing of coal with a petroleum resid. Molybdenum was added to the catalyst at concentrations up to 2 wt%. X ray photoelectron spectroscopy (XPS) analysis of the promoted catalyst indicated that both sulfur and molybdenum are preferentially adsorbed on the surface of the particle [11]. Further these studies showed the sulfur exists as SO_4^{2-} while the molybdenum is present as MoO_3. However, extended X-ray absorption fine structure spectroscopy (EXAFS) studies of the

particles conclude that the molybdenum is present as MoO_4^{2-} [12].

The promoted catalyst displayed a higher activity than the unpromoted sulfated hematite [9]. Similar loadings of a combination of oil soluble molybdenum carbonyl and iron carbonyl yielded lower activity than the molybdenum promoted sulfated hematite. Again it was concluded that the high activity was due primarily to the small particle size rather to the transient acid sites. It was also hypothesized that the sulfate group aids in preventing sintering or agglomeration of the catalyst thereby allowing the catalyst to maintain its high dispersion for extended periods. This study also reported that, while the iron increased conversion only, the hydrogenation properties of the molybdenum increased both the conversion and the hydrogen content of the liquid products.

The promising results of these studies served as the motivation for consideration of this type of particulate catalyst in this project. The high activity achieved at low promoter loadings suggested that it may be possible to improve the conversion while reducing the catalyst cost relative to the base case. Other promoter metals, such as nickel, cobalt, and tungsten, may also serve to improve the activity of the sulfated hematites at lower cost than the molybdenum. Combinations of promoter metals, such as nickel-molybdenum, which show synergistic activity on a supported catalysts may have similar effect on the sulfated hematite.

Catalyst Synthesis

The catalysts utilized in this study were produced using a aqueous precipitation of an iron salt

in the presence of a source of sulfate ions. In this project, urea was employed to effect the precipitation of ferric ammonium sulfate (iron alum), following the method of Kotanigawa et al.(3). The procedure involved the addition of 25 g of urea and 17.5 g of iron alum ($NH_4Fe(SO_4)_2 \cdot 12\ H_2O$) to 500 ml of distilled deionized water. The solution was heated to ~95°C with constant stirring for ~2 hrs. The elevated temperature caused the thermal decomposition of the urea releasing ammonia and carbon dioxide. During this time the pH of the solution increased from an initial value of ~2- to ~7 indicating completion of the reaction.

The precipitate was removed from the solution by vacuum filtration and washed with excess distilled deionized water to remove any unbound sulfate ions. The filter cake was dried in an air flow oven overnight at 100°C and then dried in a vacuum oven at 70°C for 2 hrs. While the original procedure required the particles to be calcined at 500°C for 1 hr, XRD spectra indicated that, for the small samples generated by this technique, calcining at 475°C for 15 minutes was sufficient to achieve complete conversion.

Promoter metals may be introduced by the addition of metal salts to the solution. Molybdenum was added, as ammonium molybdate, at varying concentrations to produce Mo-promoted sulfated hematites with a range of Mo concentrations up to 10 wt% of iron. Higher loadings were not considered to be economically viable and were therefore not produced. Several other metals, including tungsten (ammonium tungstate), nickel (ammonium nickel sulfate), and cobalt (cobalt sulfate) were also added by this method. In addition, the procedure may be modified to add multiple promoter metals. Several doubly-promoted

sulfated hematites have been produced by this technique: nickel/molybdenum, cobalt/molybdenum, and tungsten/molybdenum.

The catalyst particles produced in this study were characterized, both before and after calcining, by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and nitrogen BET adsorption., and elemental analysis.

Characterization

The particles were analyzed by XRD to determine their major phase and also to allow an estimation of the crystallite diameter. As shown in Figure 2, the spectrum for the as-formed particles indicates that they were not very crystalline. The principle phase was tentatively identified as α-FeOOH (goethite) although traces of α-Fe were also present. Due to the poor crystallinity associated with these samples, estimations of the particle diameters from these spectra are suspect. The addition of the various promoter metals showed no effect on the phase identification.

After calcination the particles clearly exhibit the spectrum of α-Fe_2O_3 (hematite) with traces of α-Fe still present (Figure 3). The improved crystallinity of the calcined particles allowed the estimation of particles diameters using the Debye-Scherrer relationship. Average particle diameters estimated by this method were in the range of 10-25 nm. There was no apparent

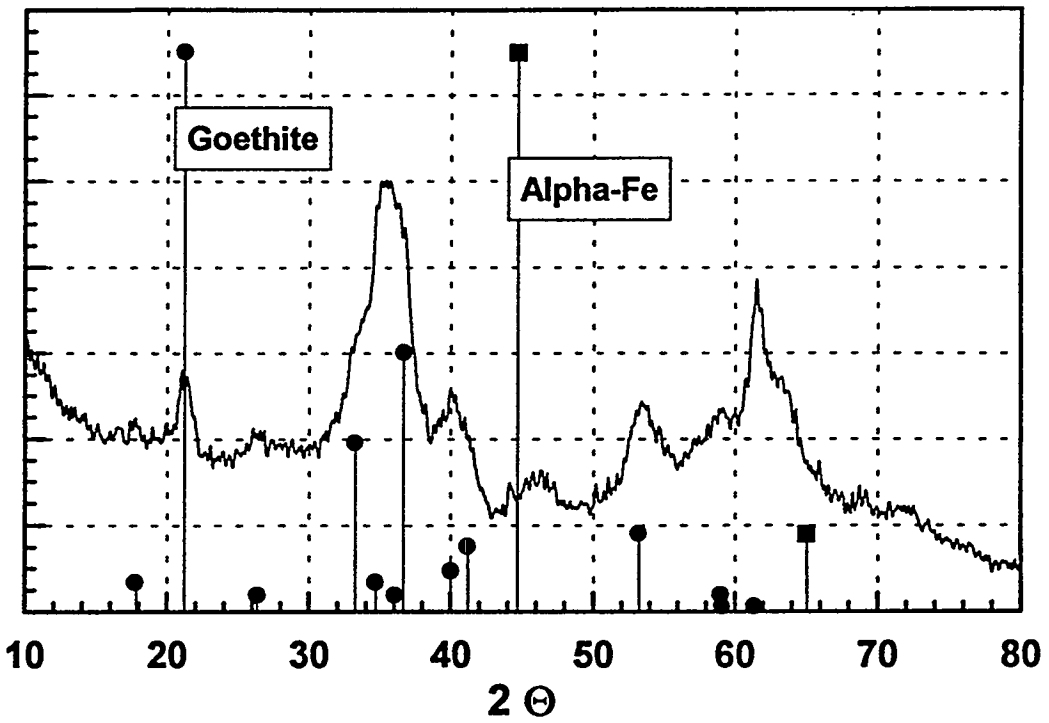


Figure 2. XRD Spectra of as-formed catalyst, goethite and alpha iron

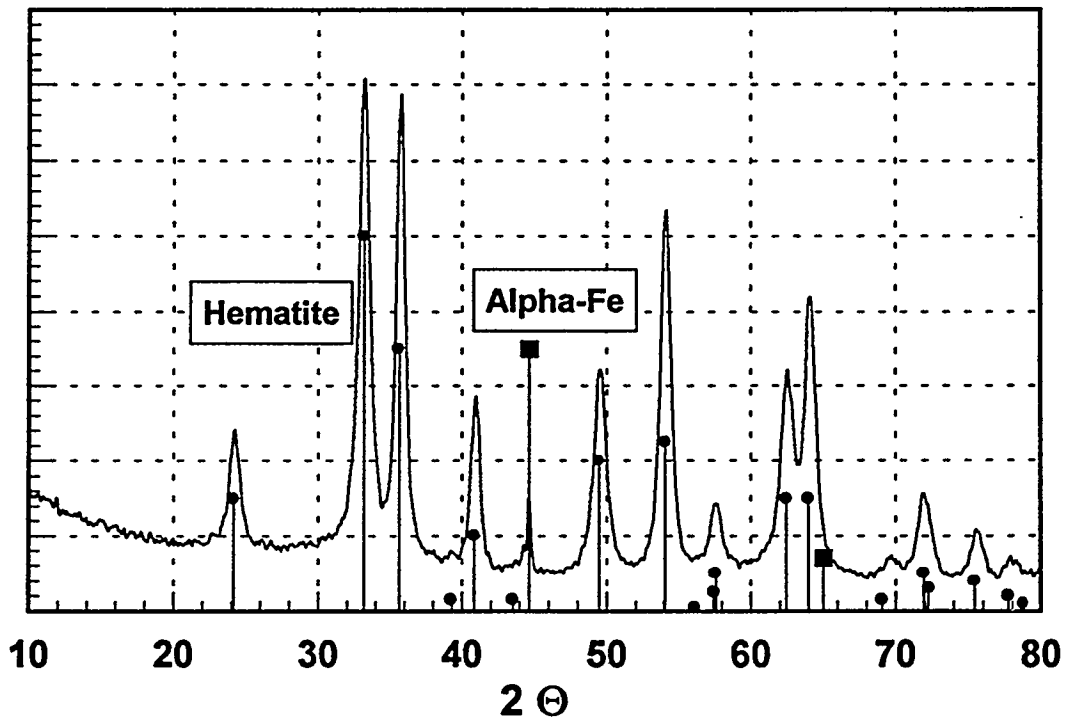


Figure 3. XRD Spectra of calcined catalyst, hematite and alpha iron

impact if the promoter metal on the phase identified by XRD, even at 10 wt% loading, indicating that the promoters were either included in the iron matrix or were present in an amorphous phase. Similarly there was little effect on the size of the particles other than a possible decrease in particle size with increasing molybdenum concentration. However, as shown in Figure 4, due to the error associated with this measurement technique, this trend is rather dubious.

The calcined particles were examined using both scanning and transmission electron microscopy (SEM,TEM). Figure 5 shows a typical SEM micrograph indicating that the particles exist as loose agglomeration of very small particles below the resolution of the instrument. These agglomerated masses were on the order of 1 μm in diameter, which corresponds well with the sizes given for these particles in the early literature[2]. However closer observation utilizing TEM show that the particles are acicular in shape with sizes of ~10x50 nm (Figure 6). Due to the agglomeration, size distributions from the TEM micrographs were not obtained.

Elemental analysis showed that the sulfur content of the precipitated particles was in the range of 2 to 6 wt%. Calcination of the particles had little effect on the sulfur content other than a slight increase in concentration resulting from a loss of water. However, the addition of other metals caused a decrease in sulfur content. In the case of molybdenum, the sulfur content was inversely related to an increase in the promoter concentration, as shown in Figure 7. Previous studies, which reported that the sulfur was present primarily on the surface, were confirmed by

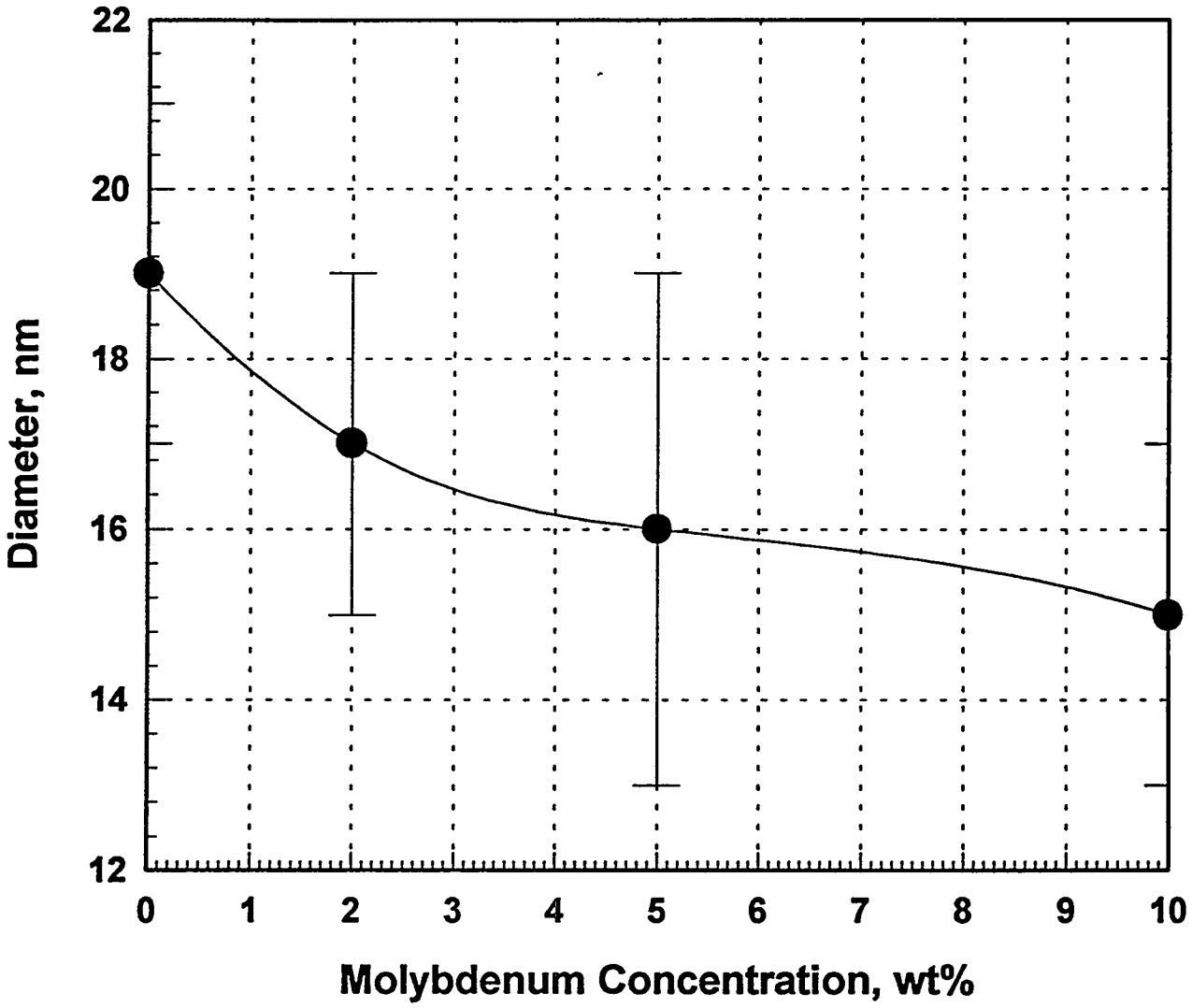


Figure 4. Effect of molybdenum concentration on particle diameter estimated from XRD

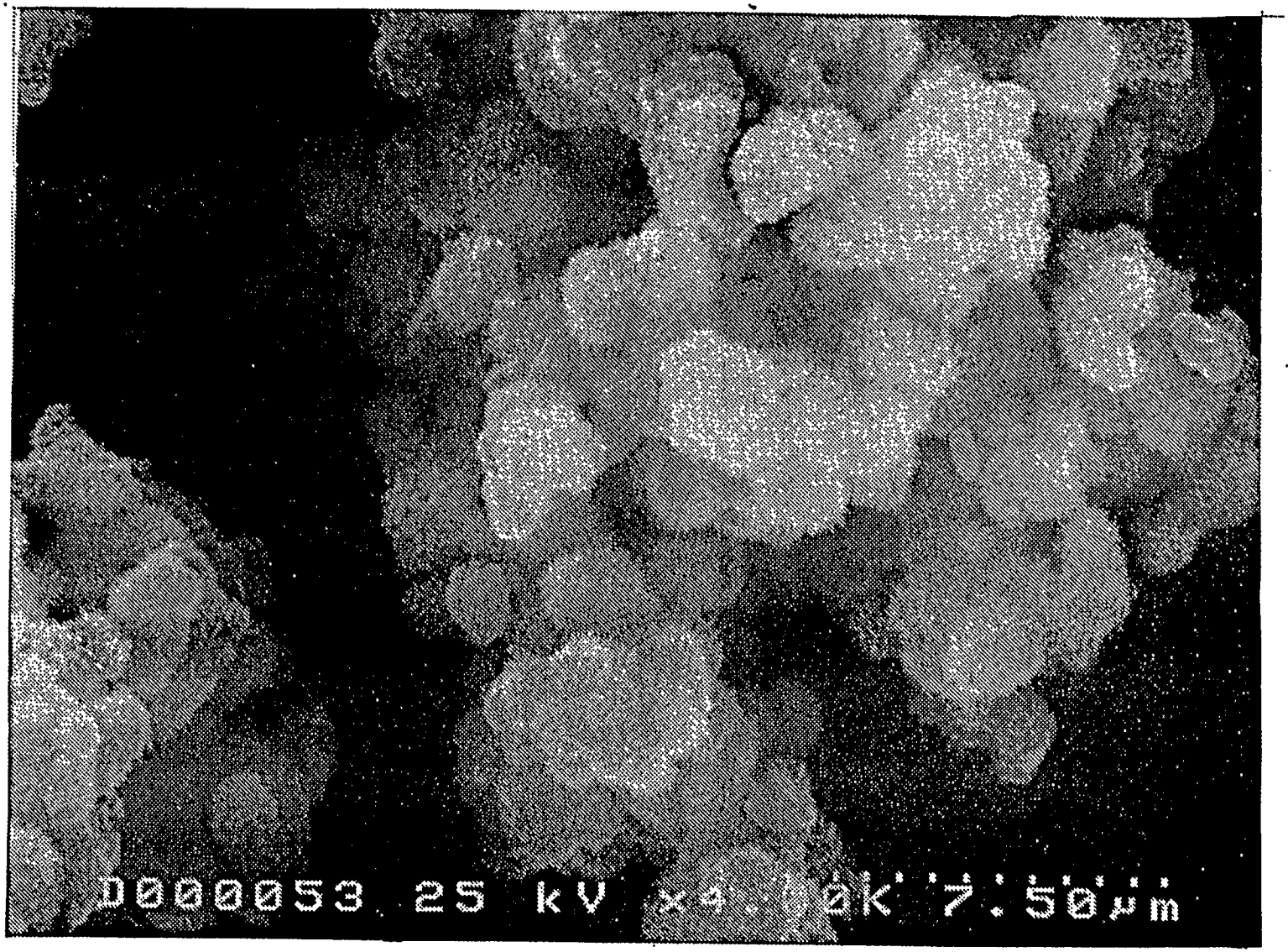


Figure 5. SEM micrograph of sulfated hematite particles.

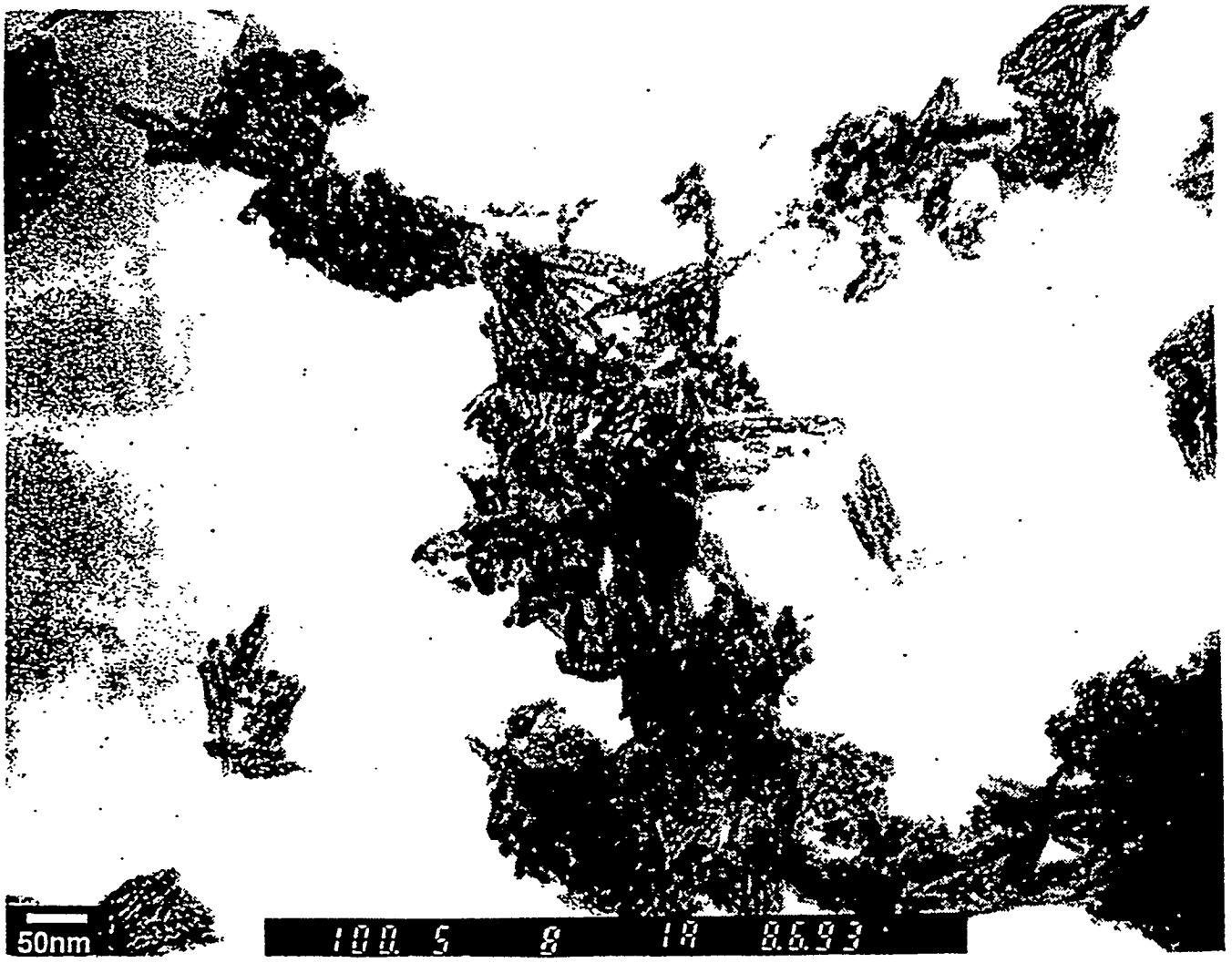


Figure 6. TEM micrograph of sulfated hematite particles.

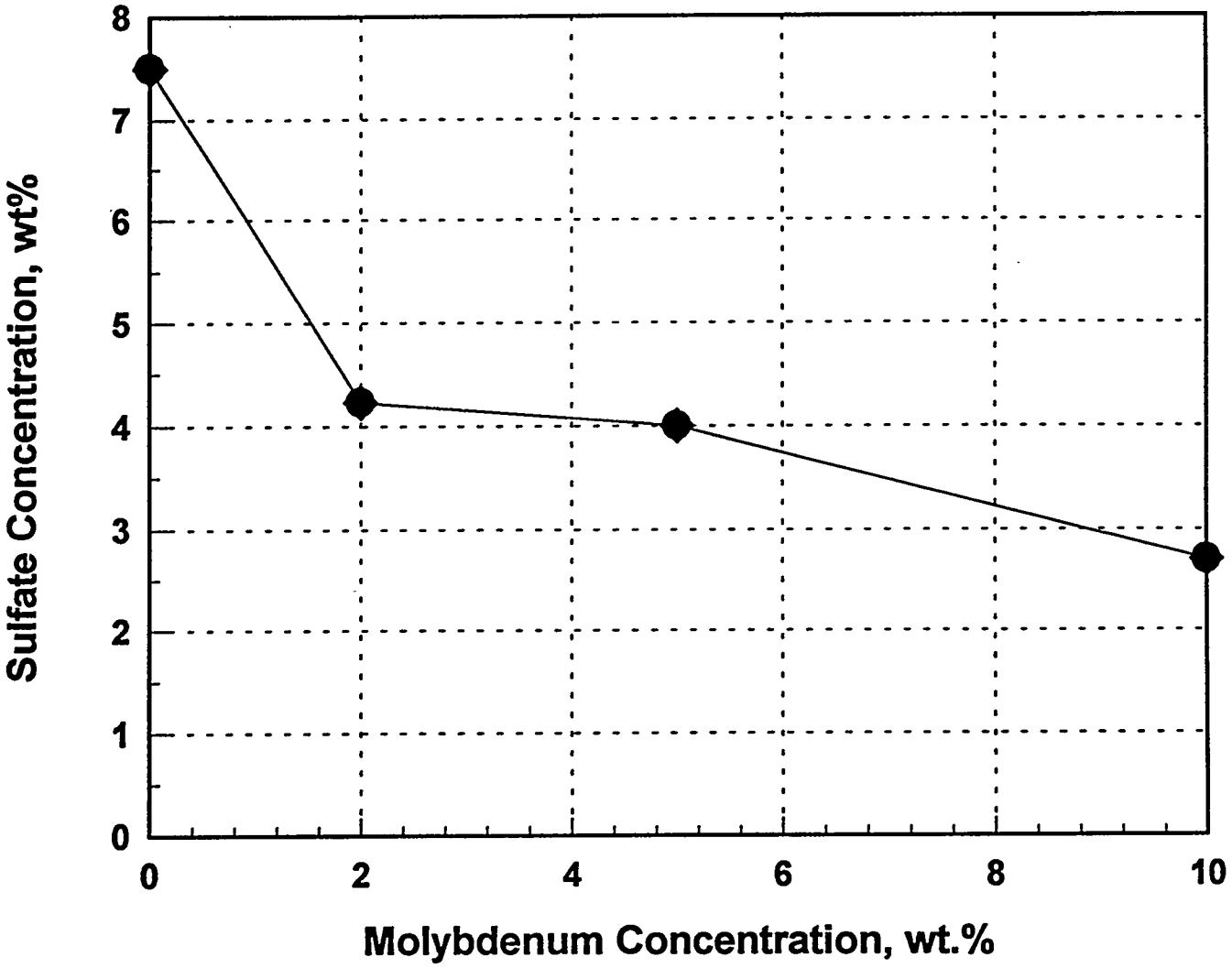


Figure7. Effect of molybdenum concentration on sulfate concentration

XPS analysis[6] Similarly, it had been reported that the molybdate ions were located primarily on the surface of the particles, possibly serving to displace the sulfate ions. This suggestion is consistent with data obtained in this study. Since the sulfur, molybdenum, and tungsten are all in their hexavalent coordination state, it would seem reasonable to expect the tungsten to also exist preferentially on the surface as tungstate ions. The results of XPS studies tend to support this hypothesis.

These results also indicate that the nickel and cobalt show similar bulk and surface concentrations. Table 1, which shows an analysis of a nickel/moly on sulfated hematite, clearly indicates that the surface concentrations of the sulfur and molybdenum are significantly higher than the bulk concentration while the nickel concentrations are the same, within experimental error. It is well known that for iron oxides and oxyhydroxides, isomorphous substitution with other metals may occur in which the Fe^{3+} in the octahedral sites may be partially replaced by similar size metals in the same oxidation state[13]. This substitution may occur without modification of the structure so that the XRD pattern will display only slight shifts in peak position.

Table 1. Comparison of bulk and surface concentrations of promoter metals on sulfated hematite.

Element	Bulk wt%	Surface wt%
Molybdenum	4	7.5
Nickel	2.3	2.5
Sulfur	2.7	4.7

The nickel and cobalt were not as easily incorporated into the sulfated hematite as the molybdenum and tungsten using this precipitation technique. For the calculated value of 5 wt % metal loading on iron, the nickel concentration, determined by elemental analysis, was only 1.4 wt %. Similarly, for the same calculated value, the cobalt concentration was measured at only 2.5 wt %. However, the molybdenum and tungsten showed the similar values for both calculated and measured metal concentration. This indicates that a portion of the nickel and cobalt were not incorporated in the catalyst and were removed with the filtrate and wash water.

Surface areas were calculated from nitrogen adsorption isotherms using the BET method. These measurements showed the particles to have surface areas in the 100-200 m2/g range. Since iron oxides have no internal porosity, the whole of this surface area is associated with the external surface, and should be available for reaction.

Model Compound Studies

The chemical structure of coal is very complex, consisting of complicated aromatic ring structures linked by alkyl as well as heteroatom bridge linkages. The primary heteroatoms in coal are oxygen, sulfur, and nitrogen. Because these heteroatoms can act as catalyst poisons, one of the goals of coal liquefaction is to break the heteroatom linkages, followed by

heteroatom removal. This is accomplished by reacting the coal at high temperatures in the presence of hydrogen. The process of nitrogen removal is termed hydrodenitrogenation (HDN). Similarly, oxygen and sulfur removal are termed hydrodeoxygenation (HDO) and hydrodesulfurization (HDS), respectively.

As mentioned previously, the structure of coal is very complex. Therefore, it is quite difficult to determine the effect of the catalyst on the liquefaction process. For this reason, model compounds are utilized. A model compound is one which contains a functional group present in coal, and is used as a representative for different coal structures. By using model compounds, one can more easily determine the effect of different catalysts for reactions similar to those encountered in a coal liquefaction process. It may then be possible to predict the response of coal liquefaction reactions to the catalyst.

For this research project, model compounds used were naphthalene to represent polyaromatic hydrocarbons, diphenylether to represent etheric linkages, benzothiophene to represent sulfur containing linkages, and quinoline to represent nitrogen containing linkages. The purpose of the project was to determine the effect of various promoter metals on the activity of an iron-based catalyst.

The synthesis and characterization of the catalysts have been described in detail earlier. The catalytic activity of several catalysts were examined. An unpromoted sulfated hematite was utilized as a base case for this type of catalyst. The effect of promoter metals nickel, cobalt,

and molybdenum, on the activity of the sulfated hematite could then be determined. Table 2 shows the elemental composition of the catalysts used in the model compound experiments.

Table 2. Elemental analysis of promoted sulfated hematite catalysts.

Catalyst	Ni	Co	Mo
Ni Promoted	2.0	0	0
Co Promoted	0	1.8	0
2% Mo Promoted	0	0	2.2
8% Mo Promoted	0	0	8.0
Ni/Mo Promoted	0.6	0	1.0
Co/Mo Promoted	0	0.4	0.9

Experimental

Model compound reactions were carried out in stainless steel, horizontal microautoclave reactors with volumes of approximately 20 ml. Model compounds were added to the reactors as a 5 wt% solution of the model compound in hexadecane. The model compounds utilized in this study were naphthalene, diphenylether, benzothiophene, and quinoline. In addition to 5 g of the model compound/hexadecane solution, 0.0125 g of catalyst and 0.0176 g of dimethyldisulfide (DMDS), a sulfiding agent, were added to the reactor. Elemental analyses of the catalyst used in this study are shown in Table 2. The reactors were sealed and then purged and pressurized to 800 psig with H_2. All reactions were carried out at 380 °C in a heated fluidized sand bath in which the reactors were vertically agitated at 400 cycles per minute. All model compounds were tested with each catalyst, and run times ranged from 5-60

minutes.

At reaction completion, each reactor was cooled to room temperature in a cool fluidized sand bath. The gas was released from the reactor and discarded, and finally the products were removed from the reactor by washing into a vial using tetrahydrofuran (THF).

Products were analyzed using a Hewlett Packard 5890 Series II gas chromatograph (GC). The GC utilized both a 30 m x 0.32 mm ID DB-5 column having a film thickness of 0.25 μm, and a 30 m x 0.32 mm Supelcowax 10 column having a film thickness of 0.5 μm. Signals from the dual flame ionization detectors were analyzed by a Hewlett Packard 3690 integrator.

Reaction products were analyzed to obtain percentage conversion and product distribution. Conversion is defined as rate of disappearance of the model compound rather than rate of formation of other products. Furthermore, desirable products are those in which the heteroatom has been removed.

Results

Naphthalene Hydrogenation:

Conversion of naphthalene to tetralin was utilized to determine the activity of the catalysts for hydrogenation of polyaromatic compounds. As shown in Figure 8, the blank, which was free of catalysts, showed very minimal conversion of the naphthalene to tetralin after 60 minutes, specifically only ~7%. In relation, the sulfated hematite and Ni and Co promoter metals

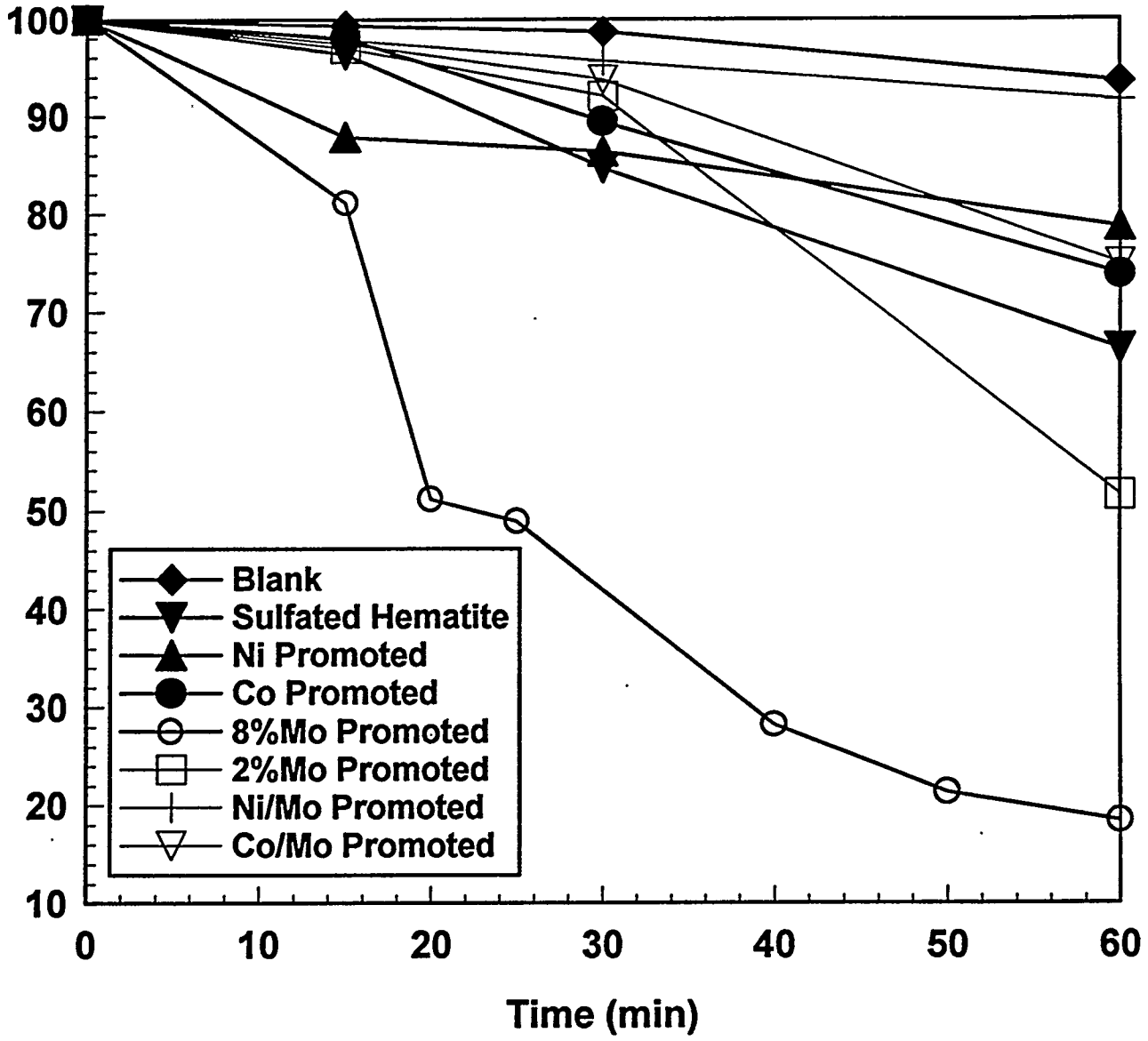


Figure 8. Effect of catalyst on hydrogenation of naphthalene

displayed slightly better results with conversions ranging from 21% and 26% for the Ni and Co promoted catalysts, respectively, to 34% for the sulfated hematite. However, conversion sharply increased for the 8 wt% Mo promoted sulfated hematite, with a conversion of ~92%.

These results clearly indicate that Ni and Co have no advantageous effect as promoter metals for the hydrogenation of polyaromatic compounds. This is shown by the fact that conversion was higher for the sulfated hematite than for either the Ni or Co promoted catalysts. On the other hand, Mo has shown to be an excellent promoter metal for this reaction, exhibiting high conversion at 60 minutes. This may be due to the well known hydrogenation properties of Mo. Ni is also known to be a good hydrogenation catalyst. The lack of activity obtained from the Ni promoter may be explained by its location inside the iron oxide lattice, which may limit the number of active surface sites.

Hydrodeoxygenation of Diphenylether:

Conversion of diphenylether was utilized to determine the activity of a catalyst for hydrodeoxygenation (HDO), or removing the oxygen atom from diphenylether. As demonstrated in Figure 9, the HDO mechanism proceeds through two different steps, ultimately resulting in four different compounds. These compounds are cyclohexane, cyclohexanol, phenol, and benzene. Our goal, however, is to maximize HDO of DPE, resulting in formation of cyclohexane and benzene, the two oxygen-free compounds.

As shown in Figure 10, all catalytic reactions showed increased conversion over the thermal

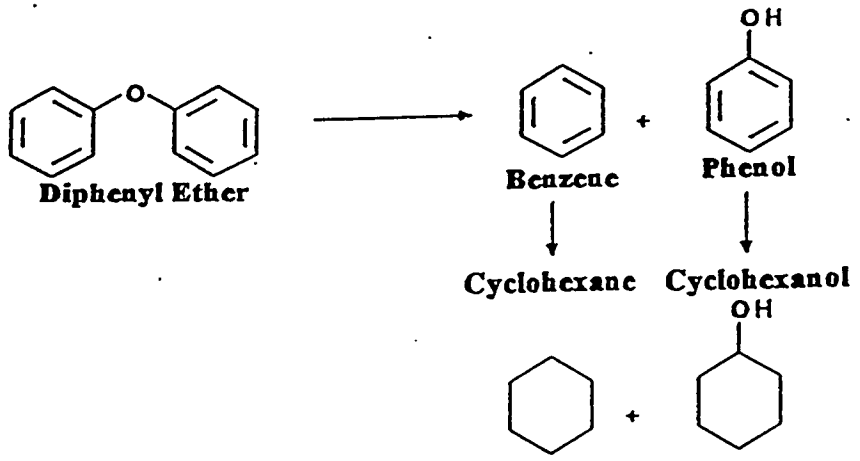


Figure 9. Reaction pathway for hydrodeoxygenation of diphenylether

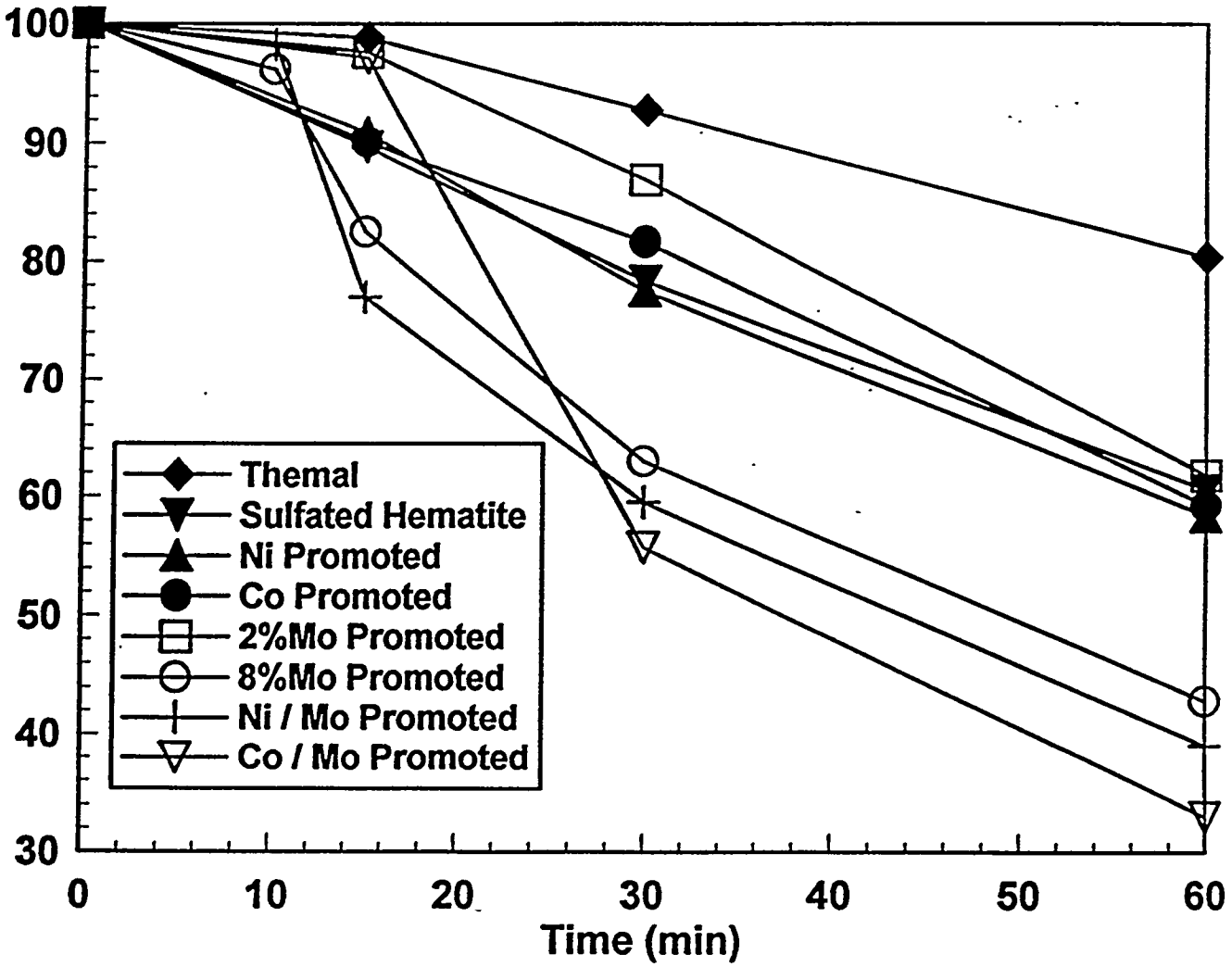


Figure 10. Effect of catalyst on hydrodeoxygenation of diphenylether

reaction. However, the Ni, Co, and 2% Mo promoter metals did not display any increase in activity over the sulfated hematite, therefore their utility as promoter metals is negligible. On the other hand, the combinations Ni/Mo and Co/Mo as promoter metals, along with the 8% Mo, clearly showed an increase in activity over the sulfated hematite. This fact displays the synergistic effect of the Ni and Co in combination with Mo because the conversion at 60 minutes is higher for the Ni/Mo and Co/Mo combination promoter metals than it is for the 8% Mo promoter metal alone.

It is also interesting to note the slow onset of activity for the Co/Mo promoted catalyst. While the reason for the delayed onset of activity is still under investigation, it has been reported that, on an alumina support, Ni compounds are more readily reduced than Co compounds[14]. While both catalyst show an initial period of relative inactivity, this may explain the longer time required to activate the Co/Mo promoted catalyst compared to the Ni/Mo promoted catalyst.

While the success of the Ni/Mo, Co/Mo, and 8% Mo promoter metals in cleaving the etheric linkage is evident, their utility for HDO is minimal at these conditions. Product distribution data from gas chromatography analysis indicated that none of the catalysts were successful in the HDO of DPE, resulting in less than ~10% HDO for even the most active catalysts. This is evidenced by the nearly equal molar ratios of benzene and cyclohexane to phenol and cyclohexanol. Therefore, it appears that the tested promoter metals have little utility in HDO reactions under these conditions. However, other studies have shown that at 475 °C in the presence of added sulfur without a catalyst the amount of oxygen removal was minimal at

times less than 4 hours [7]. This suggests that more severe conditions may be required for significant oxygen removal.

In sum, Ni and Co alone have no beneficial effect as promoter metals on the sulfated hematite, but display a synergism with Mo to create a relatively high conversion rate. Further, unlike the Ni and Co, Mo alone used at higher concentrations appears helpful in conversion of DPE. However, none of the catalysts displayed an appreciable amount of HDO although substantial cleavage of the etheric bond was observed.

Hydrodesulfurization of Benzothiophene:

Conversion of benzothiophene (BZT) was utilized to determine the activity of a catalyst for hydrodesulfurization, or removal of the sulfur atom from the BZT structure. The reaction mechanism, as shown in Figure 11, proceeds through two different initial pathways, resulting in three possible sulfur-free compounds. They are ethylbenzene (EB), ethylcyclohexane (ECH), and methylcyclohexane (MCH), all desirable HDS products.

Metal promoted catalysts proved to be quite successful in conversion of BZT, as demonstrated in Figure 12. While the thermal and sulfated hematite runs had relatively high conversions of ~57% and ~70%, respectively, after 60 minutes, the metal promoted catalysts resulted in virtually complete conversion in the same time interval. Although all metal promoted catalysts resulted in almost total conversion, their activities differed widely. The sulfated hematite showed ~50% conversion after the first 15 minutes, then leveled off dramatically,

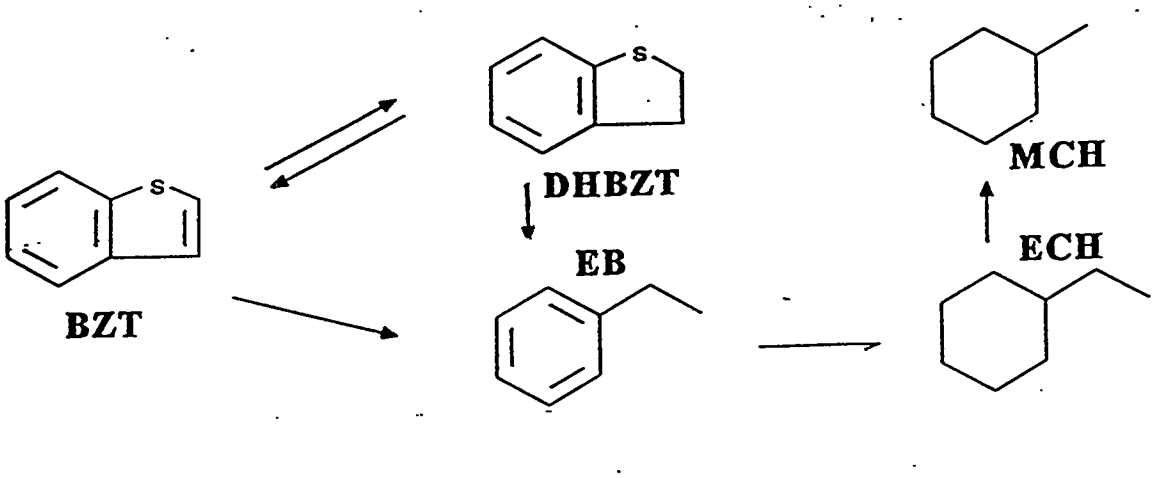


Figure 11. Reaction pathway for hydrodesulfurization of benzothiophene

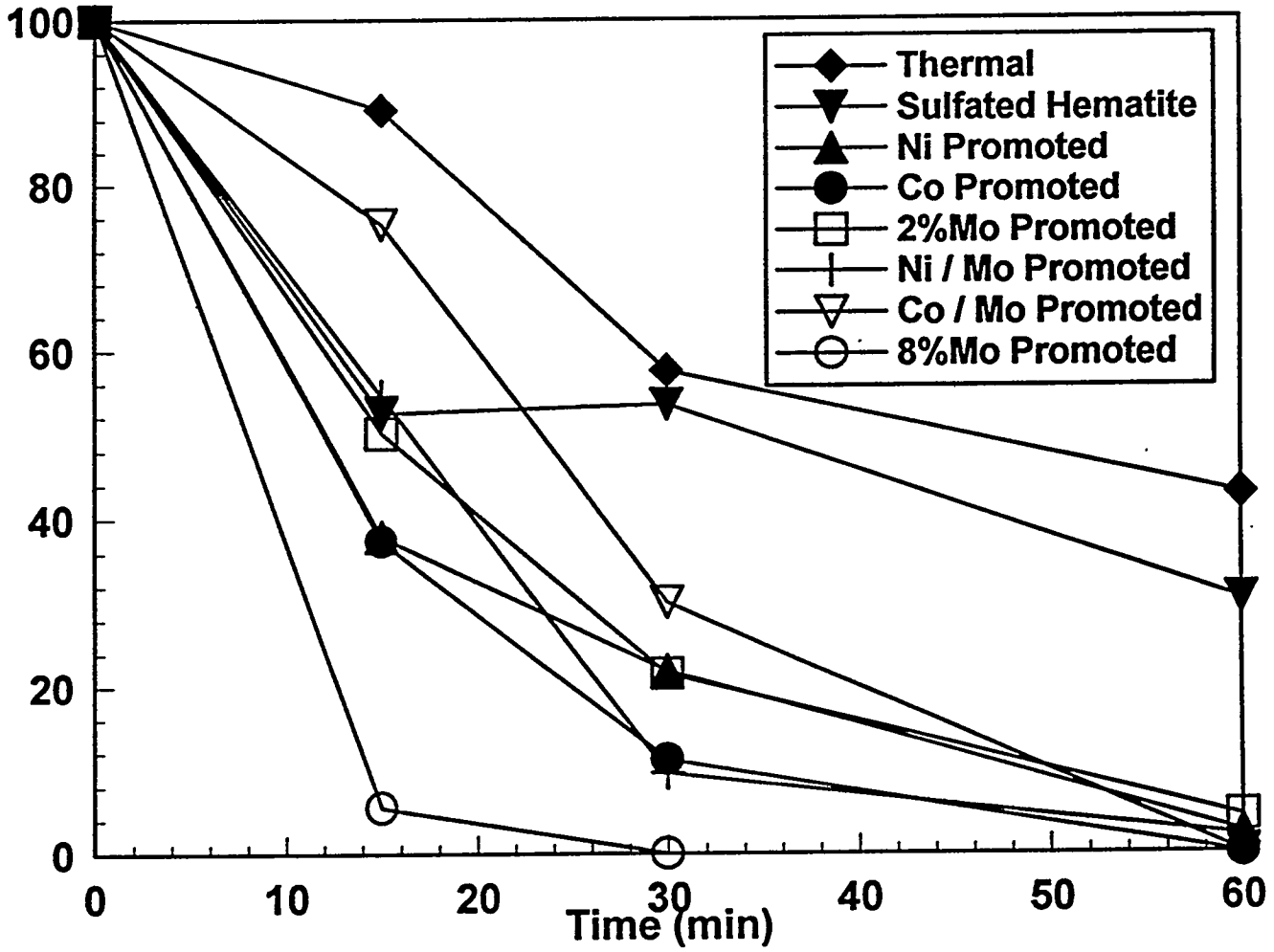


Figure 12. Effect of catalyst on hydrodesulfurization of benzothiophene

converting only 20% more in the next 45 minutes. In comparison, the Ni, Co, and 2% Mo promoted catalysts showed a similar though slightly more rapid onset of activity in the first 15 minutes followed by continued increase in conversion to near 100% at 60 minutes for each of these catalysts. The highest activity was displayed by the 8% Mo promoted catalyst which yielded a conversion of ~93% at 15 minutes and 100% conversion within 30 minutes.

The use of multiple promoter metals on the sulfated hematite had a more varied effect. As observed previously in the HDO results, the Co/Mo promoted catalyst displayed a rather slow onset of activity, converting only ~25% BZT in the first 15 minutes, which is even lower than the sulfated hematite conversion. However, after converting to the active phase, conversion steadily increased resulting in ~100% after 60 minutes.

A slight delay of onset of activity for the Ni/Mo promoted catalyst, was also observed, although much less pronounced than the Co/Mo promoted catalyst. This appears to indicate that the Co/Mo promoted catalyst is slower to convert to an active phase but may exhibit a similar activity after this transformation has occurred. Both Ni and Co in combination with Mo appear to have a nearly additive effect on the activity of the sulfated hematite. In sum, all metal promoted catalysts proved effective in conversion of BZT, however, the 8% Mo promoted is obviously most efficient.

In order to determine the effectiveness of these catalysts for HDS of BZT, it is necessary to examine product distributions. After 60 minutes, all products from catalytic runs displayed >

91% EB formation, with small amounts of DHBZT, ECH, and MCH present also. In comparison, the thermal run had only ~78% EB formation, with ~19% DHBZT formation. This fact emphasizes the utility of catalysts, especially the metal promoted catalysts, for sulfur removal.

Hydrodenitrogenation of Quinoline:

Conversion of quinoline was utilized to determine the activity of a catalyst for hydrodenitrogenation (HDN), or cleaving the nitrogen containing linkages followed by removal of the nitrogen. In order to obtain compounds free of nitrogen, quinoline must first go through several intermediate steps. One possible mechanism for this reaction is shown in Figure 13. Clearly, the desired products are either propylbenzene (PB) or propylcyclohexane (PCH) due to the fact that the nitrogen atom has been removed.

Experimental results reached an apparent equilibrium conversion, ~94-95%, after 60 minutes. According to Figure 14, even the thermal and sulfated hematite runs resulted in this equilibrium conversion after 60 minutes. The distinguishing factor between the catalysts for these experiments appears to be rate of conversion. As expected, the thermal run displayed slower conversion relative to all catalytic runs, finally reaching maximum conversion after 60 minutes. On the other hand, all catalytic runs exhibited maximum conversion within 30 minutes. More specifically, the sulfated hematite and Ni and Co promoted sulfated hematites reached maximum conversion at ~30 minutes. Again, the use of Ni and Co promoters had no significant effect on the activity of the catalyst.

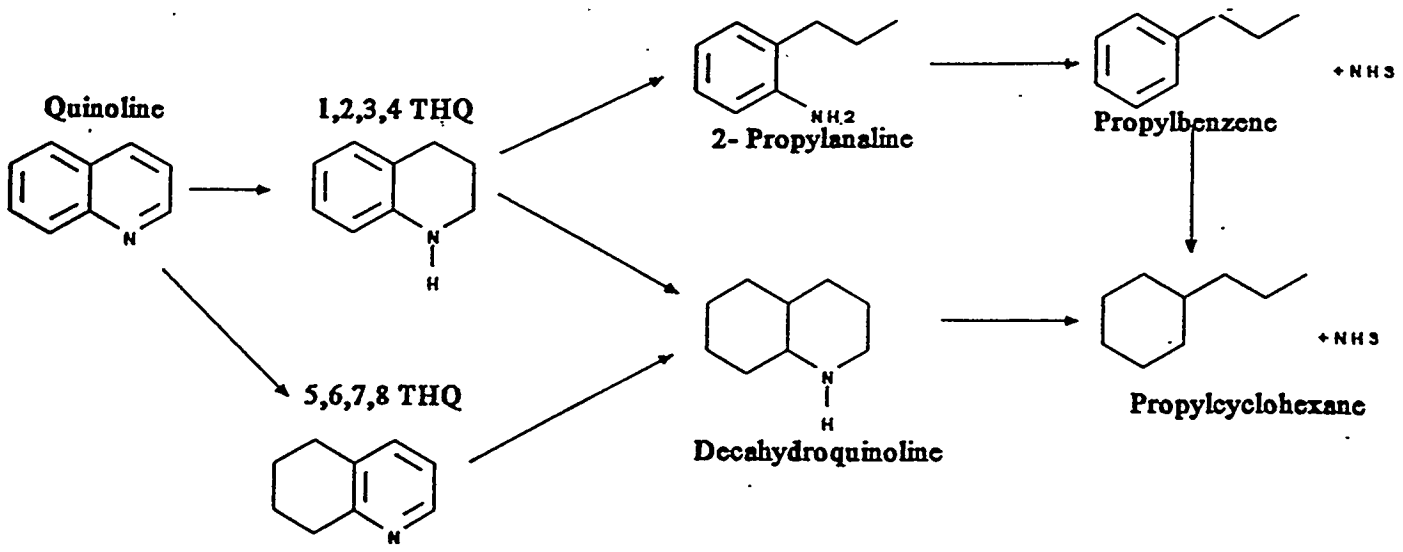


Figure 13. Reaction pathway for the hydrodenitrogenation of quinoline

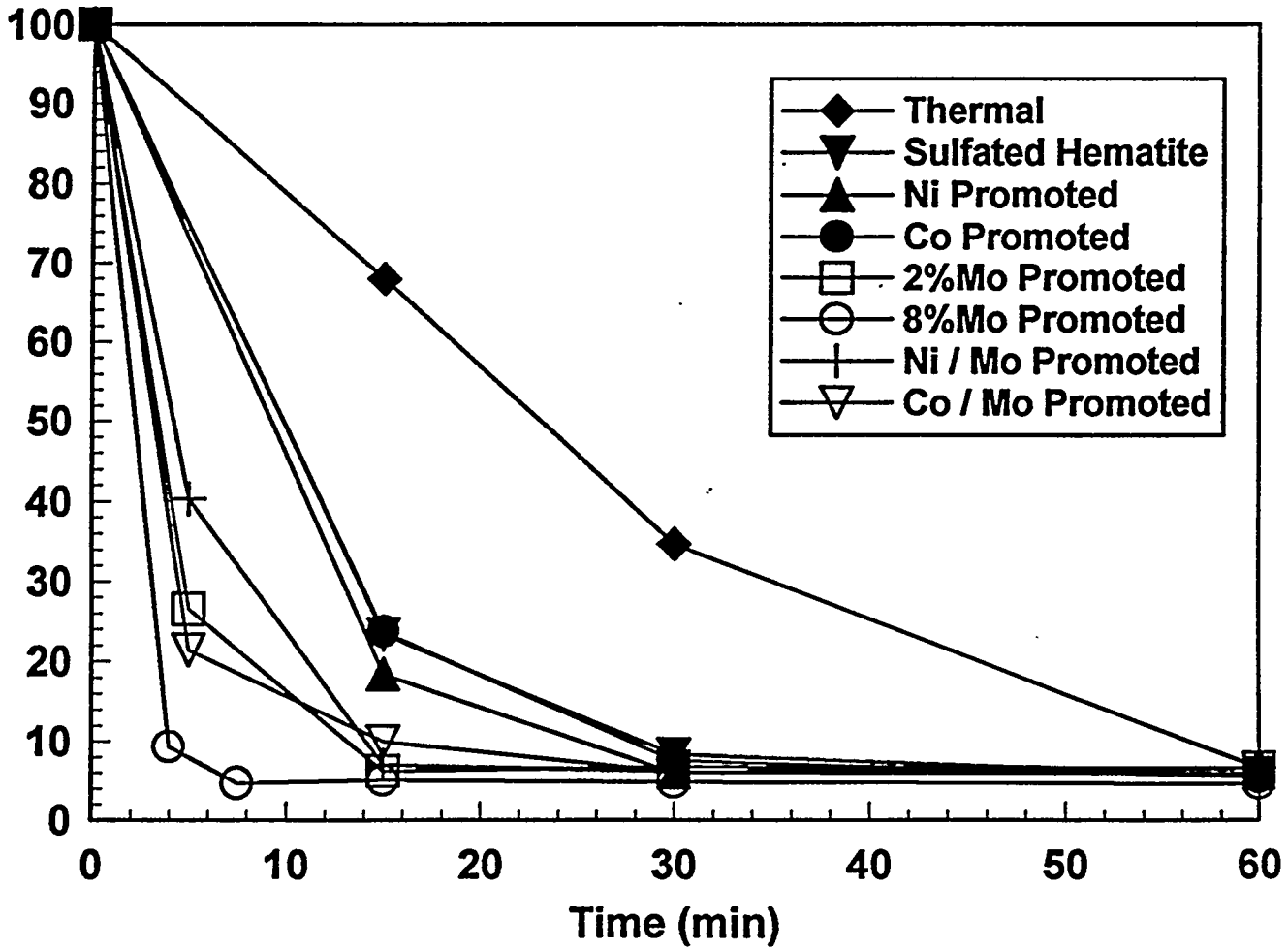


Figure 14. Effect of catalyst on the hydrodenitrogenation of Quinoline

However, the 2% Mo, Ni/Mo, and Co/Mo promoter metals facilitated maximum conversion after only 15 minutes, and the 8% Mo promoted catalyst displayed maximum conversion after only ~7 minutes. One possible explanation for this rapid rate of conversion for Mo promoter metals may be explained by the fact that both oxides and sulfides of Mo are highly active in HDN.[4] This may also explain the fact that no delayed onset of activity was observed for any of the catalyst studied. In sum, all promoted catalysts appear to enhance the conversion rate of quinoline.

Although conversion of quinoline was very high for all catalysts, gas chromatography analysis showed the reaction essentially halted at the first intermediate, 1,2,3,4 tetrahydroquinoline (THQ), a nitrogen containing compound, for all run times. Specifically, after 60 minutes all reaction products were >93% THQ except for the 8% Mo, which was 88% THQ. Only minimal amounts of decahydroquinoline and 2-propylaniline were present after 60 minutes, and trace quantities of PCH, the desirable product, were detected. A proposed mechanism for HDN reactions involves the saturation of the ring structure followed by cracking on an acid site to abstract the nitrogen. The promoted catalyst studied yielded >90% saturation of the heteroatom containing ring clearly demonstrating their high hydrogenation activity. However, the lack of nitrogen removal indicates the absence of any acid functionality. This is further substantiated by the lack of observed hydrocracking of the solvent hexadecane during these reactions. In sum, although catalysts facilitated increased conversion rates, none proved beneficial for HDN of quinoline due to failure in removing the nitrogen atom.

Summary

At concentrations of ~2 %, neither Ni nor Co when used singly as a promoter on the sulfated hematite, had any significant effect on either conversion or selectivity in HYD, HDO, or HDN reactions. This is supported by the fact that neither displayed an appreciable amount of activity in relation to the sulfated hematite. They did, however, enhance conversion of the BZT, and consequently proved useful in HDS.

On the other hand, Mo appeared to be more active than Ni and Co, depending on the concentration. The 2% Mo tended to closely resemble the activities of Ni and Co for HYD, HDS, and HDO, resulting in similar conversions and product distributions. In the HDN reactions 2% Mo caused a very rapid rate of conversion. The 8% Mo demonstrated the highest activity of all catalysts, except in HDO of DPE. This higher concentration of promoter metal resulted in increased conversion rates and greater amounts of heteroatom removal, where removal was observed. This is expected given the high activity of the MoS_2 presumed to form at the reaction conditions.

Despite their lack of activity as single promoters, Ni and Co displayed a different effect when used in combination with Mo in the doubly promoted catalysts. Both the Ni/Mo and the Co/Mo catalysts exhibited a synergistic effect for the HDO and HDS reactions. These combinations of promoters showed an additive effect for the hydrogenation of quinoline. Each of the catalysts demonstrate a period of relatively low activity followed by a period of high activity for all reactions other than HDN. This is presumably associated with the

transformation of the catalyst from the oxide precursor to the active sulfide phase. However, the Co/Mo catalyst shows the slowest conversion to the active phase. This may be related to the fact that on an alumina support, Ni compounds are more readily reduced than Co compounds[4]

The results of the experiments on HDO of DPE appear to indicate that the catalysts exhibit a period of relative inactivity which may last up to 15 minutes at 380 °C. After this period the catalysts exhibit a very high activity for the cleavage of the etheric linkage. The period of inactivity probably correlates with the conversion of the oxide precursor to the sulfide phase. It has been reported in the literature that pyrrhotite is more active for this reaction than the oxide precursor [7]. Further, it has been shown that the activity of the catalyst is related to the partial pressure of hydrogen sulfide in the system which, in turn, is directly related to the stoichiometry of the pyrrhotite. A maximum activity was achieved with a partial pressure of H_2S of 5%. Further increases in H_2S partial pressure up to 10 % yielded minimal increases in activity.

While the effect was most pronounced for the Co\Mo catalyst, each of the catalysts appeared to display some delayed onset of activity. The cause of this delay may be related to the transformation of the catalyst from iron oxide to pyrrhotite. However, as shown in Figure 15, the XRD analysis of the spent catalyst from the model compound experiments appear to indicate that the phase transformation is complete within 5 minutes. It is important to note

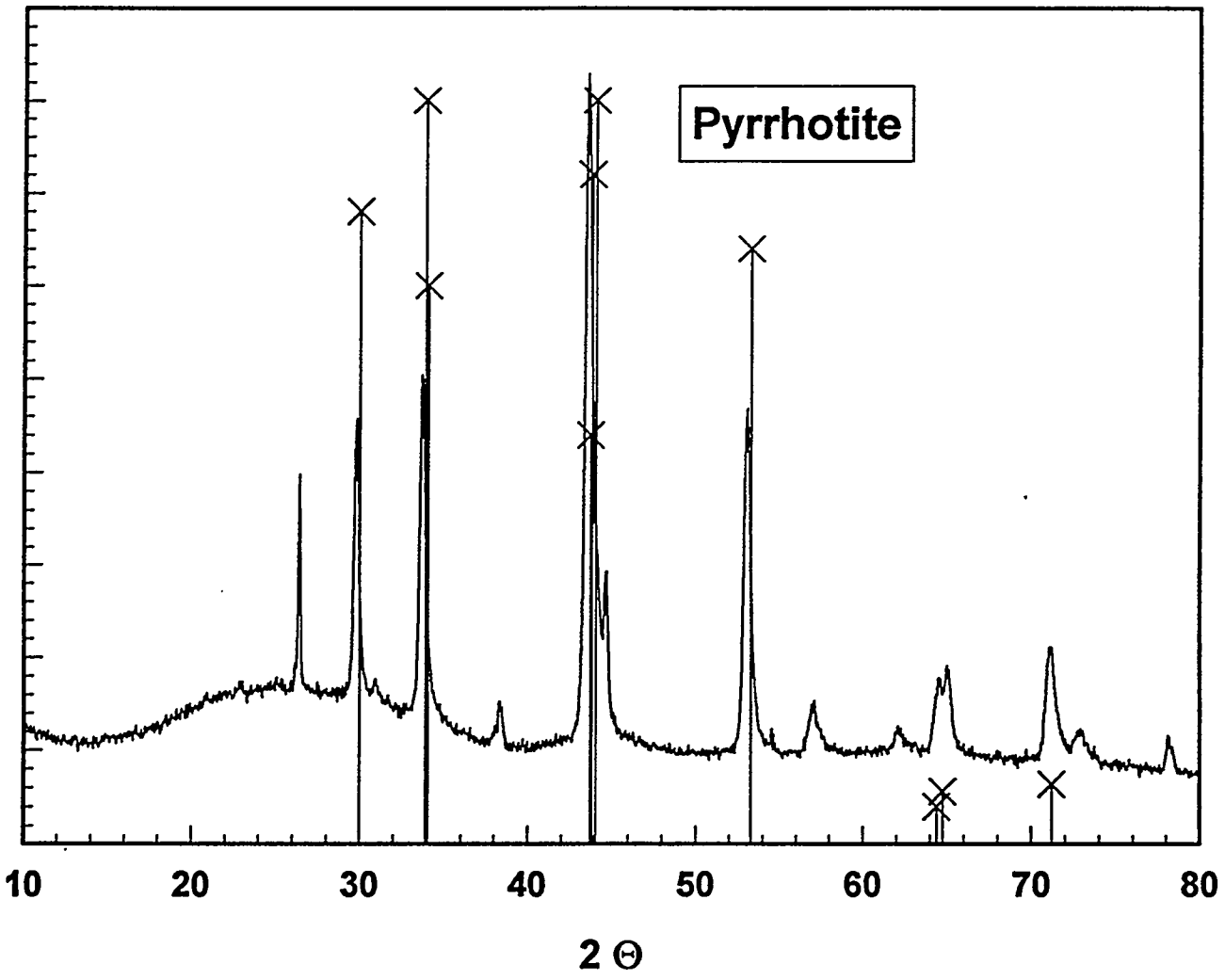
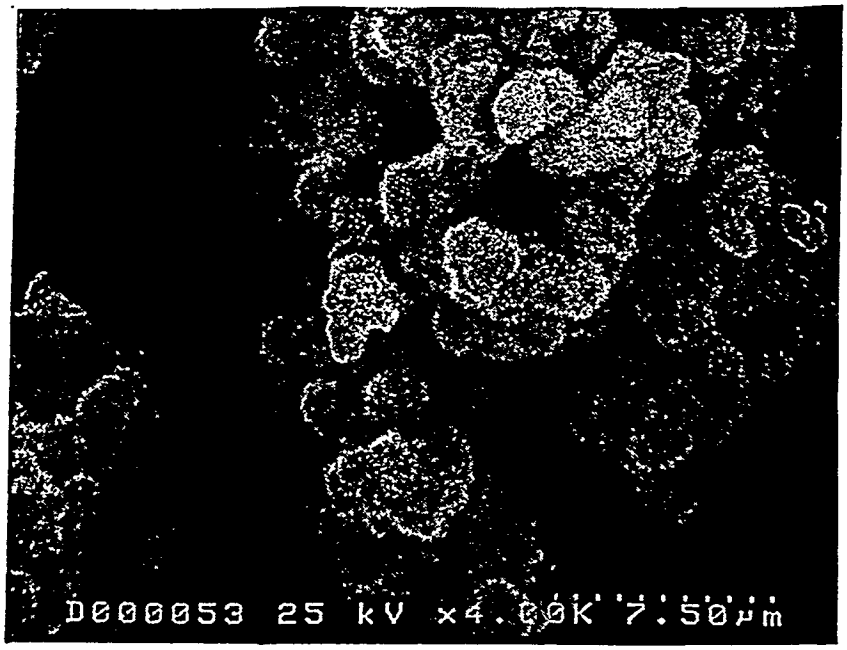


Figure 15. XRD Spectra of Spent Catalyst.

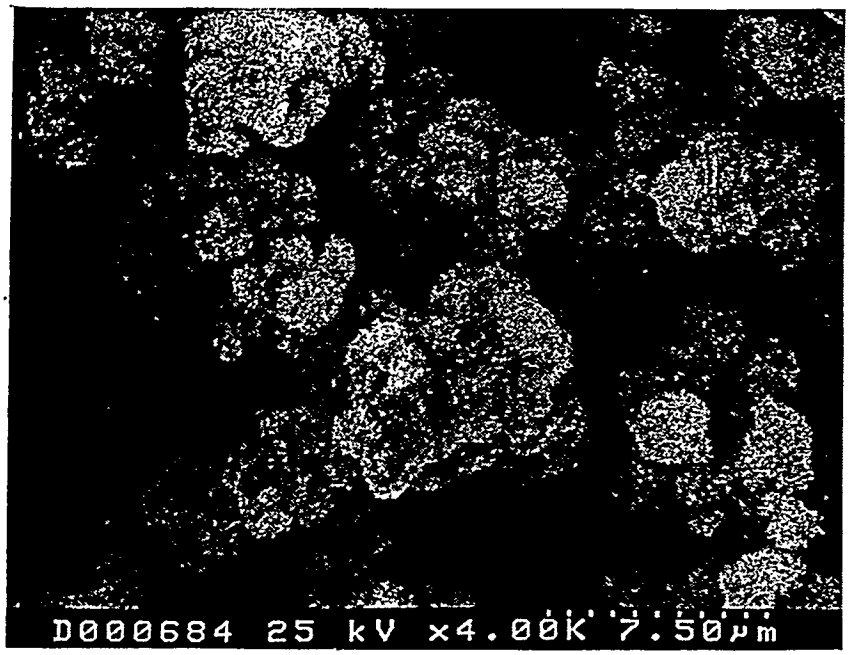
that the results of XRD analysis only show the major phases present and do not indicate the completeness of the transformation. Furthermore, it is difficult to determine the stoichiometry of the pyrrhotite from the XRD spectra obtained. The difference between the time of the apparent phase transition and the onset of activity maybe related to a change in the particle stoichiometry.

Particle diameters estimated from these spectra using a Debye-Scherrer relationship indicated no significant increase in particles size during the reaction. It is important to note that this method is useful in estimating the crystallite diameter and may not yield accurate results for these particles during transition. However, SEM micrographs of the spent catalyst appear to be very similar to those of the oxide precursor. As shown in Figure 16, both precursor and spent catalyst appear as loose agglomerations of particles below the resolution of the instrument. The agglomerated clusters have diameters of ~1 μm. TEM of the spent catalyst will confirm the actual particles size and morphology.

Finally, it has been reported in the literature that the sulfate group on the surface of the hematite particles forms a solid superacid[3],[4]. This has been proposed to be one possible explanation for the high activity of sulfated hematite and molybdenum promoted sulfated hematite. An important result of this study was the finding that neither the promoted nor the unpromoted catalyst displayed any acidic behavior under these reaction conditions. This is demonstrated by the absence of cracking of the solvent hexadecane and the lack of nitrogen removal in the HYD reactions.



a)



b)

Figure 16. SEM micrographs showing aggoleration of a) fresh catalyst and b) spent catalyst.

Coal Liquefaction in Tetralin

Experimental

The catalytic activity of the sulfated hematites for coal liquefaction was assessed through microautoclave experiments, using Black Thunder subbituminous coal, with tetralin as a hydrogen donor solvent. The 50 ml horizontal microautoclaves were loaded with 3 g of as-received coal, 5 g tetralin and 0.07 g dimethyldisulfide (DMDS) as a sulfiding agent. Catalysts were added at an iron loading of 1 wt% with respect to maf coal. The reactors were sealed, purged, and pressurized to 1000 psig (cold) with hydrogen. Reactions were conducted in a heated fluidized sand bath at 415°C for 60 minutes, with agitation at 400 cycles/minute. After reaction the reactor was quenched by immersion in a cool fluidized sand bath. The use of this system allowed the rapid attainment of reaction temperature thereby eliminating errors associated with prolonged heating times.

Conversions and yields were determined by solubility class using Soxhlet extraction. The total conversion was defined as THF soluble while the THF soluble, pentane insoluble fraction was defined as preasphaltenes + asphaltenes (PA&A). The gas yield was determined directly by gas chromatograph and the oil yield was determined by difference. All runs were done in duplicate to ensure reproducibility and all yield data are reported on an maf coal basis.

Results

The use of the sulfated hematite resulted in a substantial increase in total conversion over the

blank thermal baseline run. The increase in conversion was due entirely to an increase in PA&A yield, as shown in Figure 17, with no substantial change in oil or gas yield. This conversion compares favorably with the results obtained using a super fine iron oxide (SFIO)[9] catalyst at similar iron loadings. This despite the fact that the SFIO has smaller diameter (3 vs 19 nm) and higher surface area (190 vs 100 m2/g) compared to the sulfated hematite. The gas yield was unaffected by any of the catalysts utilized in this study.

The addition of 1 wt % molybdenum as a promoter metal to the sulfated hematite resulted in no significant increase in total conversion. However, as shown in Figure 17, there is a slight increase in selectivity to oils. This agrees well with reports in the literature that molybdenum increases the hydrogen content of the liquid products[9]. The molybdenum concentration of 1 wt% with respect to iron oxide corresponds to a 100 ppm molybdenum loading on maf coal. At this low loading the effect of molybdenum is very modest.

Increasing the promoter concentration to 5 wt% molybdenum on iron oxide results in a significant increase in total conversion to 92% compared to 88% for the unpromoted sulfated hematite. Further, an increase in oil yield and a decrease in PA&A yield is also observed for this catalyst compared to the sulfated hematite. This indicates a significant improvement in the activity and selectivity of the sulfated hematite at a molybdenum loading of only 500 ppm on maf coal.

Increasing the promoter concentration to 10 wt% molybdenum on iron results in a further

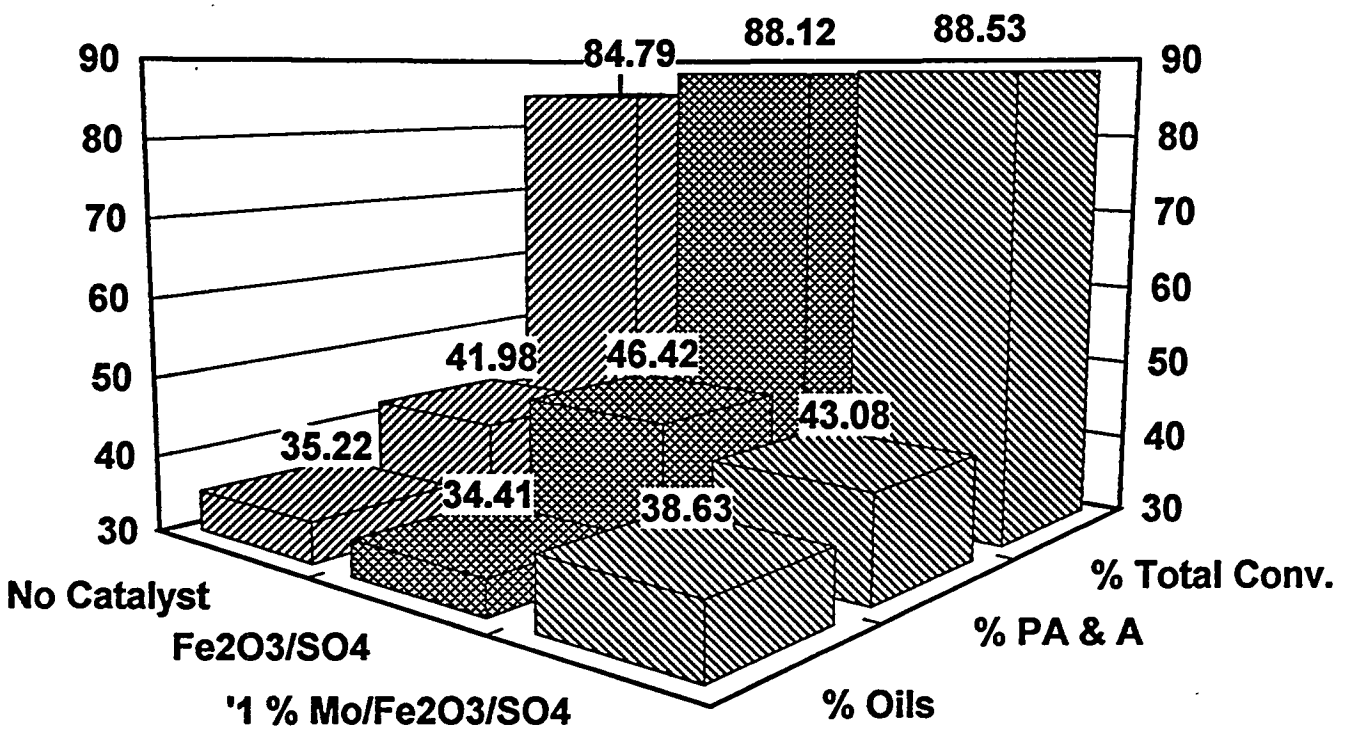


Figure 17. Effect of 1 wt % Fe as unpromoted and molybdenum promoted sulfated hematite on Conversion

increase in both conversion and selectivity. As shown in Figure 18, the increase in total conversion results from an additional increase in oil yield and a decrease in PA&A yield. The net result of the 1000 ppm molybdenum on maf coal loading is an overall increase in total conversion of 6% and an increase in oil yield of 14% compared to the unpromoted sulfated hematite. Figure 19 shows the effect of molybdenum concentration on the conversion of the Black Thunder coal in tetralin.

The addition of 1.4 wt % nickel on the sulfated hematite resulted in a slight increase in total conversion over the unpromoted sulfated hematite. This increase was due entirely to an increase in PA&A yield as the oil yield remained constant, within experimental error, as shown in Figure 20. This represents the most significant increase in total conversion and the lowest selectivity to oils of each of the promoter metals, excluding molybdenum. The addition of 2.5 wt % cobalt resulted in negligible increase in total conversion compared to the unpromoted sulfated hematite but a slight increase in oil yield. The effect of 4 wt % tungsten yielded the same results as the 2.5 wt % cobalt, within experimental error. This indicates that 500 ppm tungsten and 250 ppm cobalt on maf coal have very similar catalytic activity for coal liquefaction, while 140 ppm nickel on maf coal had slightly higher activity for total conversion but lower selectivity to oils.

The results of this study clearly indicate that the molybdenum promoted sulfated hematite displays the highest activity and also the greatest selectivity to oils. Further, both the activity and selectivity of the catalyst increase with increasing molybdenum concentration. However,

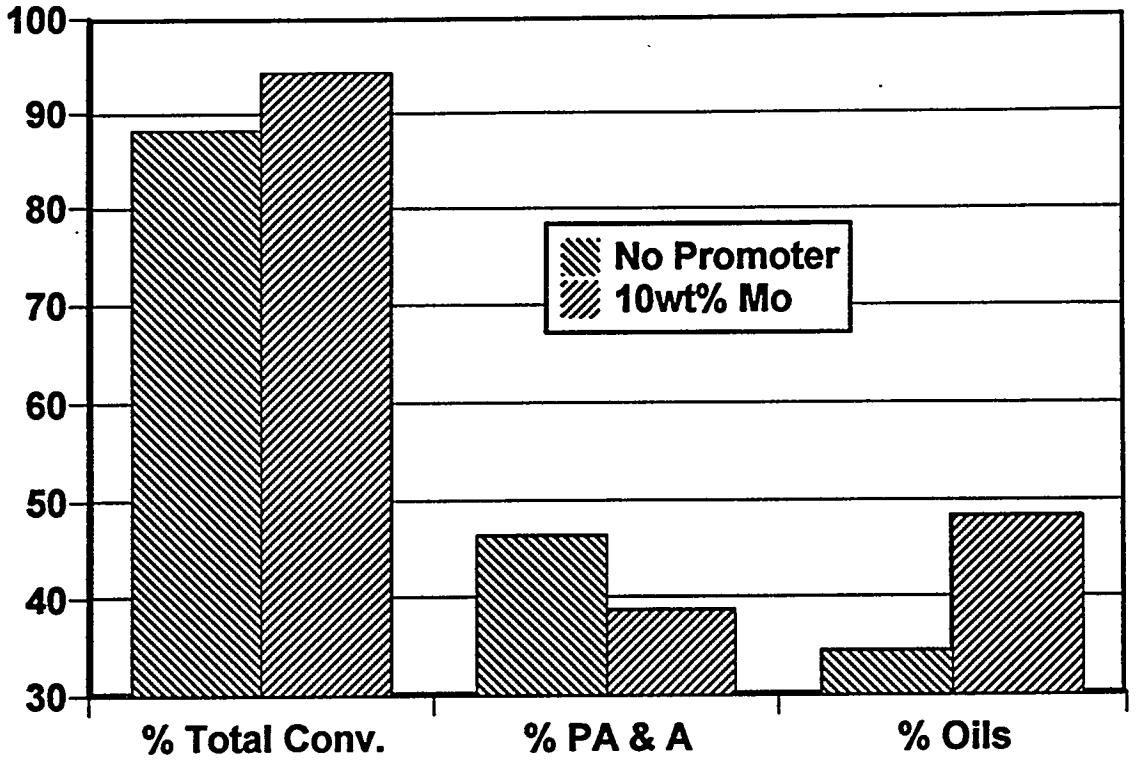


Figure 18. Effect of 10 wt% molybdenum the activity of sulfated hematite.

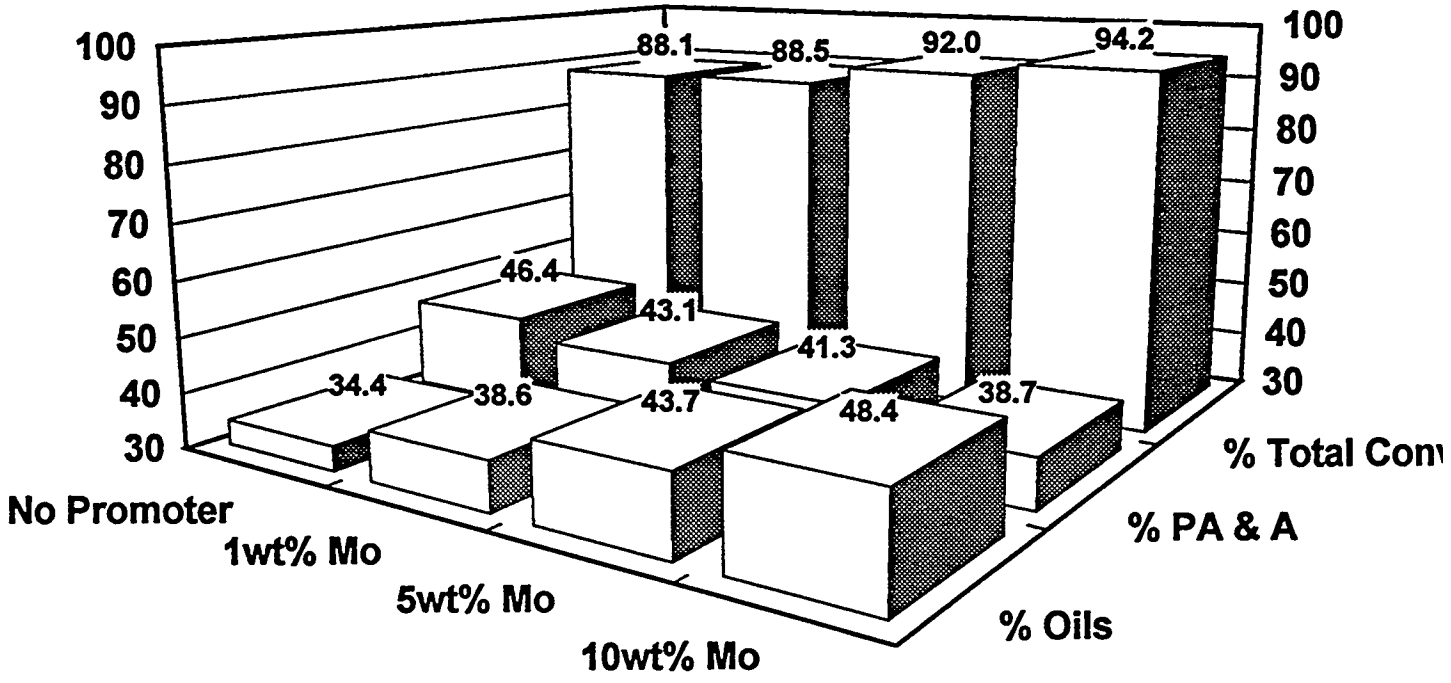


Figure 19. Effect of molybdenum loading on the activity of sulfated hematite

due to the significant cost associated with molybdenum, a loading of 1000 ppm on maf coal would be prohibitively expensive. Therefore the use of other promoters in combination with the molybdenum was explored.

The use of a cobalt /molybdenum promoted sulfated hematite demonstrated considerable catalytic activity. As shown in Figure 21 the addition of 1 wt % molybdenum and 0.5 wt % cobalt to the sulfated hematite increased the total conversion substantially. The total conversion was close to that obtained with 5 wt% molybdenum, and greater than that obtained with 2.5 wt % cobalt on sulfated hematite. This appears to indicates an synergistic effect between the molybdenum and the cobalt promoters. The oil yield was increased to 40 %, only slightly higher than the oil yield obtained for 1 wt % Mo. This indicates that at a promoter concentration of 100 ppm molybdenum and 50 ppm cobalt on maf coal, the activity of the catalyst for total conversion approaches that of 500 ppm molybdenum, although the selectivity to oils is somewhat lower.

Similar results were obtained for the combination of molybdenum with tungsten as promoter metals on sulfated hematite. The addition of 1 wt% molybdenum and 0.8 wt % tungsten resulted in an increase in total conversion to 92 % and an increase in oil yield to 40%. Figure 22 shows the comparison of this catalyst with the 5 wt% molybdenum and with 4 wt% tungsten on sulfated hematite. These results show the similar effect of cobalt and tungsten when added with molybdenum to the sulfated hematite.

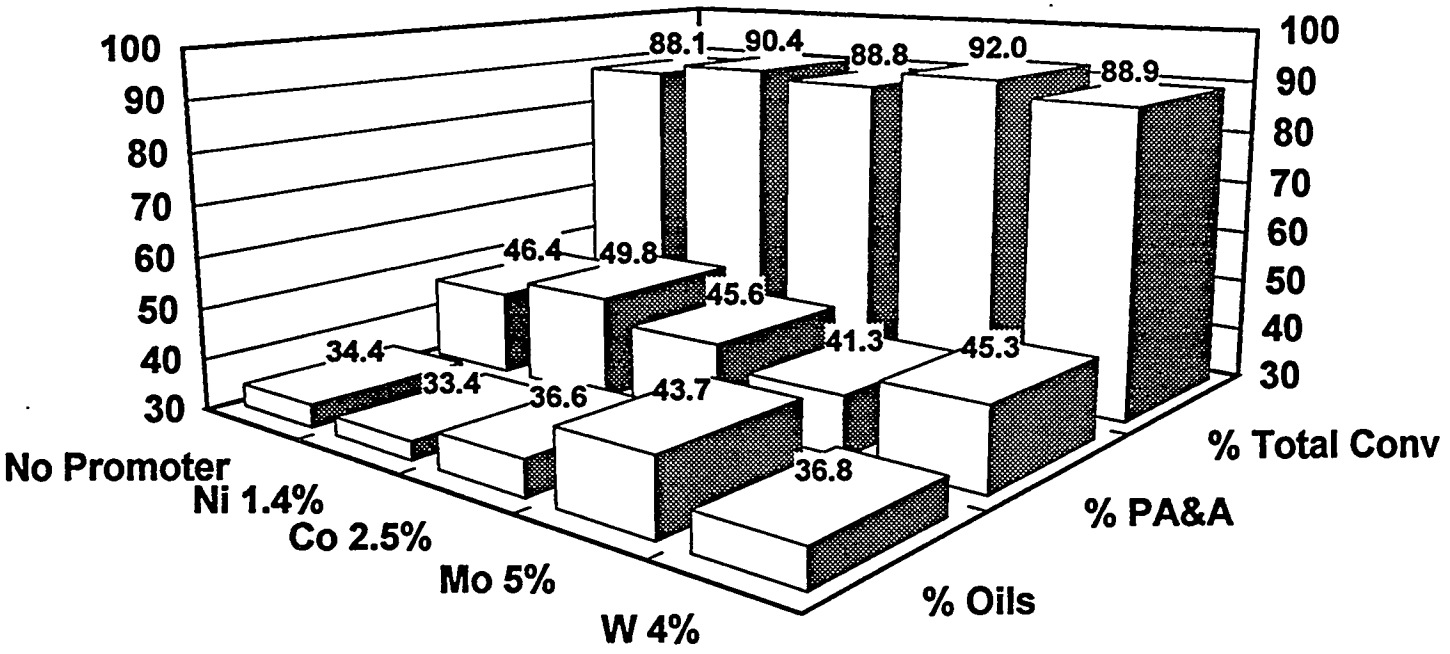


Figure 20. Effect of promoter metals on the activity of sulfated hematite

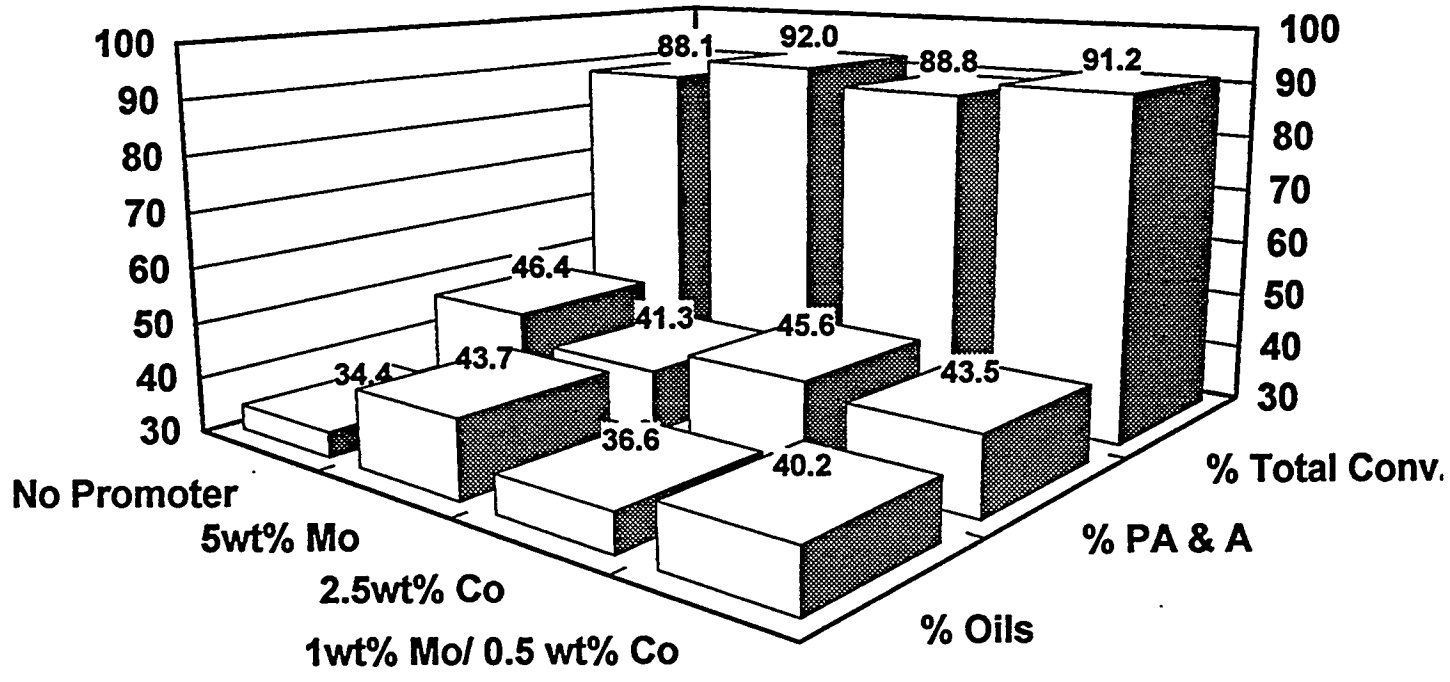


Figure 21. Effect of molybdenum and cobalt on the activity of sulfated hematite

The combination of nickel and molybdenum yielded somewhat better results. The use of 0.9 wt % molybdenum and 0.7 wt% nickel as promoters on sulfated hematite resulted in marginally higher total conversion compared to the cobalt/molybdenum and tungsten/molybdenum promoters shown previously. More importantly, however, is the fact that the selectivity to oils is higher for this sample than for the previous samples. As shown in Figure 23, the oil yield is higher than that obtained for 5 wt% molybdenum on sulfated hematite. This indicates a synergistic effect between the nickel and molybdenum which results in the high selectivity for oils. The combination of 90 ppm molybdenum, 70 ppm nickel, with 1 wt% iron on maf coal resulted in the highest selectivity to oils of the multi-promoted catalysts tested.

The effect of the variation of the cobalt/molybdenum concentrations on total conversion is shown in Figure 24. In general, as the total promoter concentration increases, the total conversion also increases. However, there appears to be a synergistic effect between the cobalt and molybdenum. This is demonstrated by the fact that 4% molybdenum, 1.2% cobalt catalyst yields a significantly higher conversion (95.3%) than either 5% molybdenum (92%) or 2.5% cobalt (88.8%) alone. Changing the molybdenum and cobalt concentrations to 0.9% and 1.3% respectively continued to demonstrate this synergism with a total conversion of 94.2%. The reduction of cobalt content to 0.5% with molybdenum at 1% continued to show significant gains in total conversion compared to 1%molybdenum or 2.5% cobalt, although it

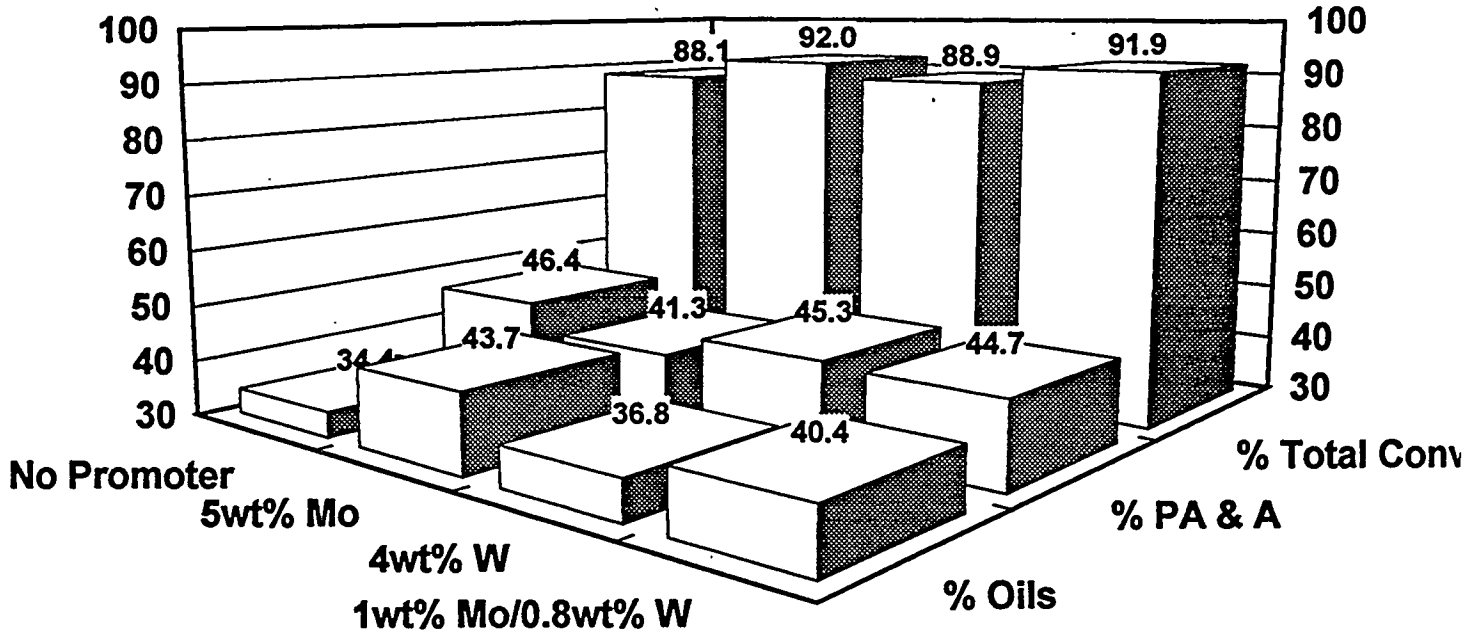


Figure 22. Effect of molybdenum and tungsten on the activity of sulfated hematite

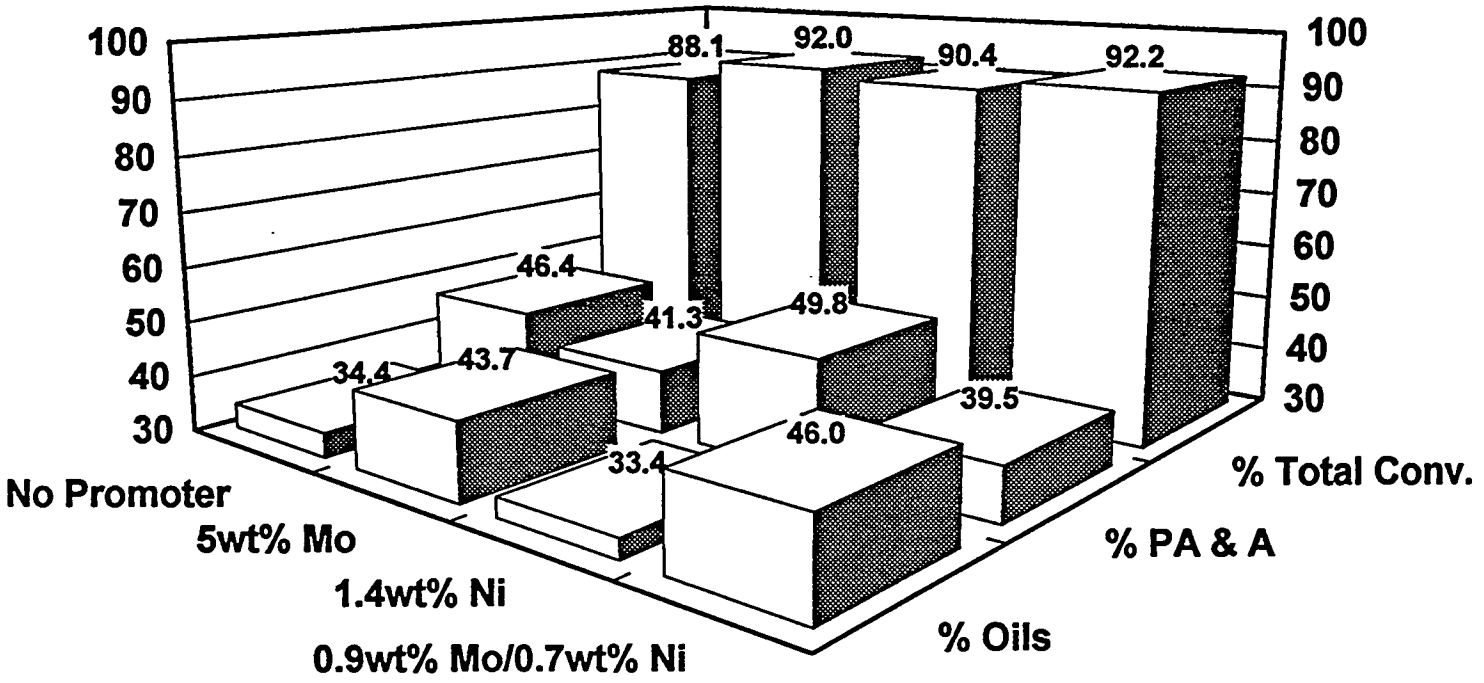


Figure 23. Effect of molybdenum and nickel on the activity of sulfated hematite

was less than that achieved with 5% molybdenum.

Similarly, the increase in oil yield showed the same trend, shown in Figure 25, yielding a maximum conversion of 48% for the 4% molybdenum, 1.2% cobalt catalyst. This represents a 14% increase in oil yield over the unpromoted sulfated hematite. Again, changing the promoter metal concentrations to 0.9% molybdenum and 1.3% cobalt continued to show significant increases of 6.1% and 8.1% over the 1% molybdenum or the 2.5% cobalt respectively. Further reducing the cobalt content to 0.5% while maintaining the molybdenum content at 1% significantly diminishes the synergistic effect, although slight gains(1.6%) in oil yield over the 1% molybdenum alone are still observed.

The results of these studies indicate that the catalyst activity is more sensitive to cobalt concentration than to molybdenum concentration. By reducing the molybdenum concentration from 4% to 1% the total conversion is reduced by only 1% while the oil yield drops by 3.5%. These represent conversions higher than those obtained with 5% molybdenum alone. However, since the cost of cobalt is >4 times that of molybdenum, the increase in conversion does not offset the increased cost of the catalyst. Further reduction of the cobalt concentration to 0.5% reduced the activity below the level obtained with 5% molybdenum.

The effect of promoter metal concentration on total conversion for the molybdenum, tungsten system are shown in Figure 26. The higher conversion is obtained at the highest promoter metal concentration, 4% molybdenum and 3.1% tungsten. This represents an increase of

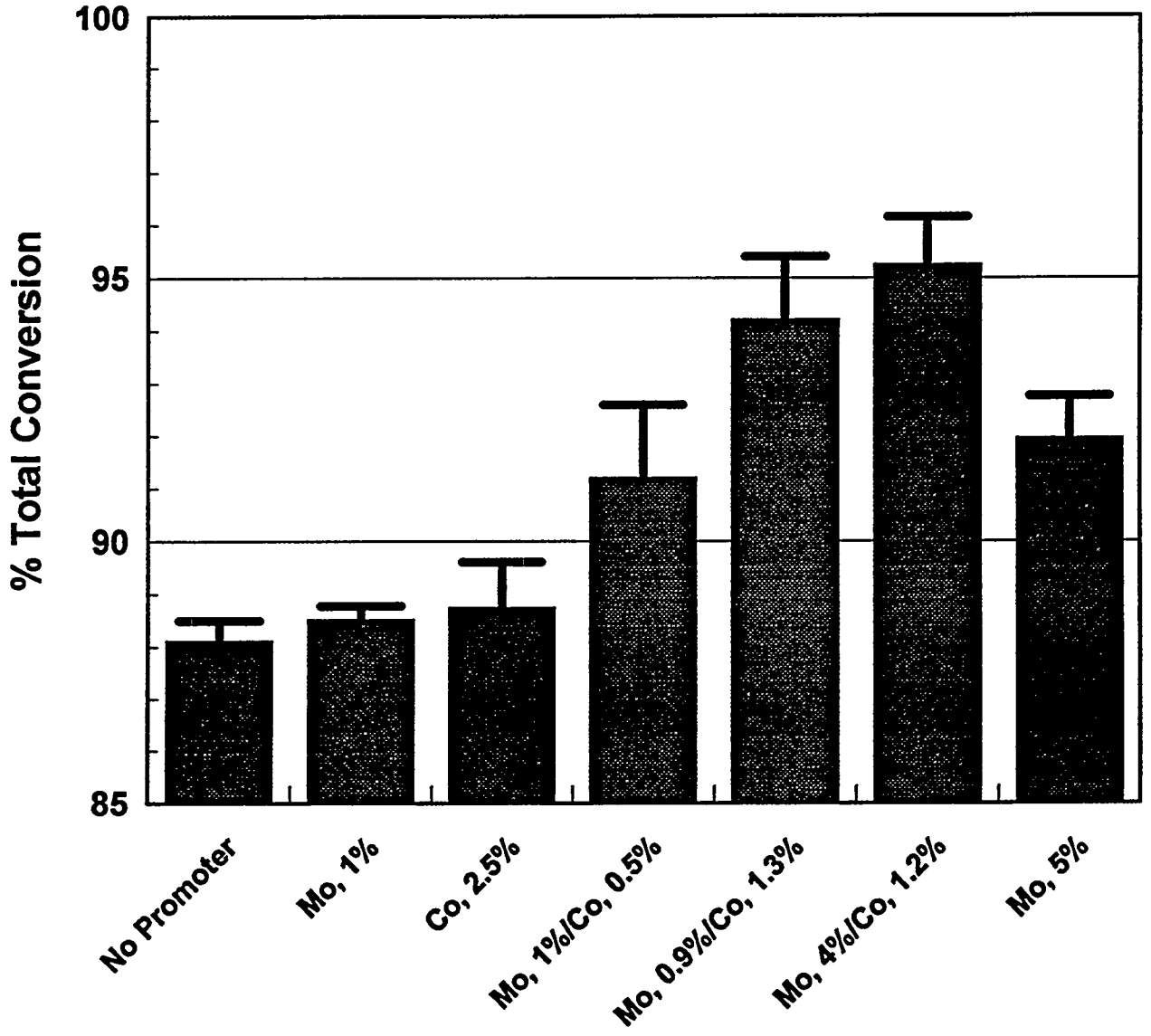
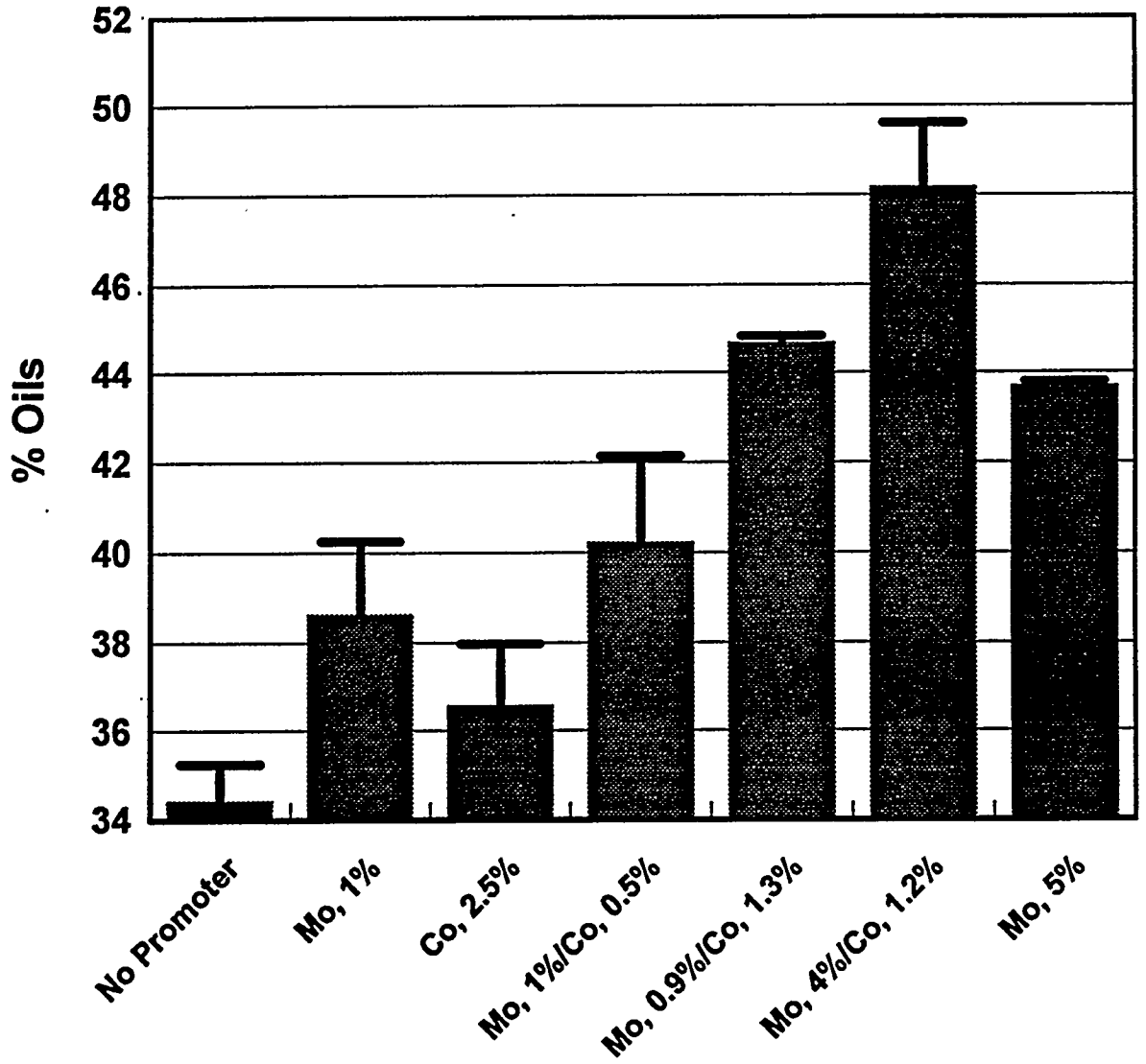


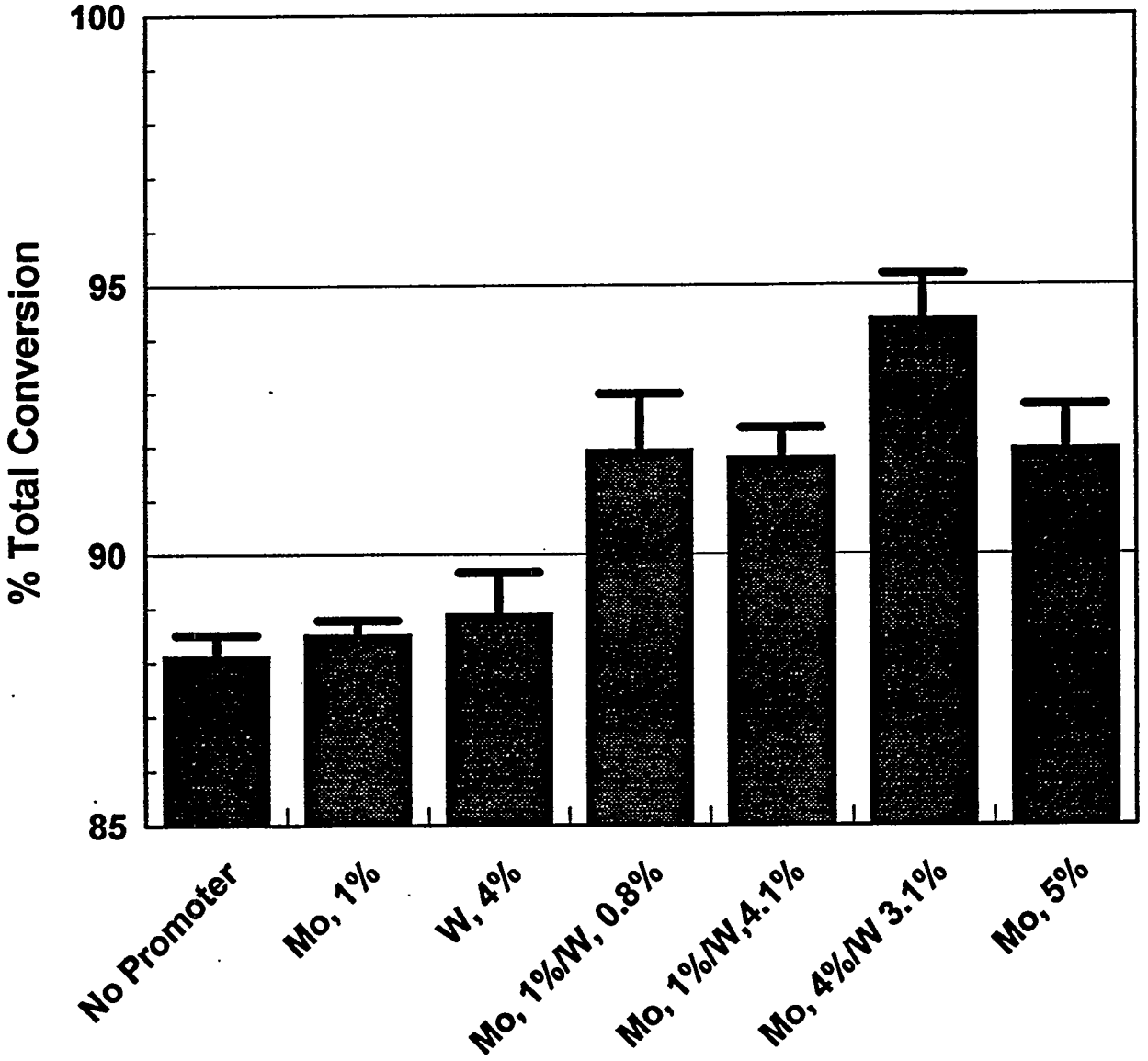
Figure 24. Effect of cobalt and molybdenum on the activity of sulfated hematite for total conversion.

1 wt% on Fe = 100 ppm on maf coal



1 wt% on Fe = 100 ppm on maf coal

Figure 25. Effect of cobalt and molybdenum on the activity of sulfated hematite for conversion to oils.



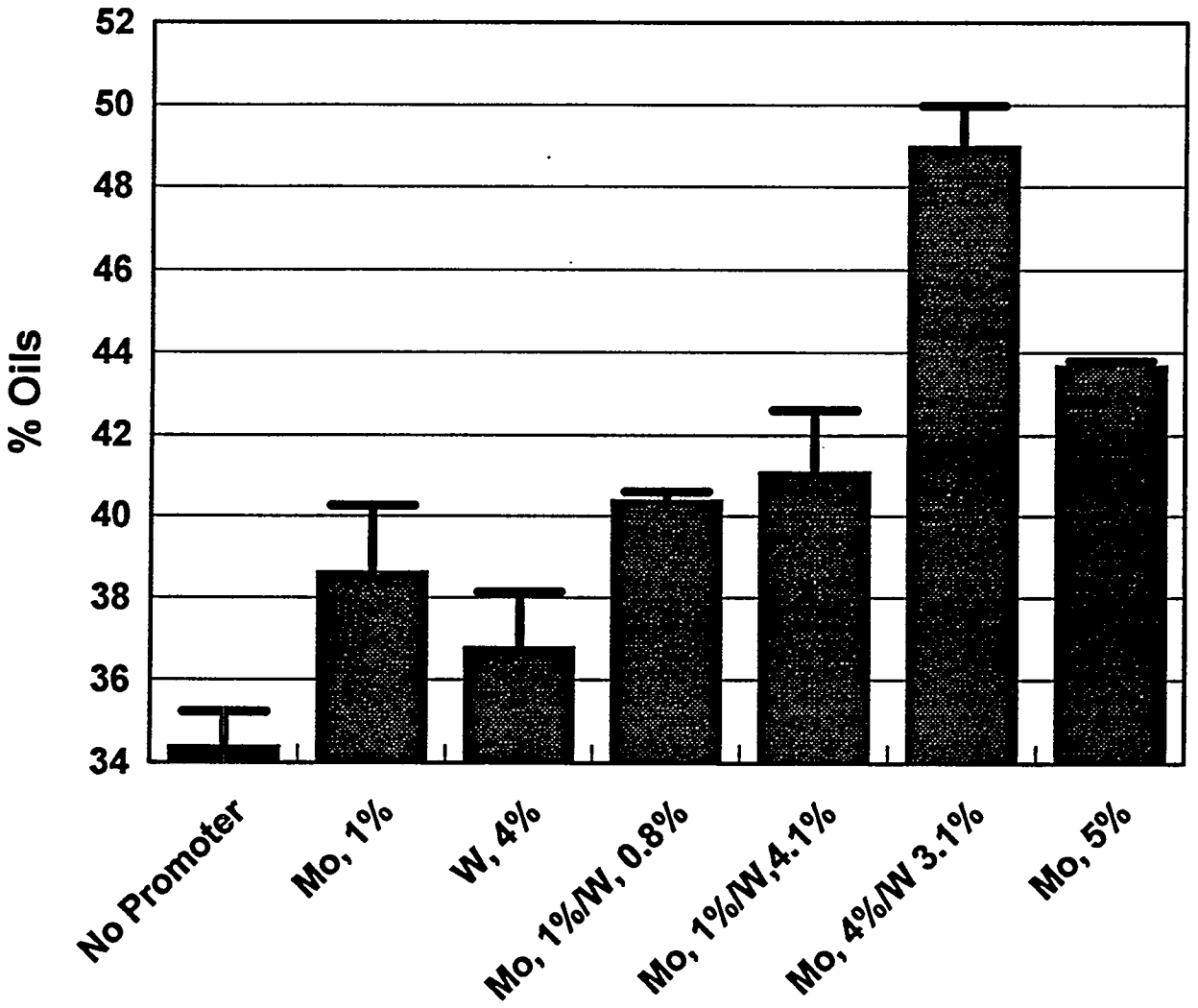
1 wt% on Fe = 100 ppm on maf coal

Figure 26. Effect of tungsten and molybdenum on the activity of sulfated hematite for total conversion.

2.4% and 5.5% over 5% molybdenum and 4% tungsten, respectively, indicating a synergistic effect at these concentrations. Reduction of the molybdenum concentration to 1% while increasing the tungsten concentration to 4.1% appears to maintain the synergistic effect, yielding results (91.8%) significantly higher than either 1% molybdenum (88.5%) or 4% tungsten (88.9%) alone. Reducing the tungsten concentration to 0.8% while maintaining the molybdenum concentration at 1% showed no significant effect on the total conversion (91.9%).

The effect of tungsten and molybdenum concentrations on oil yield followed a similar trend, as shown in Figure 27. The maximum yield was obtained for 4% molybdenum, 3.1% tungsten with an oil yield of 49%. This represents a significant increase over either the 4% tungsten or 5% molybdenum alone, 12.2% and 5.3% respectively. Changing the molybdenum and tungsten concentrations to 1% and 4.1%, respectively, reduced the oil yield to 41.1%. This is lower than that obtained with 5% molybdenum yet still shows a slight increase over the 1% molybdenum or 4% tungsten yields. The further reduction of the tungsten concentration to 0.8% had only a slight effect on the oil yield.

These results indicate that the catalytic activity is significantly more sensitive to variations in molybdenum concentration than to changes in tungsten concentration. This may indicate that further lowering the tungsten concentrations may still enhance the total conversion in the presence of molybdenum. While the high concentrations of molybdenum and tungsten showed significant gains in total conversion and oil yield, the high cost of the tungsten may



1 wt% on Fe = 100 ppm on maf coal

Figure 27. Effect of tungsten and molybdenum on the activity of sulfated hematite for conversion to oils.

inhibit the economic efficiency of these catalysts.

The combination of nickel and molybdenum showed some surprising trends with variation in promoter concentration. Increasing the nickel concentration appeared to adversely impact the total conversion. As shown in Figure 28, maximum total conversion was achieved through the use of 4.3 % molybdenum and 0.7 % nickel. The total conversion (94.7%) represented an increase over 5% molybdenum and 1.4% nickel of 2.7% and 4.3%, respectively. Reducing the molybdenum concentration to 0.9% at the same nickel loading reduced the total conversion (92.2%) to near that of 5% molybdenum. At this concentration a synergistic effect between the nickel and molybdenum becomes apparent.

Unlike the other promoter metals, increasing the nickel concentration appears to adversely effect the total conversion. At a concentration of ~4% molybdenum, increasing the nickel concentration from 0.7% to 2.3% decreases the total conversion by 7.6%, to near the same level of the unpromoted sulfated hematite. Similarly, at a molybdenum concentration of 0.9%, increasing the nickel concentration from 0.7% to 2.0% resulted in a decrease in total conversion to 91%, though the effect at these conditions is less dramatic. This appears to indicate that an optimum nickel concentration may exist near the 0.7% loading.

The effect of nickel and molybdenum on oil yield is shown in Figure 29. The maximum oil yield (46%) is obtained at a promoter concentration of 0.9% molybdenum, 0.7% nickel. This clearly shows the synergistic effect between nickel an molybdenum. Increasing the

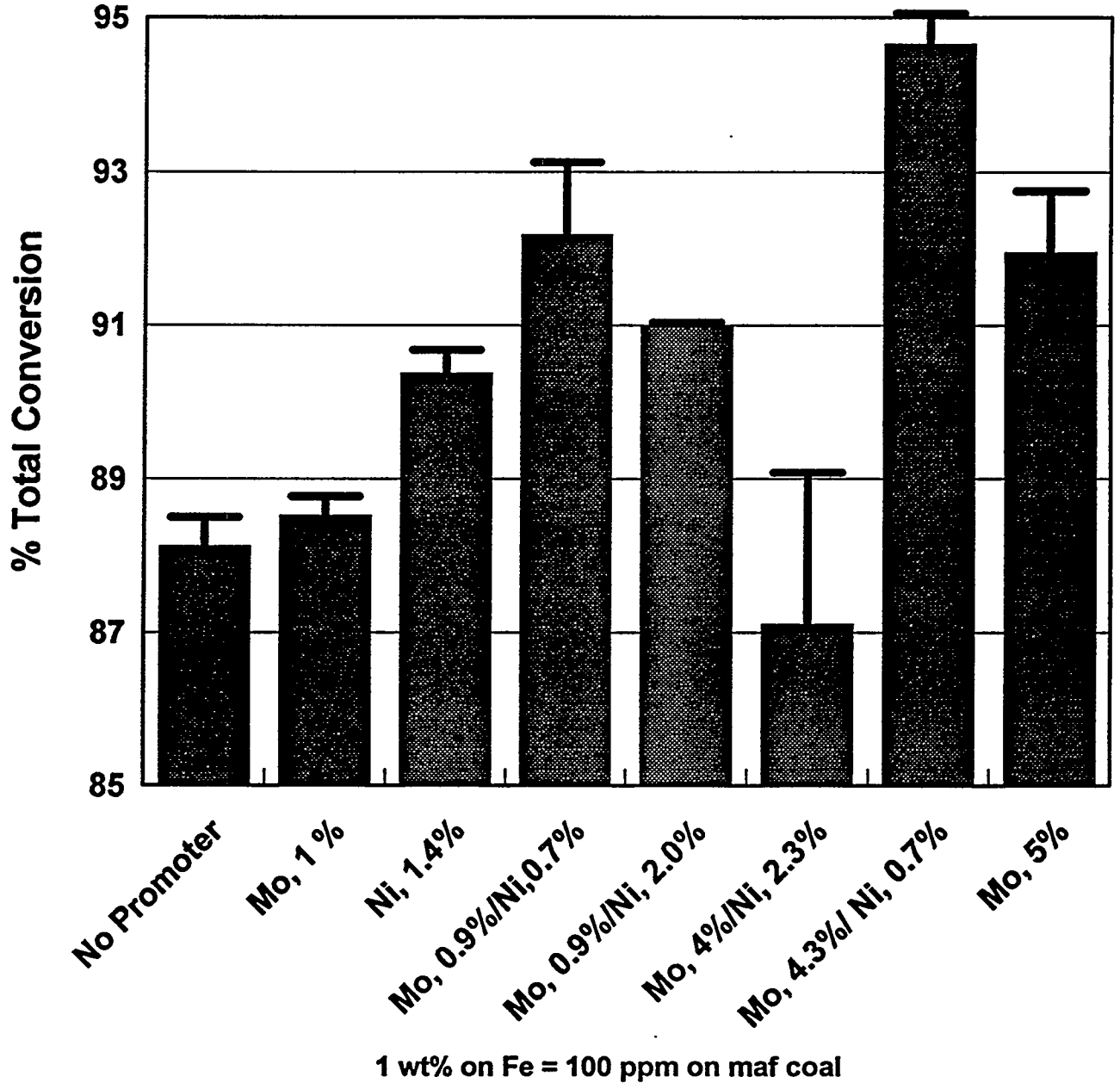
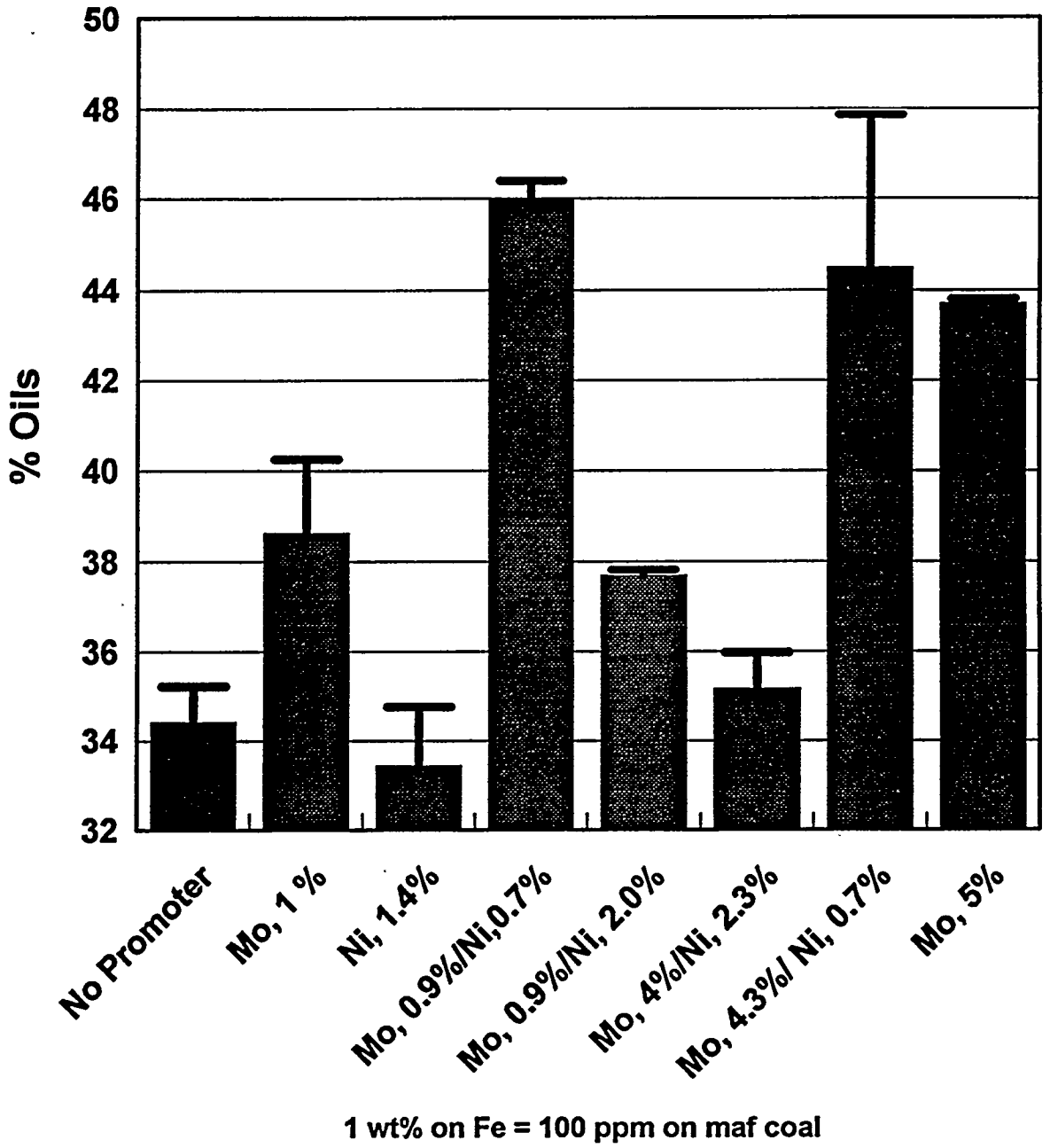


Figure 28. Effect of nickel and molybdenum on the activity of sulfated hematite for total conversion.



1 wt% on Fe = 100 ppm on maf coal

Figure 29. Effect of nickel and molybdenum on the activity of sulfated hematite for conversion to oils.

molybdenum loading to 4.3% resulted in a slight decrease in oil yield to 44.5%. As previously noted, an increase in nickel concentration to ~2% results in a decrease in catalytic activity.

These results indicate that nickel and molybdenum show the greatest amount of synergism of the catalyst tested here. The catalytic activity appears to be very sensitive to both molybdenum and nickel concentrations while the selectivity to oils is more sensitive to variations in nickel concentrations. Unlike the other promoter metals tested, nickel shows a distinct maximum in both total conversion and oil yield at a concentration of 0.7%. Increasing the concentration to ~2% significantly reduces the catalyst activity. The effect of small variations of nickel concentration near 0.7% are not known at this time. Given the relatively low cost of nickel compared to the other metals tested, the use of the 0.9% molybdenum, 0.7% nickel catalyst may have a favorable impact on the overall process economics.

Coal Liquefaction in V-131b

Experimental

In order to determine the activity of the catalysts in a recycle solvent, experiments were conducted utilizing V131b, the recycle stream from run 258K at Wilsonville. The details of this solvent and have been describe previously. This solvent contains a mixture of resid, and heavy distillate. The ash contains the recycled iron oxide used as a catalyst during Run 258K. It was apparent during these experiments that the recycled catalyst still possessed significant activity which made it difficult to discern the absolute effect of the fresh catalyst. An analysis

of the resid is shown in Table 3.

Table 3. Analysis of V-131b from Run 258K.

% Ash	11
% Iron	1.39
% IOM	15.5
% Distillate	51.2
% Resid	48.8

Microautoclave experiments were utilized to evaluate the activity of some of the promoted sulfated hematite catalysts for coal liquefaction in the presence of a recycle solvent. The experimental procedure used a horizontal 50 ml tubing bomb reactor loaded with 3.0 g Black Thunder coal and 5.4 g V131b. Except as noted in the text, the catalyst was loaded at ~1 wt% Fe2O3 on maf coal and DMDS was added as a sulfiding agent after which the reactor was sealed, purged and pressurized to 1000 psig (cold) with H2. The loaded reactors were placed in a heated fluidized sand bath at 440 C for 22 minutes and agitated at ~400 cycles/minute. Post reaction cooling was accomplished in a cool fluidized sand bath. Unless noted elsewhere, all experiments were conducted a minimum of twice to ensure reproducibility of the data. Figures reported represent an average of all runs.

Samples of the gas phase of the reactors were collected and analyzed by gas chromatography. The remaining reactor contents were analyzed by THF extraction followed by vacuum

distillation of the THF solubles to an atmospheric equivalent of 1050 F. Catalyst activity was inferred from THF conversion, resid conversion, and distillate yield. These terms are defined as follows.

$$THF\ Conversion = \frac{[maf\ Coal_{initial} - (IOM_{total} - IOM_{resid})]}{maf\ Coal_{initial}}$$

$$Resid\ Conversion = \frac{[(>1050F + maf\ Coal)_{initial} - >1050F_{final}]}{(>1050F + maf\ Coal)_{initial}}$$

$$Distillate\ Yield = 1 - \%Gas - \frac{>1050F_{final} - >1050_{initial}}{maf\ Coal}$$

Results

Baseline runs conducted with Wilsonville iron oxide (WIO) and Molyvan L (MVL) show the high activity of this catalyst combination. This catalyst system, loaded at 1 wt% WIO and 100 ppm Mo on maf coal, yielded a THF conversion of 102.0%, a resid conversion of 29.7% and a distillate yield of 52.7%. Most of the activity was attributed to the high dispersion of molybdenum achieved by use of the MVL precursor. Replacing the WIO with an unpromoted sulfated hematite resulted in a significant increase in activity. As shown in Figure 30, the use of the sulfated hematite with MVL at the same loadings resulted in an increase in resid conversion and distillate yield of 3.1% and 5.8% respectively. THF conversion also showed an improvement of 6.5%, shown in Figure 31. These numbers reflect the fact that the sulfated hematite/MVL system demonstrated the highest activity observed during this study.

In this study, the MVL loading represents ~100 ppm molybdenum on maf coal while the P-2

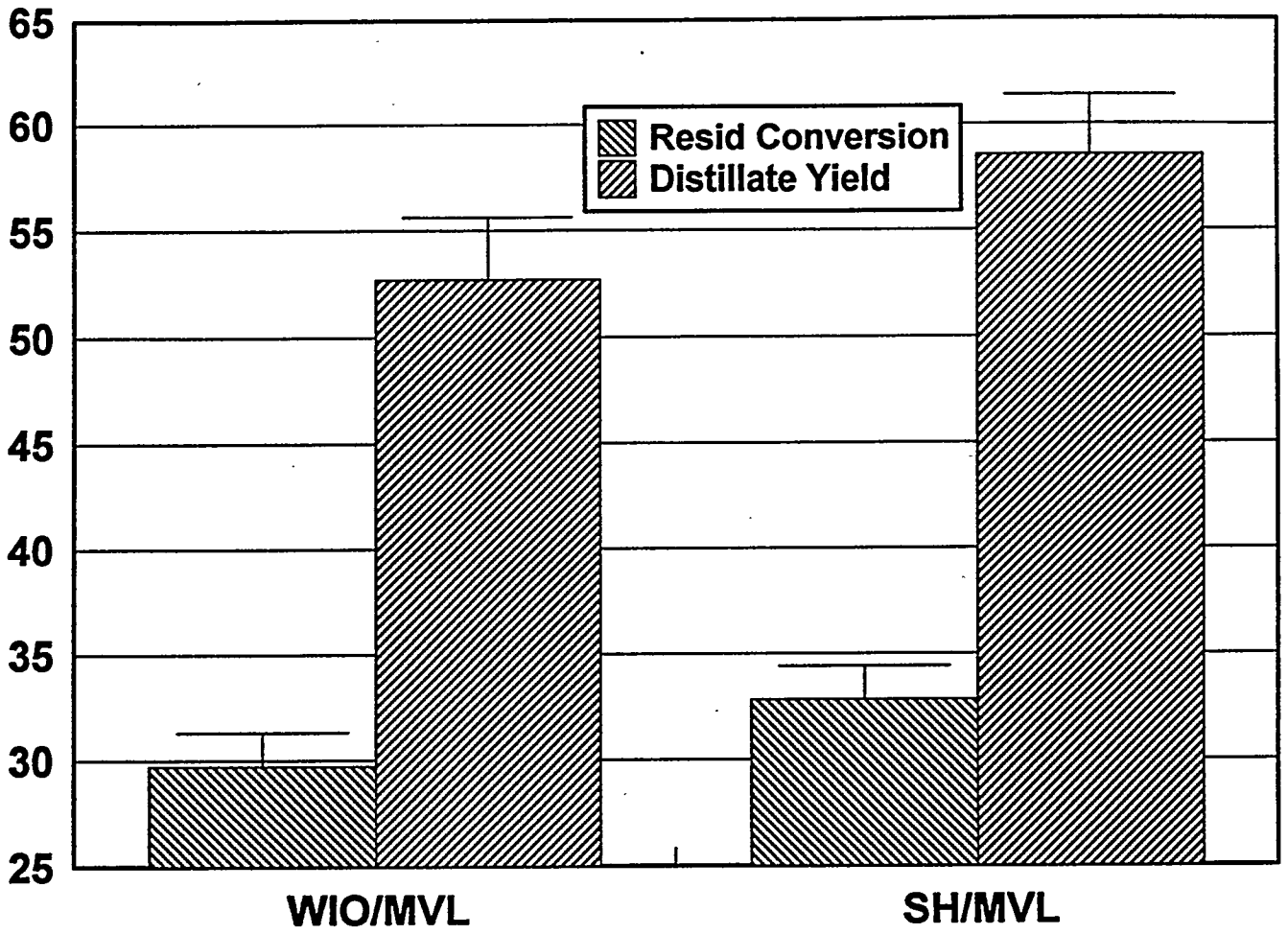


Figure 30. Comparison of the activity of sulfated hematite and WIO in the presence of 100 ppm molybdenum as MVL.

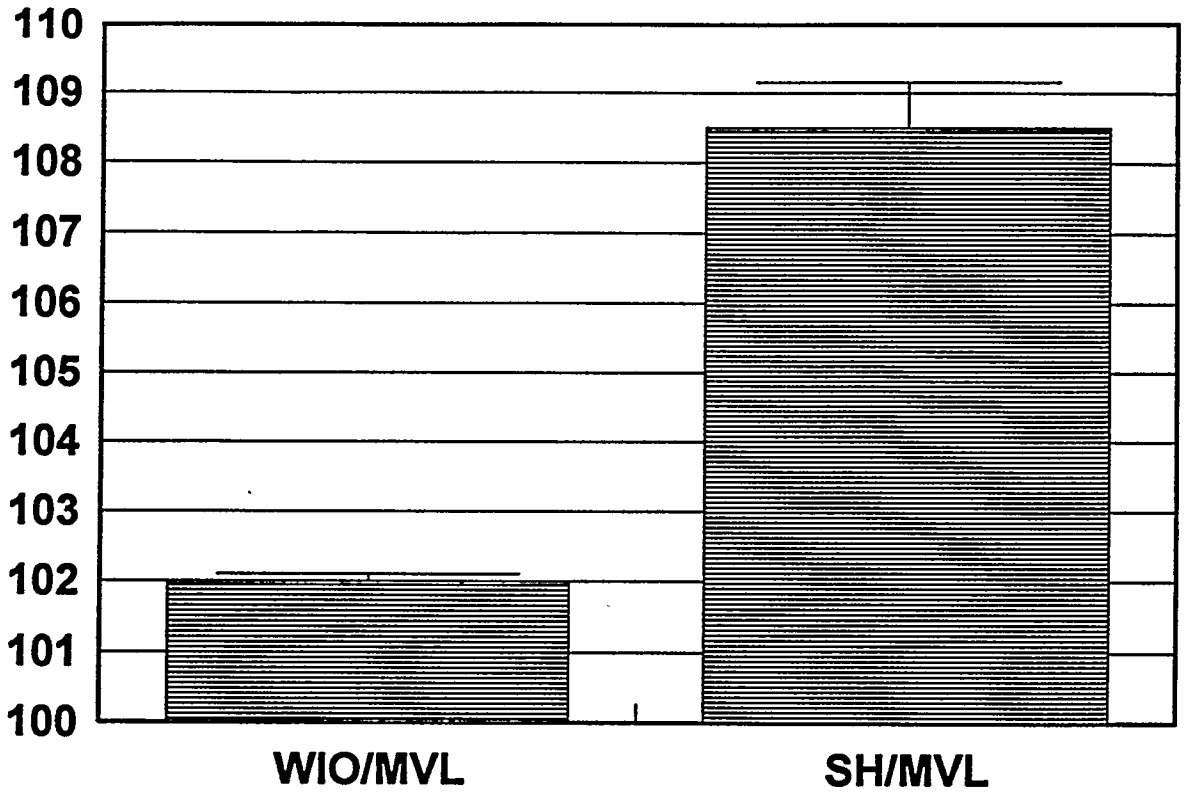


Figure 31. Comparison of the activity of sulfated hematite and WIO in the presence of 100 ppm molybdenum as MVL.

catalyst loading represents ~800 ppm molybdenum on maf coal. This higher loading is offset by the lower cost of the ammonium molybdate used for the P-2 compared to the cost of the MVL. A comparison of the P-2 catalyst with the WIO/MVL system shows a similar activity for resid conversion and distillate yield (Figure 32). However the THF conversion obtained with the P-2 catalyst, shown in Figure 33, was significantly higher than that obtained with the WIO/MVL catalyst. This appears to indicate a difference in the functionality of the two catalysts. The molybdenum promoted sulfated hematite appears to favor the conversion of the coal to a soluble material with a high average boiling point. The WIO/MVL system appears to exhibit more hydrogenation activity resulting in a lower boiling point product but less total breakdown of the coal molecule. This may indicate that the product derived using the P-2 catalyst may be more suitable to upgrading in a second stage reactor. Further studies in a continuous bench scale unit are needed to confirm this hypothesis.

The effect of the concentration of molybdenum on the promoted sulfated hematite for THF conversion is shown in Figure 34. As expected, an increase in molybdenum concentration from 2.2 wt % to 8.0 wt % on the sulfated hematite resulted in an increase in total conversion from 104.7% to 108.0%. These catalysts represent a loading of 220 ppm and 800ppm molybdenum on maf coal, respectively. Increases were also observed in both distillate yield and resid conversion as shown in Figure 35.

To help differentiate the effect of the iron and the molybdenum a catalyst was prepared which contained ~16% molybdenum on sulfated hematite. This catalyst was loaded at 0.6% catalyst

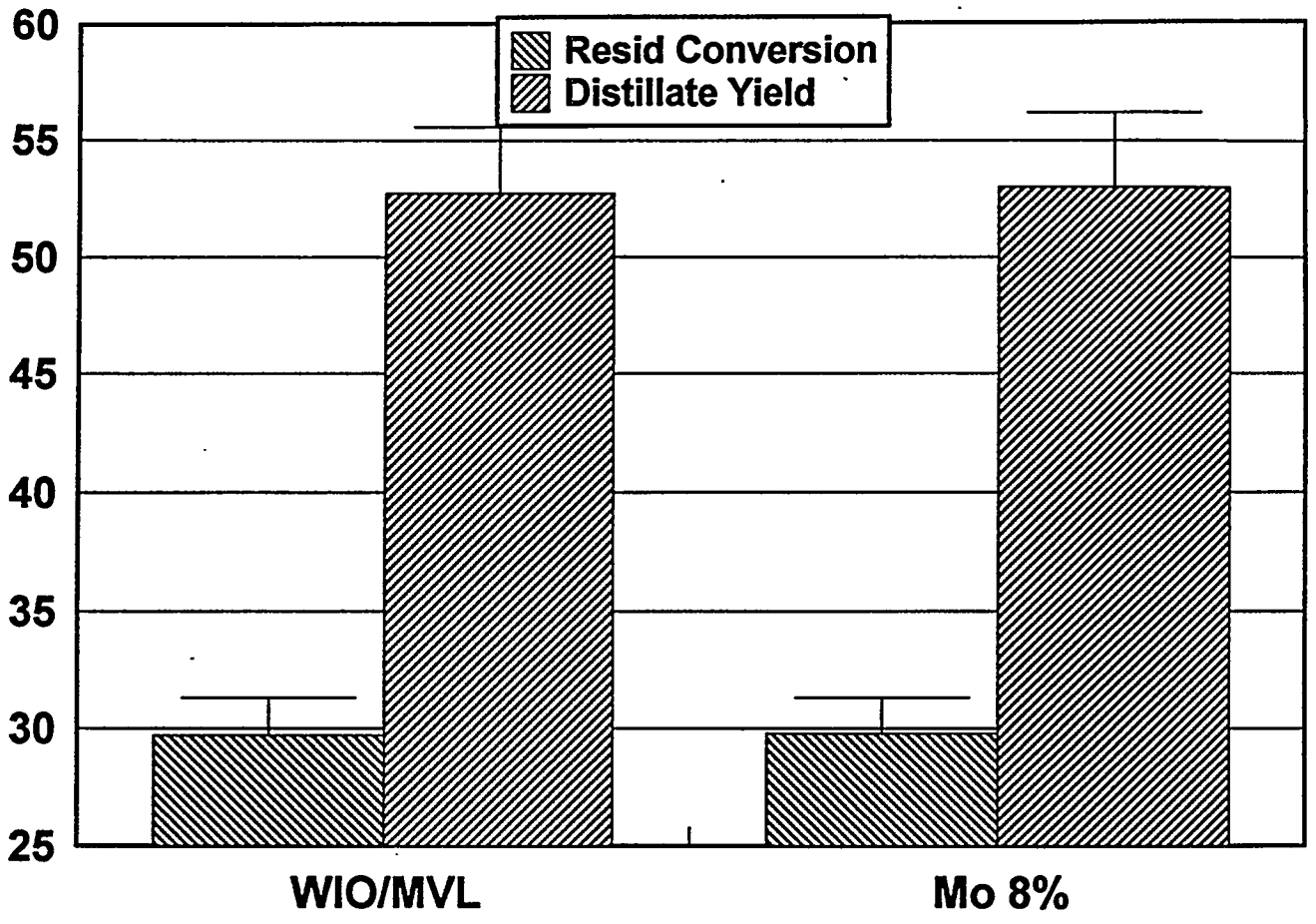


Figure 32. Comparison of activity of WIO/MVL with 8%Mo on sulfated hematite.

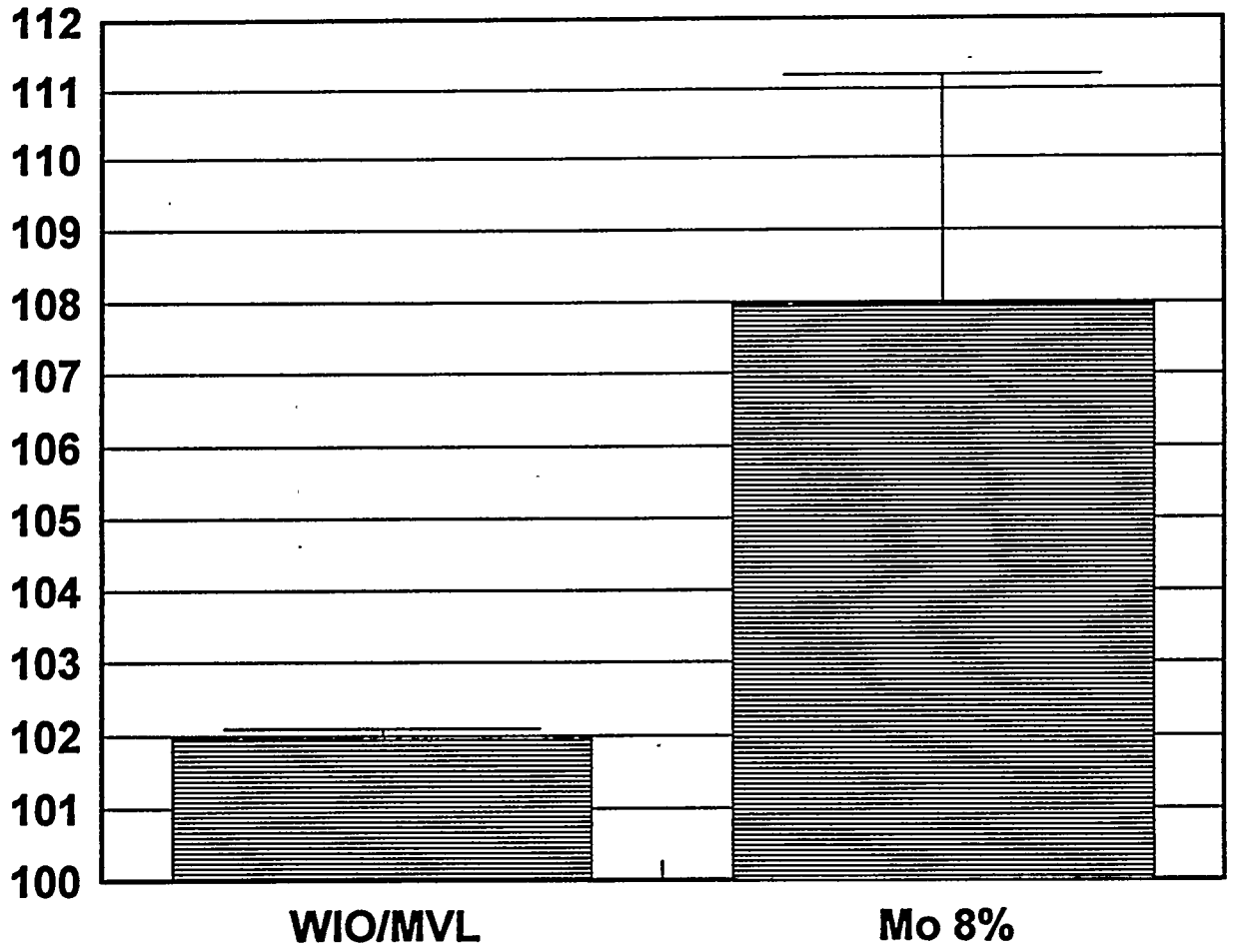


Figure 32. Comparison of activity of WIO/MVL with 8%Mo on sulfated hematite.

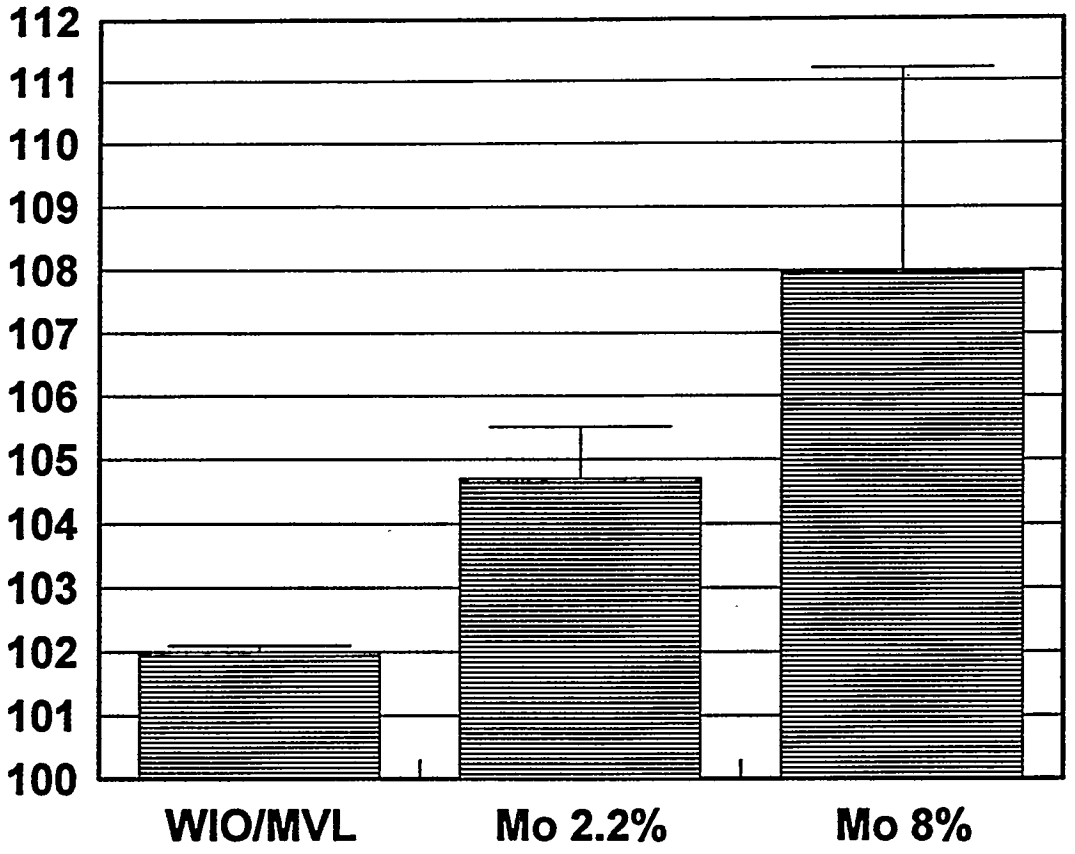


Figure 34. Effect of molybdenum concentration onTHF conversion

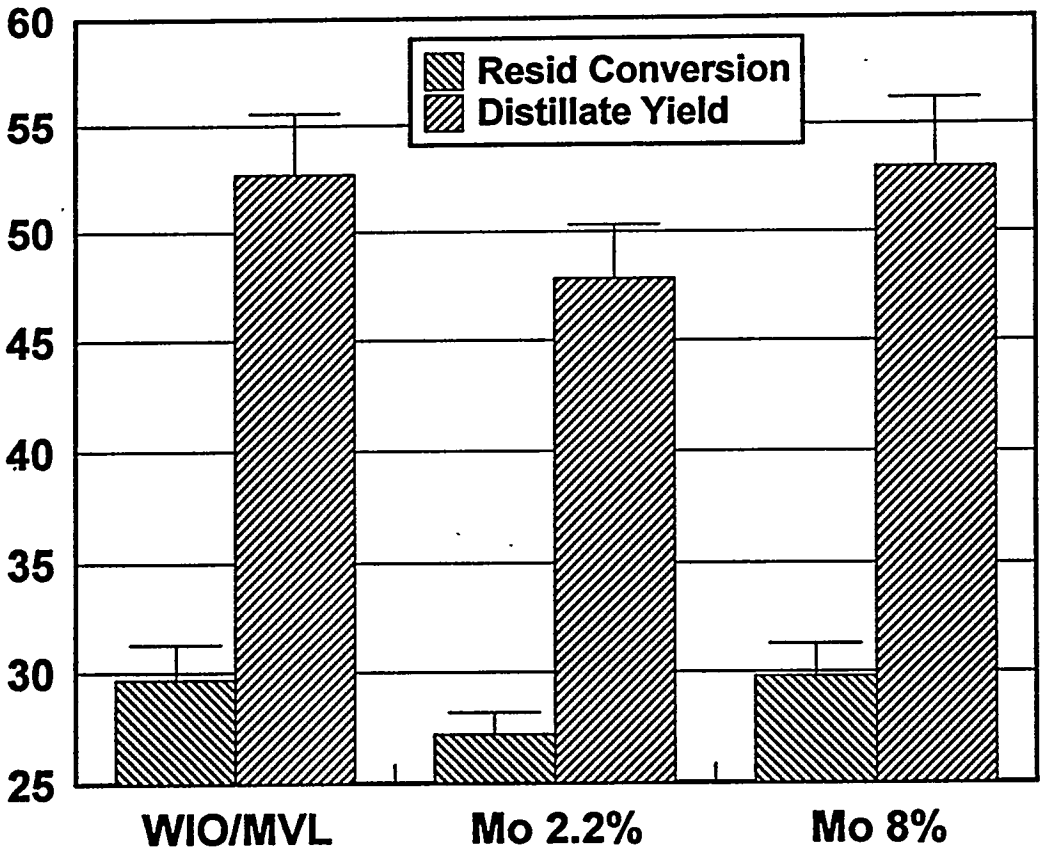


Figure 35. Effect of molybdenum concentration on resid conversion and distillate yield

on maf coal, representing a molybdenum loading of ~900 ppm on maf coal, and DMDS was added as a sulfiding agent. The results indicate that at this loading the high molybdenum catalyst exhibits similar activity to the P-2 catalyst as shown in Figures 36 and 37. Further reducing the loading to 0.3% catalyst on maf coal, corresponding to ~450 ppm molybdenum on maf coal, resulted in slight decrease in the resid conversion and distillate yield. However, the THF conversion was substantially reduced. This seems to indicate that the THF conversion correlates well with the iron loading while the resid conversion and distillate yield correlate with the molybdenum loading. This finding agrees well with previous studies which have shown that while iron is very active for conversion of coal to methylene chloride solubles, molybdenum is more active for hydrogenation of the soluble products [9].

Both nickel and cobalt were tested as co-promoters with molybdenum on the sulfated hematites. The results, shown in Figures 38 and 39, show that both nickel and cobalt have similar effects on the activity of the catalyst at very low concentrations. Although the conversions obtained with the addition of nickel to the molybdenum promoted catalyst were slightly lower than those obtained with the 8 wt% molybdenum promoted catalyst, this may be partially offset by the substantially lower cost of the nickel relative to the molybdenum. When compared to the 2.2 % molybdenum promoted catalyst the addition of ~ 0.5 % nickel or cobalt to ~1% molybdenum resulted in nearly identical activities, within experimental error. This corresponds to a reduction in molybdenum concentration, on a maf coal basis, from ~220 ppm to ~100 ppm with the addition of ~50 ppm nickel. Given the relative costs of nickel and molybdenum this would indicate nearly 50% reduction in the cost of the promoter metals.

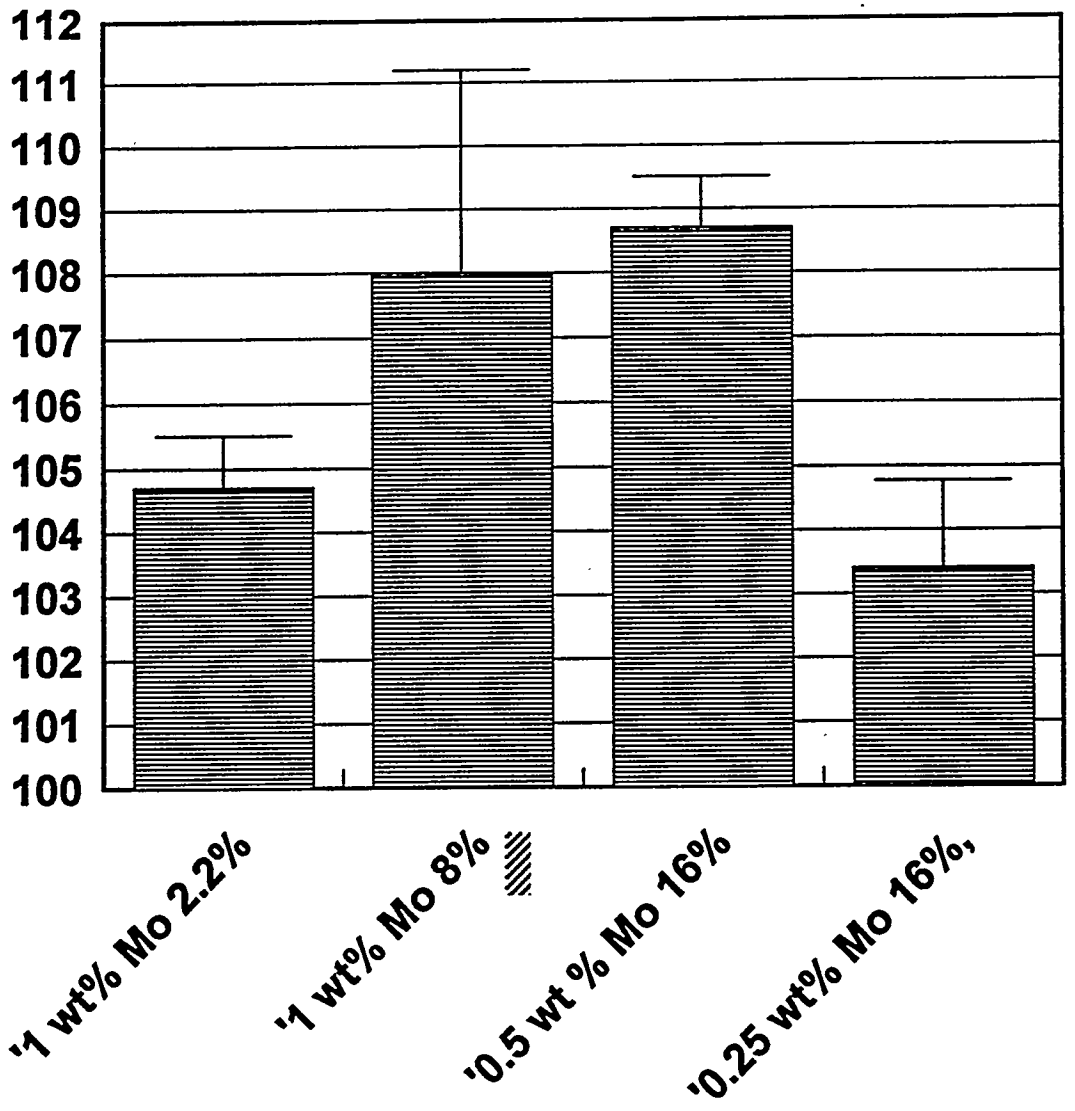


Figure 36. Effect of molybdenum loading on THF conversion. Axis label indicates wt% total catalyst loading and molybdenum concentration on catalyst.

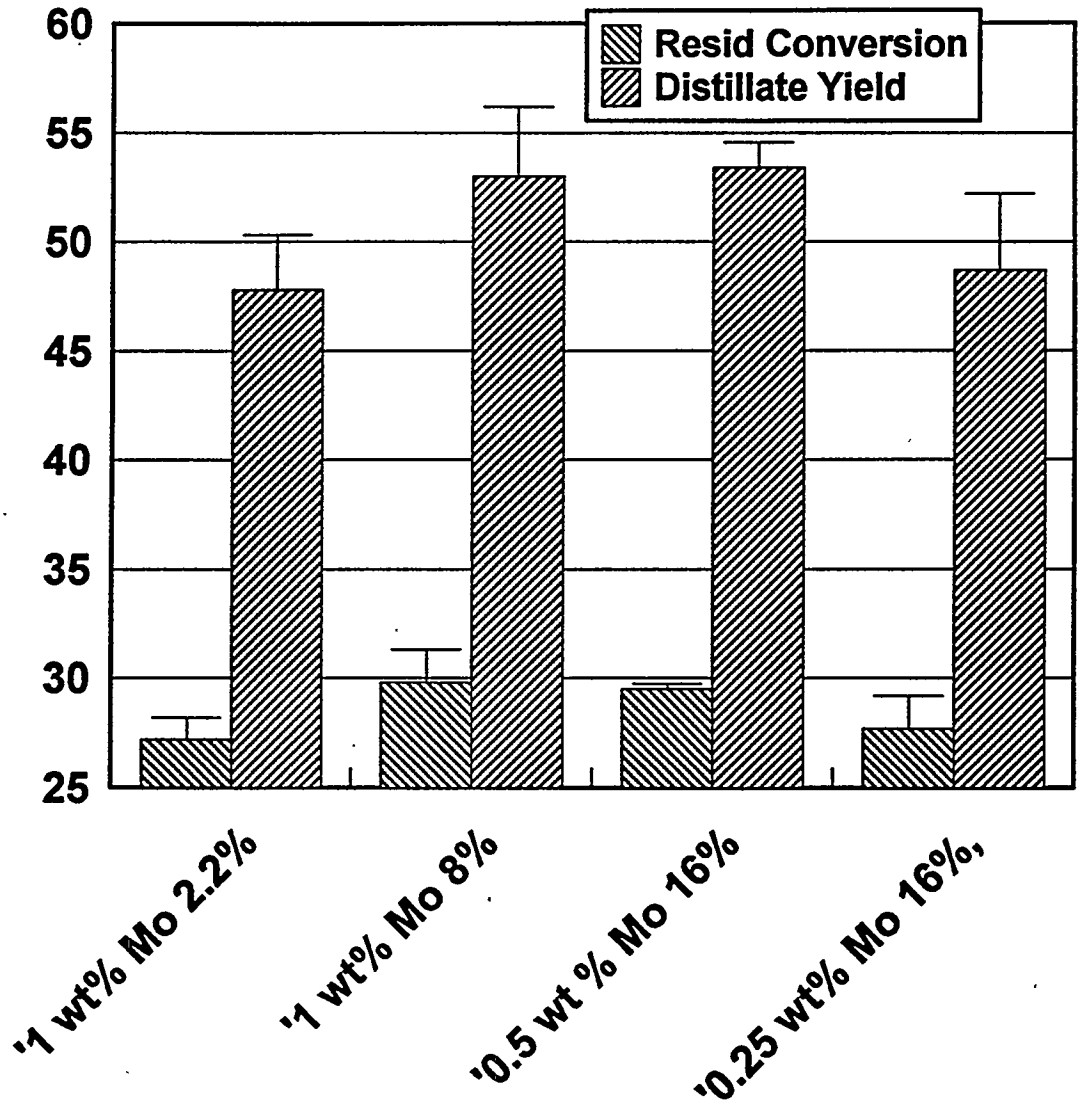


Figure 37. Effect of molybdenum loading on resid conversion and distillate yield. Axis label indicates wt% total catalyst loading and molybdenum concentration on catalyst.

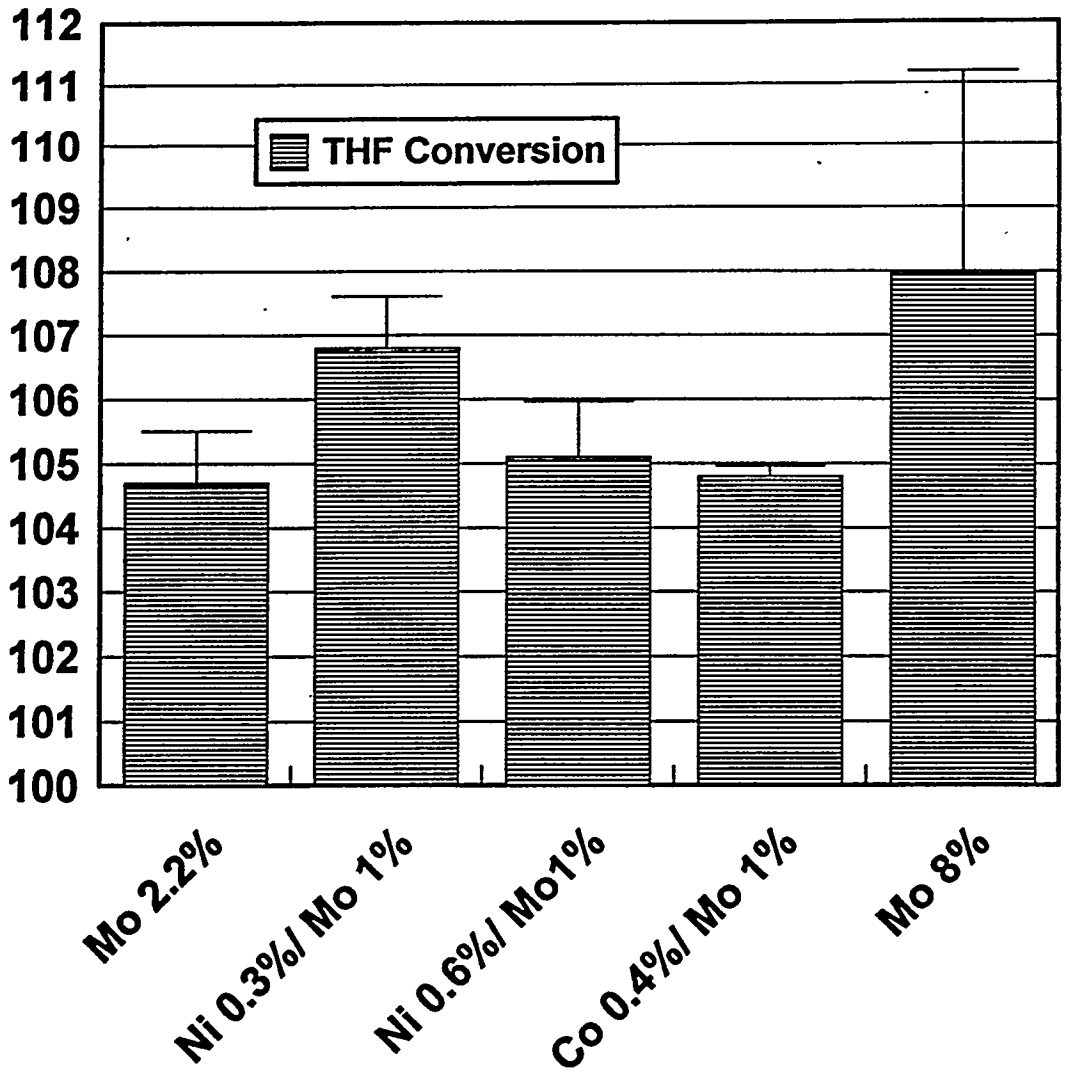


Figure38. Effect of co-promoter on the molybdenum promoted sulfated hematite.

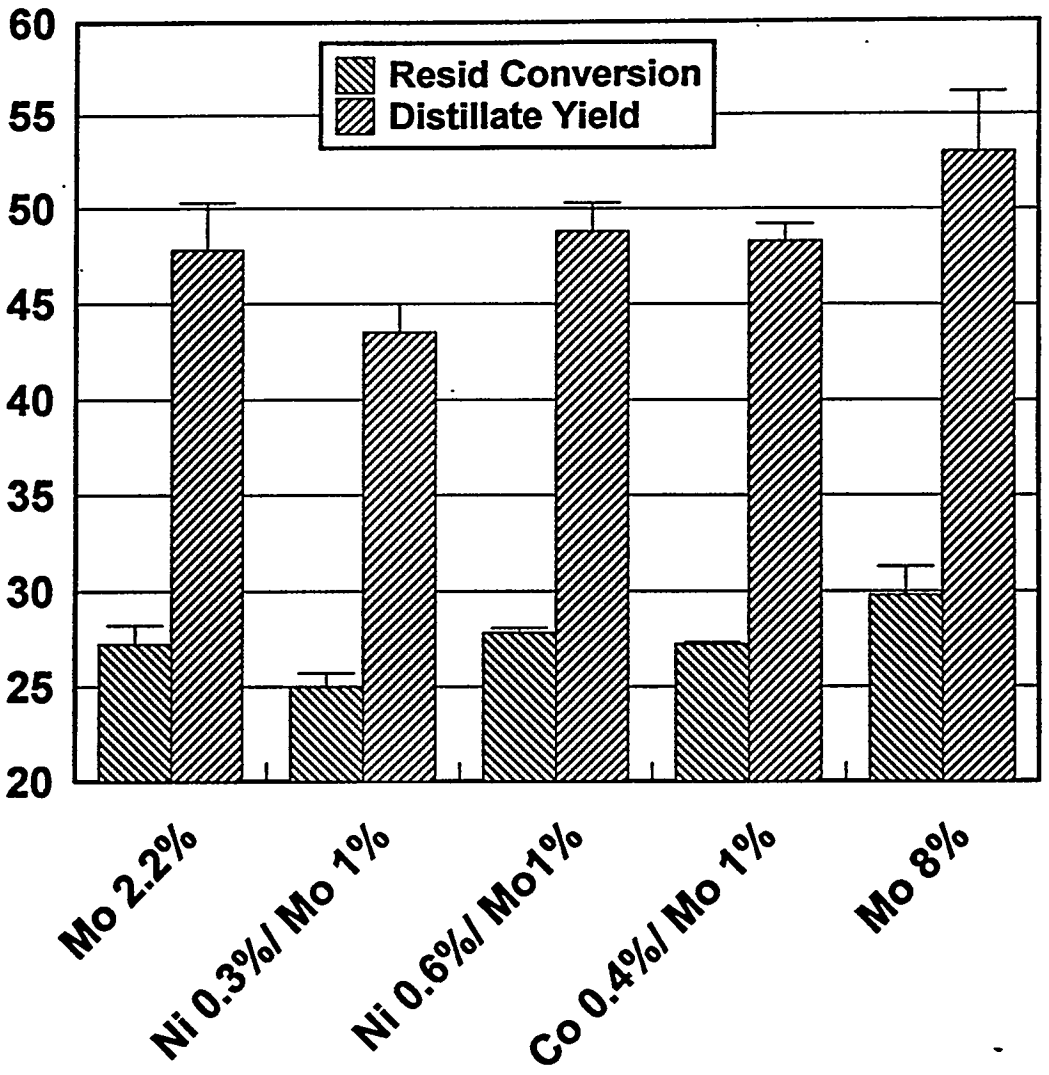


Figure 36. Effect of co-promoter on the molybdenum promoted sulfated hematite.

Further reduction of the nickel content to ~0.25% reduced the activity of the catalyst for distillate production but resulted in a slight increase in THF conversion. This catalyst would then contain ~25 ppm nickel and ~100 ppm molybdenum on maf coal. Cobalt may have a similar effect though this possibility was not explored. These results infer that by manipulating the ratio of the promoter metals it may be possible to maximize either the THF conversion or the distillate yield.

Conclusions

Promoted sulfated hematites have shown promising results as catalysts for the liquefaction of Black Thunder coal in the presence of a recycle donor solvent. A comparison of these catalysts with the WIO/MVL system has shown that it is possible to realize higher conversions, although higher molybdenum concentrations were required to achieve higher distillate yields. All the promoted sulfated hematite catalyst displayed a higher activity for THF conversion than the WIO/MVL system.

The unpromoted sulfated hematite displayed superior activity compared to the WIO when used in combination with the MVL resulting in the highest conversions and distillate yield observed in this study. This may be attributed to the higher surface area and dispersion of these particles. The use of a sulfated hematite promoted with molybdenum resulted in activity similar to the WIO/MVL system. However the molybdenum concentration was 8 times that

used in the WIO/MVL system. The higher molybdenum concentration may be offset by the lower cost of the precursor compared to the MVL.

Using a high molybdenum loading on sulfated hematite it was found that high conversions could be maintained at low catalyst loadings. The reduction in the catalyst loading did not adversely effect the product slate. The use of the high molybdenum catalyst would allow a 50% decrease in catalyst mass while maintaining high activity. This would result in significant reduction in the size of the catalyst production facilities thereby improving the overall process economics.

These studies also illuminated some differences in the activity provided by the iron and molybdenum. The addition of iron appeared to have a greater influence on the conversion to THF solubles than on distillate yield. On the other hand molybdenum had a profound impact on the quality of the liquids produced in the reaction. This agrees well with other data reported in the literature.

By using small amounts of nickel or cobalt as co-promoters, the molybdenum concentration may be reduced by 50% without loss of activity. This promising result demonstrates the possibility of significantly reducing the cost of the particulate catalyst by replacing a portion of the molybdenum with less expensive nickel or cobalt. These results were obtained for a molybdenum concentration of 2% on sulfated hematite. In light of the results obtained using high molybdenum concentrations, higher loadings of both molybdenum and the co-promoter

would appear to be indicated to achieve higher activity while reducing the total mass of catalyst required. This may not be possible as the ability to add the nickel and cobalt appears to be limited. Further, the optimum ratio of promoter metals has yet to be determined.

It was not possible in this study to differentiate between the activity of the fresh catalyst and the acitivity of the recycled iron oxide. Unlike the fresh catalyst, the recycled catalyst is in its active phase during the initial period of reaction and may therefore play am important role in the initial reactions occuring during this period.

The Effect of Recycle Ash on Activity

As previously mentioned, the activity of the sulfated hematite for coal liquefaction was confirmed in recycle solvents from both Wilsonville Runs 258K and 262E. Run 258K solvent was obtained from a run made at Wilsonville when 1% iron oxide catalyst was being added to the feed while Run 262 solvent were generated when adding 1% iron oxide in combination with 100 ppm molybdenum as Molyvan L. Since these solvents contained small amounts of recycled catalysts the relative influence of the particulate catalyst compared to the recycled catalyst was unknown. It is assumed that the recycle catalyst is in its most active phase at the beginning of the reaction while model compound studies have indicated that the particulate catalyst may experience a period of relatively low activity prior to activation.

In order to isolate the effects of the fresh and recycled catalysts, a deashed solvent which contained little or no recycle ash was prepared in order to obtain a better indication of their

intrinsic activity. Comparison of the activity in the deashed and ashy solvents should give an indication of the activity of the recycled catalyst.

Ash Free Materials

Recycle solvents from Runs 258K and 262E at Wilsonville have been utilized in this study. The material from recycle material from Run 262E consists of a mixture of ashy resid, deashed resid, and heavy distillate. The ashy resid was feed to the Rose-SR unit while the deashed resid was the product from the unit. The ash-free Run 262E solvent was prepared by eliminating the ashy resid from the mixture and replacing it with a calculated amount of deashed resid.

The recycle stream from Run 258, denoted as V-131B, was utilized in an as-received form in the previous studies. The separated streams were not available for this run. In order to determine the effect of recycled iron on the conversion, a hot vacuum filtration method was employed to remove the ash. The V-131B was heated in a beaker to reduce the viscosity. The hot solvent was then poured through Whatman GF/D glass fiber filter paper in a heated Buchner funnel. This paper has been reported to retain particles larger than 2.7 μm. Although the external temperature of the funnel was maintained at >170 C for the duration of the filtration, the paper fouled fairly rapidly allowing only small quantities of sample to be filtered during each run.

The products of the filtrations were ground and mixed prior to analysis. The results of the analysis, shown in Table 4, indicate that the filtration was successful in removing over 95% of the ash and over 99% of the iron. A substantial portion of the IOM was also removed, however the

resid/distillate ratios remain similar. This is due to the loss of some light distillate during the heated filtration process. The importance of this loss is unclear at this time.

Table 4. Analyses of as-received and filtered Run 258K V-131B.

	As-Received	Filtered
% Ash	11	0.25
% Iron	1.39	0.009
% IOM	15.5	6.4
% Distillate	51.2	52.3
% Resid	48.8	47.7

Experimental

The liquefaction experiments were carried out as previously described. The amount of solvent utilized for each run was adjusted to reflect the ash-free amounts utilized in previous runs. The ash free solvent from Run 262E consisted of 2.06 g deashed resid with 2.32 g heavy distillate while the ash free solvent from Run 258K consisted of 4.48 g filtered V-131B. The runs were carried out for 22 minutes at 440 °C with 3 g of as received coal.

Two catalysts were studied during this period. The sulfated hematite catalyst promoted with 8 wt% molybdenum was utilized at a concentration of 1 wt% catalyst on maf coal. It was desired to determine the activity of a similar concentration of molybdenum and iron loaded as Molyvan L (MVL) and Wilsonville iron oxide (WIO), respectively. Therefore WIO was loaded at 1 wt% on maf coal and MVL was added as 1000 ppm molybdenum on maf coal.

An investigation of the effect of concentration on total conversion and resid conversion was also undertaken during this reporting period. These experiments were conducted utilizing molybdenum promoted sulfated hematite and the filtered Run 258K recycle solvent to minimize the effects of recycled catalyst. Also, based on the results from the Process Simulation Test (PST) series, the use of the recycle solvent from Run 258K appears to yield more significant variation with reaction conditions and catalyst addition.

Results

The results of the liquefaction testing are summarized in Table 5. The use of the recycle solvent from Run 262E resulted in substantially higher resid conversion than that obtained with the Run 258K recycle solvent, i.e. 36.4% vs. 29.5%, respectively. The corresponding 1050 °F- yields were 70.1 and 52.6%, respectively. The removal of the ash from these solvents did not appear to have a significant effect on this trend. The ash free Run 262E solvent resulted in a slightly higher THF conversion (89.8%) than the filtered Run 258K V-131B solvent (87.3%), in the presence of molybdenum promoted sulfated hematite. The use of 1 wt% WIO and 1000 ppm MO as Molyvan L showed a slightly higher THF conversion in the filtered Run 258K V-131B solvent (93.0%) than in the ash free Run 262E solvent (91.6%), however these numbers are not statistically different given the error in the experiments. The relative activities of the catalysts are clear with the WIO/Molyvan L yielding a THF conversion 5.7% higher than the promoted sulfated hematite catalyst in the filtered Run 258K solvent. In the ash free Run 262E solvent a similar trend was observed, with the WIO/Molyvan L being 1.8% higher than the promoted sulfated hematite catalyst case. Both cases indicate a higher sensitivity of the filtered Run 258K

recycle solvent to catalyst addition.

While the difference in the THF conversion was small, the effect of recycle solvent on resid conversion and 1050 °F⁻ distillate yield was significant. Substantially higher values were obtained with the addition the promoted sulfated hematite for the ash-free Run 262E solvent as compared to the filtered Run 258K solvent. This same trend was seen with the addition of the WIO/Molyvan L catalyst. The relative activities of the catalysts is also clearly indicated. The WIO/Molyvan L catalyst gave a 2.3% higher resid and 4.2% higher 1050 °F⁻ distillate yield than molybdenum promoted sulfated hematite catalyst in the filtered Run 258K recycle solvent. For the ash free Run 262E recycle solvent, the molybdenum promoted sulfated hematite catalyst and WIO/Molyvan L catalysts were nearly identical. The lack of response in the Run 262E recycle solvent to different catalysts was also observed for the Run 262E solvents containing ashy materials during the PST runs.

Table 5. Summary of Liquefaction Data for Ashy and Ash Free Recycle Streams

Catalyst	Solvent[a]	Resid Conv.	THF Conv.	1050 °F⁻	% COx	% HC gas
Mo / SH	V-131B	29.5%	107.3%	52.6%	5.8%	3.3%
Mo / SH	Filtered V-131B	24.2%	87.3%	38.4%	5.8%	2.8%
Mo / SH	WRO	36.4%	107.3%	70.1%	5.4%	3.6%
Mo / SH	Ash free WRO	37.0%	89.8%	56.5%	5.2%	3.0%

WIO/ MVL	Filtered V-131B	26.5%	93.0%	42.6%	5.7%	3.0%
WIO/ MVL	Ash free WRO	36.7%	91.6%	56.3%	5.8%	2.7%
a. V-131B is Run 258K V131B; WRO is Run 262E recycle solvent.						

The effect of filtration or deashing of the recycle solvent on conversion is complex. The THF conversions reported for the PST runs were generally greater than 100% indicating conversion of a portion of the IOM in the recycle solvent. The filtration process reduced the IOM concentration of the Run 258K recycle solvent from 15.5% to 6.4%. Similarly, the ash free Run 262E solvent contained only 3.3 % IOM compared to 14% for the Wilsonville recycle oil (WRO). This reduction in IOM is most likely a major factor in the reduction in THF conversion. The reduction of catalyst in the recycle solvents probably also plays a role in the reduction in THF conversion. The relative contributions of these two factors has not been determined.

The filtration of the Run 258K V-131B solvent resulted in a decrease in THF conversion of 20.0% when used with the molybdenum promoted sulfated hematite. Similarly, the use of ash free Run 262E resulted in a decrease of 17.5% in THF conversion with the same catalyst compared to the full range recycle solvent. The possible reasons for these decreases have been given earlier. Deashing of the solvents clearly had an effect on both resid conversion and 1050 °F- distillate yield. The use of the filtered Run 258K recycle solvent with molybdenum promoted sulfated hematite resulted in a decreases of 5.3% in resid conversion and 14.2% distillate yield compared to the unfiltered solvent. This follows the same trend as

the THF conversion and may be due to reduced recycle catalyst or loss of reactive resid in the filtration process. In contrast, the ash free Run 262E recycle solvent with same catalyst displays no change in resid conversion and a 13.6% drop in distillate yield.

The explanation may lie in the different method of ash removal. The ash was removed from the Run 262E recycle solvent by a critical solvent deashing (CSD) method which yields a substantially different product distribution than the hot filtration process. The filtration method results in significantly less resid removal than the CSD method. The resid which was removed was probably of higher molecular weight and less reactive than the retained resid. This would account for the high resid conversion but lower distillate yield obtained using the Run 262E derived solvents.

The effect of loading of molybdenum promoted sulfated hematite on resid conversion and distillate yield is shown in Figure 40. From this it can be seen that at a loading of 0.25 wt% catalyst on maf coal the effect on resid conversion and distillate yield is apparent. Further increases in concentration up to 1 wt% catalyst on maf coal yield very little additional resid conversion and distillate yield. However, the THF conversion continues to increase with increasing concentration up to 1 wt% catalyst.

Conclusions

The results from this study indicate that the solvent from Run 262E exhibits higher activity than the solvent from Run 258K regardless of the recycle ash content. The ash free Run 262E

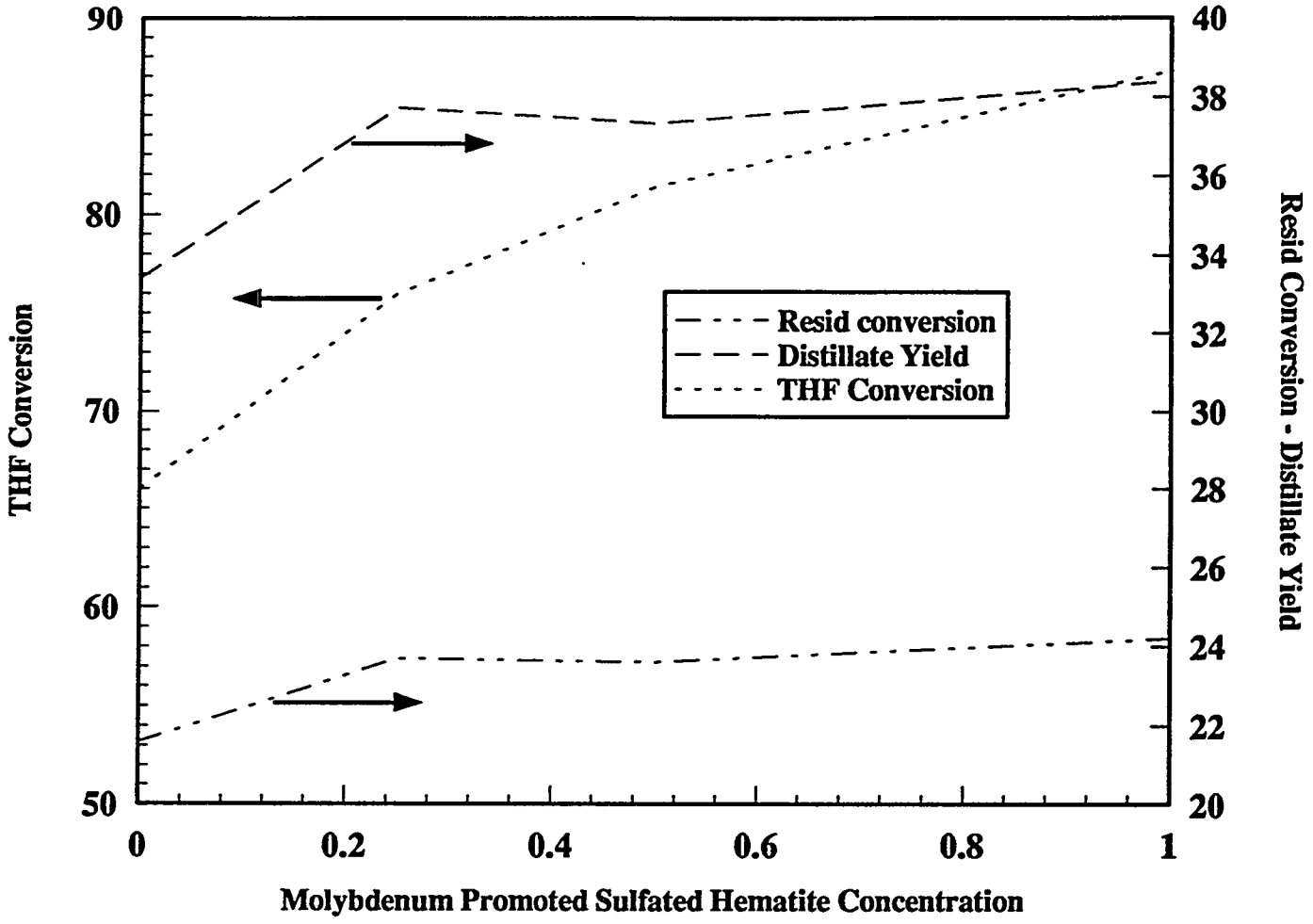


Figure 40 Effect of concentration of molybdenum promoted sulfated hematite on conversions and distillate yield.

solvent yielded higher resid conversions than the filtered Run 258K solvent with both molybdenum promoted sulfated hematite and WIO/Molyvan L catalysts. However, the filtered Run 258K solvent showed higher sensitivity to catalyst addition. In addition to the removal of recycled catalyst, the method of de-ashing appears to play a role in the activity of the ash free solvent.

From these results it is clear that the activity of the recycled catalyst in the Run 262E recycle solvent is higher than that from Run 258K. The recycled catalyst in both solvents exhibit considerable activity which interferes with the determination of the activity of fresh catalysts added to the system. In the absence of recycled ash it is apparent that the activity of the molybdenum promoted sulfated hematite is comparable with that of the WIO/Molyvan L catalyst system. This is particularly important given the slightly higher molybdenum concentration in the WIO/Molyvan L system.

An analysis of the effect of catalyst loading on activity indicates that the maximum resid conversion and distillate yield may be obtained at significantly lower loadings than those suggested in the base case. Loadings as low as 0.25 wt% catalyst on maf coal have been shown to yield substantial increases in resid conversion and distillate yield. However, higher catalyst loadings are required in order to maximize the THF conversion.

Summary

The results of this program have shown the high catalytic activity of the nanoscale sulfated

hematite particles. The addition of low concentrations of molybdenum has been shown to significantly enhance the activity of the sulfated hematite. The results of the model compound studies indicate that the catalysts exhibited high activity after a period of low activity. This delayed onset of activity is presumably related to conversion to an active phase. However, XRD analysis of the spent catalysts from the model compound runs showed a transformation to pyrrhotite within 5 minutes while some catalysts showed low activity for 15 minutes. Due to the inherent limitations of this analytical technique, no information about the promoter metals was generated which leaves questions about the nature of the catalyst during the initial reaction times. Further investigations into the fate of the promoter metals may shed light onto the cause for the delayed onset of activity.

The synergistic effect of nickel and molybdenum has been evident throughout this study. The use of nickel to reduce the amount of molybdenum required should result in substantial reduction in catalyst cost. There appears to be an optimum ratio of promoter metals which yields a maximum activity. The use of high molybdenum concentrations on the sulfated hematite have shown that the amount of catalyst may be reduced without sacrificing high activity. It may then be possible to further enhance the activity of these catalysts by the use of high concentrations of nickel and molybdenum, in the proper ratio, thereby reducing the cost of the catalyst.

This study has shown the high activity of the molybdenum promoted sulfated hematites for coal liquefaction in a recycle solvent. However, the activity of the catalyst when used in a

recycle mode has not been investigated. Given the slow rate of activation observed in the model compound experiments it is possible that the recycled catalyst may exhibit higher activity than the fresh catalyst.

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CHAPTER 6

Activity and Sulfur Activation of a Nanoscale Iron Oxide Catalyst for Coal Liquefaction

Introduction

Of the several approaches that have been considered in the Advanced Concepts in Liquefaction project to lower the cost of producing coal liquids (e. g., CO pretreatment of coal, coal cleaning, and recycle liquefaction solvent quality improvements), research and development activities addressed here relate to the use of low-rank coal feedstocks and dispersed catalysts to promote coal dissolution in the first stage of a two-stage process. In particular, a nanoscale iron oxide and its activation with dimethyl disulfide are investigated for enhancing Black Thunder coal liquefaction product yields and increasing hydrogen consumption. The liquefaction data are compared with data for other catalyst precursors, including a coarser grade iron oxide and a carbon black, that exhibit some, but not all of the characteristics of the nanoscale iron oxide.

The advantages of using cheaper subbituminous coal liquefaction feedstocks from the western US are well documented.[1,2,3,4] However, these low-rank coals have high moisture contents and high oxygen contents, the latter resulting in high hydrogen consumption and hence increased cost. Further, the rate and extent of conversion in thermal reaction are low, causing inefficient use of reactor space and the loss of additional product on solids separation. However, pilot plant experience[5] has shown that high conversions can be obtained by the use of appropriate

added catalysts.

Molybdenum and iron are the most commonly investigated catalyst metals, and precursors of both can be converted to an active sulfide form under liquefaction conditions.[6] Although iron catalysts are much less active, they are preferred for reasons of economy, and their use has allowed the liquefaction of subbituminous coals which could not otherwise be processed.[3] Nevertheless, the activity of these catalysts is still much less than desired and means to enhance their activity are under investigation.

The catalyst activity is determined principally by its composition and the extent of its dispersion with the coal or coal-solvent slurry. The catalyst dispersion is dependent upon the form and mode of addition of the catalyst precursor. In general, a high surface/volume ratio, along with intimate contact between the active catalyst and coal, are thought to be the controlling factors.[6] Dispersion, as normally inferred from changes in catalyst activity, may be affected by the mode of addition, the presence of solvent, and the initial composition of the precursor (e.g., soluble organometallics); and for coal-impregnated catalyst precursors, the choice of impregnation solvent[7] and impregnation conditions.

A variety of innovative strategies have been developed to introduce catalyst precursors to the liquefaction reaction while seeking to maintain particle size and distribution. These have included the use of emulsions and colloids,[8,9,10] direct addition of ultra-fine particles to the slurry,[11,12,13,14,15] addition of oil soluble organometallics and carbonyls,[16,17,18] ion exchange[19]

and impregnating the coal.[20,21,22] The results of some studies, however, indicate that even with the well dispersed organometallic and carbonyl precursors, quite large crystallites or agglomerates can be formed during liquefaction and hence the potentially high dispersion is not maintained. There is some evidence to suggest that, if introduced as fine particulates, there is less tendency for agglomeration. Andres et al.[23,24,25] earlier verified that iron particles, in various forms as oxides and oxyhydroxides, retained their small size upon conversion to pyrrhotite under coal hydroliquefaction conditions. Additionally, the studies mentioned above that used nanometer size iron catalyst particulates have reported enhanced catalytic activity.

In evaluating avenues for improved catalysts, liquefaction studies performed at CAER using a commercially prepared small particle iron oxide (Superfine Iron Oxide, or SFIO) in process derived oils from the Wilsonville Advanced Coal Liquefaction Research and Development Facility have also shown activity for coal conversion, as well as a selectivity towards the production of distillable product.[26] SFIO is prepared by high temperature air oxidation of a volatile Fe precursor, and was originally developed as a burning rate catalyst for solid rocket fuel. The SFIO, whose very high surface area is consistent with nanometer size particles, may also, upon sulfiding, give rise to small particle, high surface area liquefaction catalysts. This enhanced effectiveness for coal liquefaction prompted interest in additional studies to evaluate fundamental performance in neat tetralin, absent the complexities of working with actual process derived process oils,[27] while recognizing the hydrogen rich tetralin vehicle would tend to minimize differences among the various catalysts.[28]

A second catalyst precursor investigated is a powdered material that had been successfully used at Wilsonville in Run 263, and which was derived from Aiusruther spray roast processing of spent acid from steel pickling prepared by Bailey.[29] This iron oxide (IO) was selected to represent a coarse, commercial grade iron oxide that would provide a comparison to the performance of the specialty SFIO described above.

Additionally, liquefaction experiments were conducted using carbon black as a catalyst that would present a considerable non-Fe surface in the reaction, to investigate the importance of an Fe species present as the active catalyst, in addition to other catalyst factors that are examined for the two iron oxide precursors.

Experimental

Materials- Reagents were purchased as follows: practical grade dimethyl disulfide (DMDS) from Fluka AG; 99% purity UV grade tetralin, high purity tetrahydrofuran (THF), and high purity pentane were Burdick & Jackson Brand from Baxter S/P; Ultra High Purity Grade hydrogen was supplied by Air Products and Chemicals, Inc.

Samples of the subbituminous coal and the powdered iron oxide catalyst used at Wilsonville[29] were supplied by CONSOL, Inc. Black Thunder subbituminous coal was ground to -200 mesh, riffled and stored under nitrogen at 4°C. Proximate and ultimate analyses of the coal are presented in Table 6-1. Moisture content measurements were made at the beginning of each run, but with little change over the course of the experiments had a value of 21.9 ±

0.72 wt% (as-received basis).

A sample of Superfine Iron Oxide (SFIO) was provided by MACH I, Inc., King of Prussia, PA. This material is a nanometer size iron oxide with the following properties as determined by high resolution transmission electron microscopy (TEM): γ-Fe_2O_3 structure, average particle size of 1-3 nm (see Photomicrograph 1, at 80 k magnification), and a nitrogen BET surface area of 300 m^2/g.[30] To protect against the adsorption of moisture, samples of SFIO were stored under dry nitrogen. The iron content of 63 wt% is consistent with a composition of either Fe_2O_3 containing 10 wt% moisture or with FeOOH. Zhao[31] proposed that the dominant phase of this material is $FeOOH \cdot xH_20$ based upon X-ray absorption fine structure (XAFS) analysis, with bulk iron coordinated to six oxygen or hydroxyl groups, and with a significant additional fraction of the iron located at the particle surfaces at sites with lower coordination. After heating, an α-Fe_2O_3 begins to form, with the phase transition being complete after extended heating at temperatures $>400°C$. Considerable particle growth has been found to occur upon sulfidation in the presence of H_2S and tetralin at 380°C, with the formation of pyrrhotite with a particle size of several hundred nanometers (Srinivasan et al.[32]). However, if sulfided in the presence of coal, a much smaller particle size pyrrhotite is formed.[32,33,34,35] It has been speculated in the latter instance that coal liquefaction products encapsulate the particle with a smooth carbonaceous deposit which preserves its activity,[35] or that perhaps a secondary component present in the coal mineral matter interacts with the SFIO to inhibit growth of the pyrrhotite particles.[36] This growth-inhibition phenomenon has also been observed on Fe-impregnated carbon black,[37] and absent coal products or mineral matter, some interaction with

the carbon substrate was indicated.

The IO was used as-received, and consists of about 99% Fe_2O_3, with the specification that 95% was -325 mesh (44 μ). Scanning tunneling electron microscope (STEM) studies showed the bulk of the IO was considerably smaller than this, and present as irregular, well rounded particles of 100 nm diameter or greater. Very little material was present with particle sizes as low as 10 nm. The difference in size between the IO and SFIO is apparent when Photomicrograph 2 is compared with the much smaller SFIO in Photomicrograph 1 at the same magnification. Other metal oxides comprised the remaining 1% of the IO, by far the largest component being an oxide of manganese, at 0.35 wt %. The nitrogen BET surface area was 8.6 m^2/g, which is consistent with an average particle size about 140 nm. The IO also has a bulk density 26 times that of SFIO (1.37 vs. 0.052 g/ml). Analysis by Mössbauer spectroscopy identified the iron oxide phase as >99% hematite, α-Fe_2O_3, and X-ray diffraction (XRD) confirmed this analysis.

The carbon black was purchased from UIC, Inc. for use in the liquefaction experiments. It had a nitrogen BET surface area of 90 m^2/g, and TEM studies showed it to comprise particles 10-60 nm across, and agglomerated in larger clusters. Proximate analysis showed it to be 93% fixed carbon content.

Liquefaction Experiments- Liquefaction experiments were conducted in batch reactions using microautoclaves. The 50 cc microautoclaves used in this study were made of 1.0 x 0.120 inch

wall, 316 stainless steel tubing with Swagelok socket weld-to-tube ends, capped with two 1 inch plugs. The overall length of the reactor body was 6.0 inches with the end plugs removed. The microautoclaves were mounted with the cylinder axis horizontal, and connected at the middle of the tube body with a vertical 1/4-inch stainless steel tube to allow gas pressurizing and venting. The vertical tube was sealed at its upper end by a 316 stainless steel, non-rotating stem Whitey angle valve.

In a typical experiment 3 grams of coal, 5.4 grams of tetralin, catalyst and dimethyl disulfide (DMDS) were added to the reactor. DMDS (when used) was added at 3.0 moles S/mole Fe to ensure that complete sulfiding of the catalyst precursor could be achieved. The reactor was sealed, pressurized with hydrogen to 6.89 MPa, and leak tested. Reactions were carried out by immersing the microautoclave in a fluidized sandbath set at the specified temperature, while the reactor was continuously agitated by vertical displacement at a rate of 400 cycles per minute. At the end of the reaction period, the reactor was rapidly cooled in a sand bath at room temperature.

Product Work-up. The gaseous products were collected and analyzed by gas chromatography. The solid-liquid products were scraped from the reactor using THF and the mixture was extracted in a Soxhlet apparatus for 18 hours. The THF-insoluble material, which comprised IOM and ash, was dried (80°C/0.1 atm) and weighed. The THF solubles were concentrated by removing excess THF in a rotary evaporator. A 50:1 volume of pentane was then added to precipitate any pentane-insolubles. The mixture was placed in an ultrasonic bath

for 3 minutes to facilitate the precipitation process before filtering off the insoluble fraction (here labelled PA+A, pre-asphaltenes plus asphaltenes). The PA+A was dried and weighed. Thus the product is divided into pentane solubles (Oils), PA+A, and IOM plus ash.

The product distribution was determined assuming complete recovery of the ash plus catalyst. The iron in the catalyst precursor is presumed to convert to pyrrhotite and the weight of catalyst reporting to the ash fraction is calculated as the corresponding weight of $Fe_{0.9}S$. Experimentally, complete recovery of ash and catalyst was demonstrated. Oils are calculated by difference, and as a result, water produced during liquefaction, as well as any experimental error, is included in this calculation. No work has been done to determine the yield of water. The total of the net products equals the amount of maf coal in the feed and reflects the net make of each of the solubility fractions, while coal conversion equals 100 minus the yield of IOM.

Analytical Methods. Methane-ethylene product gases were analyzed with a Carle gas chromatograph using a refinery gas analysis column package. Pentane-soluble products were analyzed with a Hewlett-Packard 5890 gas chromatograph fitted with a DB-5 column. Mössbauer spectroscopic analyses of the IO and liquefaction residues were done with a Tracor-Northern TN-4500 programmable multichannel analyzer, and the spectra were analyzed with a MicroVAX II computer. An Air Products cryostat is used to obtain spectra as a function of temperature from liquid He to ambient. X-ray diffraction analysis was performed with a Philips 3100 XRG diffractometer equipped with a Cu K-alpha emitter (λ= 1.54056 Å), graphite monochrometer detector, and automatic sample changer. Nitrogen BET surface areas were

measured with an Omnisorp 100CX. Surface areas were calculated using the standard BET equation[38] between relative pressures of 0.05- 0.25. Prior to analysis, all SFIO samples were outgassed under vacuum for 21 hours at a temperature that was slowly increased to 145°C, in order to remove any adsorbed moisture and other species.

Results and Discussion

Liquefaction Studies. Five sets of liquefaction experiments were performed, and are referenced in the discussion by their alphabetic letter:

A. Uncatalyzed, or thermal-only,

B. IO added with DMDS,

C. SFIO added with DMDS,

D. SFIO added without DMDS, and

E. Carbon black added without Fe or DMDS.

When used, the iron oxide catalysts were typically added at 1.2% Fe (mf coal basis), a level which nominally corresponds to 1% Fe on as-received coal. Additionally, studies on the more active catalyst, SFIO, were included for various Fe addition levels, both with and without added DMDS, to expand the data collected for this material. Most experiments were conducted for 30 minutes, and each 30-minute experiment was at least duplicated (the average standard deviations for all replicated 30-minute experiments are shown in Table 6-2). Some experiments were also made for 7½ to 60 minutes reaction times to explore the effect of time on the liquefaction data. While these are typically single experiments, the consistency of the data is generally established in the trendline through the 30-minute data. The influence of the different

catalyst systems, as well as the factors considered important for each, are considered first by examining product yields, and subsequently by discussing their impacts on hydrogen consumption. For the discussion that follows, the results of the liquefaction experiments are summarized in Table 6-3 for the cases A through C. Separately, Table 6-4 reports the results of liquefaction experiments D and E.

Product Yields. The conversion of coal to THF soluble products is shown as a function of reaction time in Figure 6-1. The most notable effect is that the *addition of Fe in any form* results in a significant increase in THF conversion; the overall effect observed is essentially independent of precursor type, or the presence or absence of added DMDS. While commonly observed for sulfided forms of Fe, additional experiments would be required to determine if this increase in conversion in the absence of sulfur is typical for other iron oxides, or is unique for the high surface area SFIO. However, the effect of added Fe on both Oils and hydrocarbon gas depends on added DMDS, where both yields increase in its presence.

We can look at the overall differences between the two different types of Fe precursors (IO vs. SFIO), e.g., their particle sizes (100-140 nm vs. 1-3 nm) and nitrogen BET surface areas (9 vs. 300 m^2/g), and the particles sizes of the resulting pyrrhotites formed under liquefaction conditions collectively by comparing experiments C with B. Of these differences, one is tempted to speculate the predominant factor is the size of the pyrrhotites formed upon sulfiding, with better catalyst distribution and higher surface area resulting from smaller precursors. In addition to the increase in THF conversion for C (where total THF conversion is about 2% higher for

C vs. B), the addition of either type of sulfided Fe significantly improves the yield of Oils to the same level in both cases. Thus, all of the incremental THF conversion from C over B reported to the PA+A fraction. Nonetheless, the smaller differences in conversion between B, C and D when compared to the larger increase over A suggest that the mix of initial particle size (and the size of the resulting pyrrhotites, which have been shown to increase proportionately in size),[37] surface area and dispersion is less important than the presence of Fe *for coal dissolution.*

Referring to Table 6-3 it is also apparent that there is no significant impact on THF conversion upon increasing the concentration of sulfided SFIO from 1.2 wt% to 2.3 wt%. Similarly, there is no impact on Oils yield over this range of SFIO concentration.

Comparing experiments D with C allows a collective view of:

1) the presence of DMDS in the reaction,

2) the subsequent formation of the pyrrhotite phase from SFIO, and

3) the presence of a more reactive hydrogen donor in H_2S.[39]

For the data of D at 30 minutes' reaction time, total coal conversion ranges from 82% to 87%, comparable to the yields reported above where DMDS was added. Note that these are well above the conversions reported for the thermal cases. For the larger range of concentrations studied for D at 30 minutes' reaction time, shown in Figure 6-2, the effect on THF conversion in the absence of added DMDS is precipitous below 0.3 wt%, then increases uniformly with higher concentration up to about one standard deviation less than C at 1.2 wt% Fe, with no

difference from C at 2.3 wt% Fe. Clearly, no upper limit for THF conversion is evident from this range of Fe concentrations examined for D. However, the yield of Oils at equal Fe concentrations is significantly less for D than C. In fact, as shown in Figure 6-2, in the absence of DMDS, there is no relationship between Oils yield and concentrations of SFIO, which are the same as for the uncatalyzed case (shown as 0% in that figure), indicating higher production of PA+A from the added Fe in D. The unsulfided SFIO played little role in the production of additional Oils, but was quite active for coal dissolution. Hydrocarbon gas yields also remained nearly constant at a low level compared with the cases where Fe and DMDS were added.

To assess the impact of additional reaction surface area in the feed mixture, as-received coal and carbon black were mixed in the reactor in a 9:1 ratio. No DMDS or Fe was added (experiment E), and the same weight of tetralin was added as in the previous experiments. The carbon black had been extracted earlier with THF and found to have a slight propensity to adsorb THF (~3%). However, to determine product yields, the mf weight of carbon black that had been added was subtracted from the liquefaction residue weight without this adjustment (well within the accuracy of the experiment). Yields were calculated on an maf coal basis, as before, and the product yields are essentially the same as for A. Total conversion for A was 76.7%; while for E, 76.5%. Oils yields were 31.8% for A, and 32.4% for E. In essence, the mere presence of a carbon surface was not sufficient to enhance product yield, and thus the importance of Fe in the catalyst precursors is emphasized.

However, Charcosett et al.[40] did observe an increase in coal conversion in tetralin for

one hour at 407°C to hexane soluble products in the presence of carbon black and a 1% H_2S atmosphere, with an attendant increase in hydrogen uptake from gas. It was speculated that the additional surface present adsorbed free radicals, and slowed down the retrogressive reactions. The absence of this occurrence in the present data (where no DMDS was added with the carbon black) suggests a role for H_2S in hydrogenolysis.

Hydrogen Consumption. In addition to activity related to improved product yield structure, another property for consideration is relative hydrogenation activity. A decrease in the amount of naphthalene produced in the presence of an active hydrogenation catalyst at the end of coal liquefaction experiments using tetralin as solvent is commonly observed. Whether this is due to the ability of the selected catalyst to activate molecular hydrogen to directly cap thermally decomposed free radicals from coal in lieu of hydrogen from the donor solvent or through rehydrogenation of the naphthalene has been the subject of much research, and an overview of some of that research follows.

Cronauer et al.,[41] working with model compounds relevant to the complex reactions of coal liquefaction (e.g., cracking of dibenzyl and dibenzyl ether) found that *in the absence of a good hydrogenation catalyst*, the hydrogen required to stabilize free radicals is largely supplied by solvent or intramolecular arrangement, and not from dissolved hydrogen. In coal liquefaction studies of Datong coal in a stirred autoclave using tritium labelled hydrogen and unlabelled tetralin, Kabe et al.[42] also found that in the absence of catalyst the initial transfer of hydrogen to coal products favored the solvent over gas phase source about 2:1. However, in the presence

of $NiMo/Al_2O_3$, the H donors were reversed to favor gas over tetralin about 2.5:1. In both cases, the data showed that gas phase tritium transferred directly to coal products in the first few minutes of the reaction.

In our case, it is relevant to consider the particular ability of Fe catalysts to rehydrogenate naphthalene in conjunction with the activation of molecular hydrogen. Charcosett et al.[40]observed from liquefaction product yields using Fe, Sn and Mo catalysts in both tetralin and 1-methylnaphthalene, that along with low rehydrogenation rates of naphthalene to tetralin, hydrogen reacted preferably in its disassociated form and molecular hydrogen appeared more important in the stabilization of free radicals than the donor hydroaromatic solvents. Working with tetralin and mixed naphthalene/ tetralin solvents for the liquefaction of Wyoming coal, Suzuki[43] inferred little hydrogenation of naphthalene during liquefaction when using an $Fe(CO)_5$ precursor. Relatedly, from kinetic modelling work, the important role of the catalyst was thought to be the activation of molecular hydrogen and its transfer to coal fragment radicals. In a study by Ikenaga et al.[44], a sulfided $Fe(CO)_5$ precursor, which has been shown to produce a finely divided pyrrhotite (among other Fe species) under liquefaction conditions,[45] was found to have little ability to activate molecular hydrogen in the cracking of benzyl phenyl ether in tetralin. The precursor was shown to have activity for naphthalene hydrogenation, however. In that study, a sulfided $Mo(CO)_6$ precursor used was found to be very active, reversing the hydrogen donor supply to primarily gas phase, while suggesting the transfer of gaseous hydrogen to benzyl and phenoxy radicals. More particularly, Guin et al.[46] showed that unsulfided SFIO exhibited activity in naphthalene hydrogenation experiments, but the addition of sulfur in the

absence of coal poisoned the catalyst. These conditions may have allowed for considerable pyrrhotite particle growth.

In sum, across the range of conditions and reactants studied, varying degrees of Fe activity have been found, ofttimes viewed only in the context of more or less active catalysts. In general it would be convenient to think of hydrogen delivered from competing suppliers (with no net addition from intramolecular rearrangement), with dissolved molecular hydrogen a predominant source in the presence of an active catalyst. The amount of naphthalene present in the solvent at the end of hydroliquefaction appears to be influenced by the specific catalyst in the system, interactions with available coal radicals (affected by the selection of coal, time, and temperature), hydrogen overpressure and gas-product-solvent equilibrium factors. While we cannot expect to uniquely determine these for the data collected, we would expect that the better hydrogenation catalysts yield lower naphthalene concentrations at the conclusion of hydroliquefaction.

To better illustrate the changes in relative hydrogenation activity, Figures 6-3 to 6-6 describe the uptake of hydrogen as a function of reaction time for each of the series of liquefaction experiments. Hydrogen consumption is shown as mg/g maf feed coal, and the total is divided into two sources, that calculated from the gas phase analysis and that consumed by the conversion of tetralin to naphthalene. The latter calculation assumes that four hydrogen atoms are transferred to coal products for each mole of naphthalene formed, and that the yield of other products from tetralin is negligible. Experimental determinations show that the

composition of other products is typically less than 4%. Duplicate experiments (C at 30 minutes in Table 6-3) showed the variability in the calculation of hydrogen consumption to be ±0.4 mg/g. The average standard deviation of calculated molecular hydrogen consumption for duplicated experiments presented here is 2.1 mg/g; therefore we could estimate the certainty in total hydrogen consumption to be ±2.5 mg/g.

The data in Figure 6-3 graphically identifies the sources of added hydrogen during the uncatalyzed reactions (A), and is subsequently used as a reference case for the other figures, shown as a dashed line. In this reference case, up to 40% of the 38 mg/g maf coal added hydrogen is supplied by solvent.

B had relatively little impact on hydrogen consumption or its source (See Figure 6-4), yet had a significant effect on THF conversion, Oils yield and hydrocarbon gas yield, as was shown earlier. In contrast, C had a much greater impact on hydrogen consumption, and there is a marked difference in the total hydrogen consumed and consumption from the gas phase (Figure 6-5). Total hydrogen consumption was 15% higher for C compared with B, while consumption from gas was over 30% higher. Shown in Table 6-5, ultimate analyses of samples of PA+A for these runs show 5% higher H:C ratios for the SFIO product (there also being 5% more product), partially accounting for the higher H_2 uptake.

In contrast, as shown in Figure 6-6, hydrogen consumption was not nearly as high for D (at the higher 2.3% Fe concentration) and was comparable to the uncatalyzed case, but a

larger portion of the hydrogen was consumed from the gas. Total hydrogen consumption was lower than for the cases where DMDS was added with the Fe, while the n:t ratios are higher. Interestingly, the 2.3% Fe case without added DMDS has about the same n:t ratio as 1.2% Fe with added DMDS, although the total hydrogen consumed and Oils yield are less. Further, D at the 2.3% Fe level showed better liquefaction results than B at 1.2% Fe in two respects: total conversion and hydrogen delivery from the gas phase. Total hydrogen consumptions were the same. However, B at the lower concentration gave higher Oils yield.

Figure 6-7 shows the hydrogen consumption trends for the 30 minute experiments using increasing quantities of SFIO, still in the absence of added DMDS (D). This figure confirms the data presented above, and shows only a modest increase in total hydrogen consumption, but a linear increase in the amount of gaseous hydrogen utilized with a nearly offsetting reduction in hydrogen from tetralin. SFIO without added DMDS showed good activity for coal dissolution at low concentrations of SFIO, and appears to activate molecular hydrogen to some limited extent in proportion to the amount added. Of note, however, is how little hydrogen D required to achieve considerable incremental coal dissolution over A. Since THF conversion is not a hydrogen-intensive reaction, it may explain why, in our data, surface area and dispersion are secondary to the presence of Fe for coal dissolution.

Guin, et al.[46] in liquefaction studies using a comparably low sulfur HVA bituminous Blind Canyon coal in tetralin with SFIO as catalyst (400°C for 60 minutes) also observed catalyst activity for coal liquefaction in the absence of added sulfur, although a higher increase in

pentane solubles yield was also found. The best performance, though, was with the combination of SFIO plus added sulfur. Results presented here suggest a higher degree of synergism between SFIO and sulfur than observed by Guin for the production of pentane solubles, particularly in view of the higher hydrogen consumption numbers given for C over D.

It has been suggested that even the low sulfur content of these coals is sufficient to provide an active, sulfided SFIO surface. However, the hypothesis that surface Fe in both C and D was sulfided to the same extent would not be consistent with the increase in hydrogenation activity shown here for C compared with D. As an alternate, one could consider the liquefaction yields of SFIO as stemming from surface Fe only partially sulfided. However, the uniformly increasing catalyst effect of SFIO for coal dissolution at increased catalyst loadings (e.g., THF conversion and n:t ratios) in the 30 minute liquefaction studies would indicate sufficient available sulfur to produce the observed effect beyond that required for the penultimate catalyst load (1.2% Fe), where yields remained well below those with added DMDS. Mössbauer studies of the liquefaction residues for D showed only 10% present as a sulfide form (pyrrhotite), the remainder an oxide. If the particles retained something close to their 30 Å size through the experiments, a much greater fraction of the sulfide form would be required to cover each particle. Further, Mössbauer analysis of the 7½ minute liquefaction residues for C, with DMDS added, showed 96% of Fe present as pyrrhotite, requiring that the SFIO particles be altogether sulfided, and showing no particular inclination to selectively sulfide the surface, even at short run times.

Activity of a reduced Fe phase, formed during the liquefaction experiment from the oxide, could be considered a factor in the observed results. In that regard, Fe reduced *in situ* with potassium borohydride has been reported active for the liquefaction of Blind Canyon coal in 1-methylnaphthalene[47] and reduced Fe has been shown active for naphthalene hydrogenation.[48] Since the liquefaction residues here were exposed to air at different points in the product workup, more studies would be required to conclusively eliminate the possibility of an active, reduced Fe species present during the reaction. But we would suggest production of this phase is unlikely in the course of our experiment, and would prefer to think that while some activity of the oxyhydroxide is seen, an important ingredient (i.e., sulfur) is missing.

Not surprising given the similarity of the product yield data, hydrogen consumption data for the 30 minute, carbon black-catalyzed experiment (E) was very similar to the uncatalyzed (A) experiment at the same run time as well. Total hydrogen consumption for E was 36 mg/g, and was 38 mg/g for A (less than one standard deviation's difference). The 90 m^2/g carbon black showed no catalyst activity in either enhanced product yield structure or hydrogen uptake.

In sum, we have observed differing degrees of hydrogenation ability for each of the catalyst precursors used, and perhaps their most important function is to serve as a site where molecular hydrogen is adsorbed and dissociated for subsequent transfer between aromatic structures.[6] At the lowest level is the ability to solubilize coal, even at the outset of liquefaction, which we have observed to require little incremental hydrogen addition. Next is the ability to mobilize additional gaseous hydrogen (while either rehydrogenating naphthalene or reducing

hydrogen abstraction from tetralin) to better produce the lighter pentane soluble fraction, an important function for a practical liquefaction plant catalyst. While SFIO used without DMDS clearly showed some ability to dissociate molecular hydrogen (in direct proportion to SFIO concentration), as did IO with DMDS, a much better product results from the combination of a small particle precursor used with DMDS. The presence of the larger size pyrrhotite alone was not sufficient to give the large effects desired, nor did the addition of carbon surface area from added carbon black have any effect. We would speculate the high surface area precursor's initial propensity to mobilize gaseous hydrogen is augmented by a more reactive hydrogen donor, or a better catalyst in the smaller pyrrhotite phase formed, or both. Clearly, product yields are enhanced by smaller particle size precursors, and more intimate mixing of catalyst and coal that results.

Conclusion

In liquefaction studies of a subbituminous coal in tetralin, when compared with a larger particle iron oxide (IO) that had been used in pilot plant scale liquefaction studies, the nanometer-size SFIO proved to be a better liquefaction catalyst in many respects, e.g., THF conversion, hydrogen consumption, and naphthalene: tetralin ratio. Although both of the iron oxides studied showed activity when compared with uncatalyzed runs, we observed precursor size and follow-on dispersion to be key variables for further development. SFIO plus added DMDS demonstrated particular ability to mobilize gaseous hydrogen. Even in the absence of added DMDS, SFIO liquefaction results evidence that the high surface area SFIO has activity for coal dissolution at concentrations down to 3000 ppmw Fe, but hydrogenation activity is quite

low and the yield of THF soluble-pentane insoluble products increases. Carbon black used alone showed no catalyst activity, either in product yield structure or hydrogen consumption. Chromatographic analysis of the pentane soluble liquefaction products to determine tetralin dehydrogenation, when used along with product yield structure, aided in differentiating among liquefaction catalysts at longer reaction times (i.e., 30 minutes and over). It showed the relative importance of hydrogen donated by tetralin solvent follows the order

Carbon black, E≈ Thermal, A > SFIO, D > IO+DMDS, B > SFIO+DMDS, C

where experiments C had the highest hydrogen uptake with the least dehydrogenation of the tetralin.

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Table 6-1. Black Thunder Coal Analysis			
Proximate Analysis	(wt%, as-determined)	Ultimate Analysis	(wt%, dry)
Moisture	21.2	Carbon	68.68
Ash	5.15	Hydrogen	4.76
Volatile Matter	34.4	Nitrogen	1.21
Fixed Carbon	39.3	Sulfur	0.56
Sulfur Types	(wt%, dry)	Oxygen (diff)	18.25
Total	0.39	Ash	6.54
Pyritic	0.07	Ash, SO_3-free	5.42
Sulfate	0.09		
Organic	0.23		

Table 6-2. Average Standard Deviations for Liquefaction Product Yields	
Product	$\pm \sigma$, wt% maf Coal
HC Gases	0.1
$CO+CO_2$	0.4
Oils	2.8
PA+A	2.4
IOM	1.4

Table 6-3. Results of Liquefaction Experiments

Catalyst	A				B			C				
Added Fe, wt% mf coal	0	0	0	0	1.2	1.1	1.2	1.2	1.2	1.2	1.2	2.3
S/Added Fe mol/mol	0	0	0	0	3.0	3.0	3.0	3.2	3.0	3.0	3.2	3.1
Reaction time, mins	7.5	15	30	60	15	30	60	7.5	15	30	60	30
Products, wt% maf Coal												
HC Gases	0.3	0.5	0.7	1.0	0.9	1.4	1.7	1.0	1.2	1.4	2.0	1.8
$CO+CO_2$	4.3	4.5	5.3	5.2	5.2	5.1	4.9	5.1	6.7	5.1	7.1	5.1
Oils	21.0	20.1	31.8	42.6	29.9	37.0	46.8	21.9	31.6	36.7	46.2	35.0
PA+A	27.9	40.5	38.9	35.4	37.4	40.1	33.6	37.0	39.2	42.2	33.5	43.8
IOM	46.5	34.4	23.3	15.8	26.6	16.4	13.0	35.0	21.3	14.6	11.2	14.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
THF Conv	53.5	65.6	76.7	84.2	73.4	83.6	87.0	65.0	78.7	85.4	88.8	85.7
H_2 consumed, mg/g maf Coal												
from gas	20	22	23	30	22	28	35	31	41	37	52	36
from solvent	7	11	15	15	12	12	14	7	8	8	10	7
Total	27	33	38	45	34	40	49	38	49	45	62	43
Coal moisture, wt %	20.8	21.9	21.1	21.5	22.3	21.5	22.3	22.7	22.7	21.7	22.6	21.6
n:t ratio in Oils	.116	.180	.263	.258	.192	.195	.237	.112	.120	.137	.162	.107
Run numbers	3076-1[b]	2154-2[b]	2154-1 3291-3 3341-1 4151-2[b]	2160-2[b]	3342-1[b]	3342-2[b] 4004-1[b]	3342-3[b]	3208-1[b]	3208-2[b]	3208-3 3346-2 4151-3 4130-1[b]	3210-2[b]	4138-1 4138-2 4153-1[b]

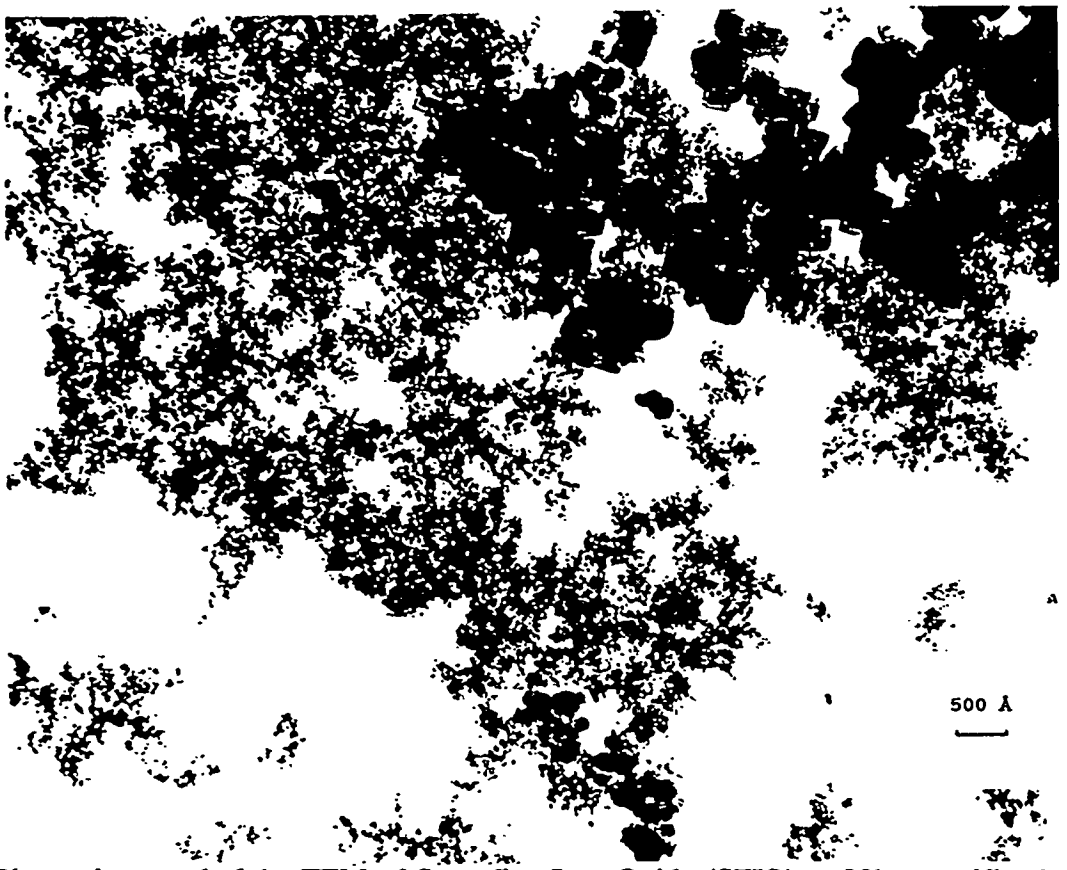
a. Liquefaction experiments at 415°C using 3 g Black Thunder coal, 5.4 g tetralin, 6.89 MPa H_2 cold. SO_3-free ash basis. Updated for forced N_2 gas composition.
b. Indicates which sample was used for Mössbauer and n:t ratios.

Table 6-4. Results of Liquefaction Experiments with SFIO but without Added Sulfur (D)							and with Carbon Black (E)
Added Fe, wt% mf Coal	2.3	0.3	0.6	1.2	2.3	2.2	14% carbon black (no Fe)
S/Added Fe mol/mol	0	0	0	0	0	0	0
Reaction time, minutes	15	30	30	30	30	60	30
Products, wt% maf Coal							
HC Gases	0.6	0.7	0.8	0.8	0.8	1.2	0.7
$CO+CO_2$	5.1	5.6	5.4	5.3	5.2	5.9	5.2
Oils	29.5	31.9	31.5	29.7	32.6	44.3	32.4
PA+A	43.3	43.6	44.7	47.6	48.3	35.8	38.2
IOM	21.5	18.2	17.6	16.6	13.1	12.8	23.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
THF Conv	78.5	81.8	82.4	83.4	86.9	87.2	76.5
H_2 consumed, mg/g maf Coal							
from gas	20	22	27	24	31	39	20
from solvent	9	13	12	12	9	9	16
Total	29	35	39	36	40	48	36
Coal moisture, wt %	20.1	21.8	21.7	21.7	21.3	19.3	20.6
n:t ratio in Oils	.141	.221	.205	.194	.144	.147	.248
Run numbers	3147-3[b]	4153-2[b] 4157-3	4143-3[b] 4143-4	4143-1[b] 4144-1	4138-3 4138-4 4144-3[b]	3145-1[b]	4091-1[b] 4091-2

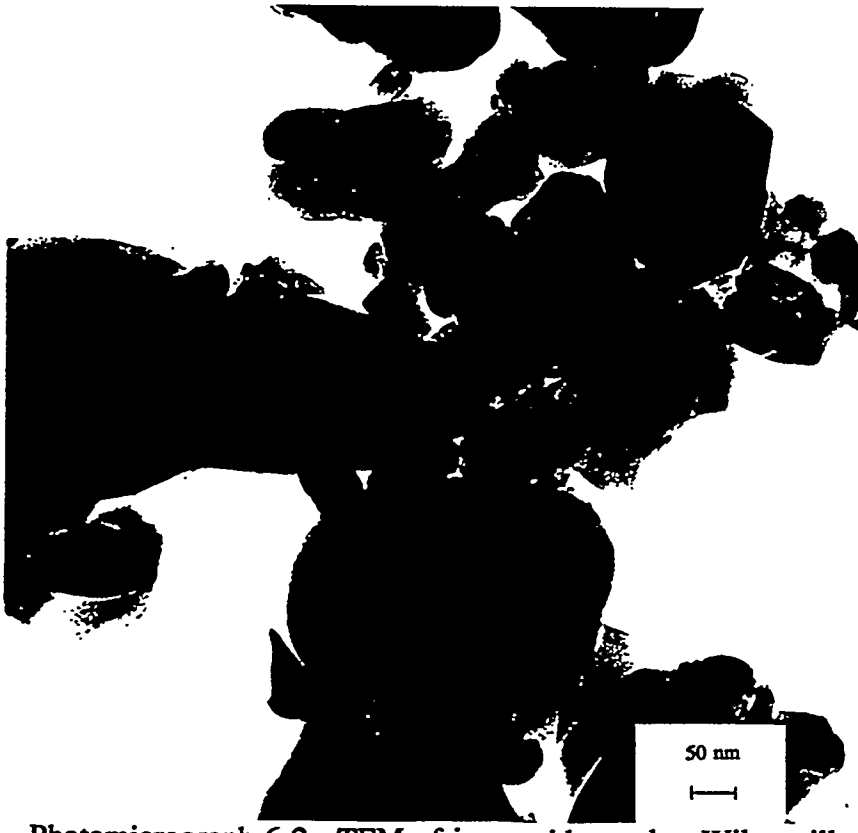
a. Liquefaction experiments at 415°C using 3 g Black Thunder coal, 5.4 g tetralin, 6.89 MPa H_2 cold. SO_3-free ash basis. Updated for forced N_2 gas composition.
b. Indicates which sample was used for Mössbauer and n:t ratios.

Table 6-5. Hydrogen-to-Carbon ratios of PA+A Liquefaction Products.[a]	
Catalyst (@% Fe on mf coal)	H/C ratio in PA+A, %
A	6.9
B (1.2%)	7.0
C (1.2%)	7.4
C (2.3%)	7.6
D (1.2%)	7.1
D (2.3%)	7.3

a. 30 minute reactions at 415°C.



Photomicrograph 6-1. TEM of Superfine Iron Oxide (SFIO) at 80k magnification.



Photomicrograph 6-2. TEM of iron oxide used at Wilsonville (IO) in Run 263, 80k magnification.

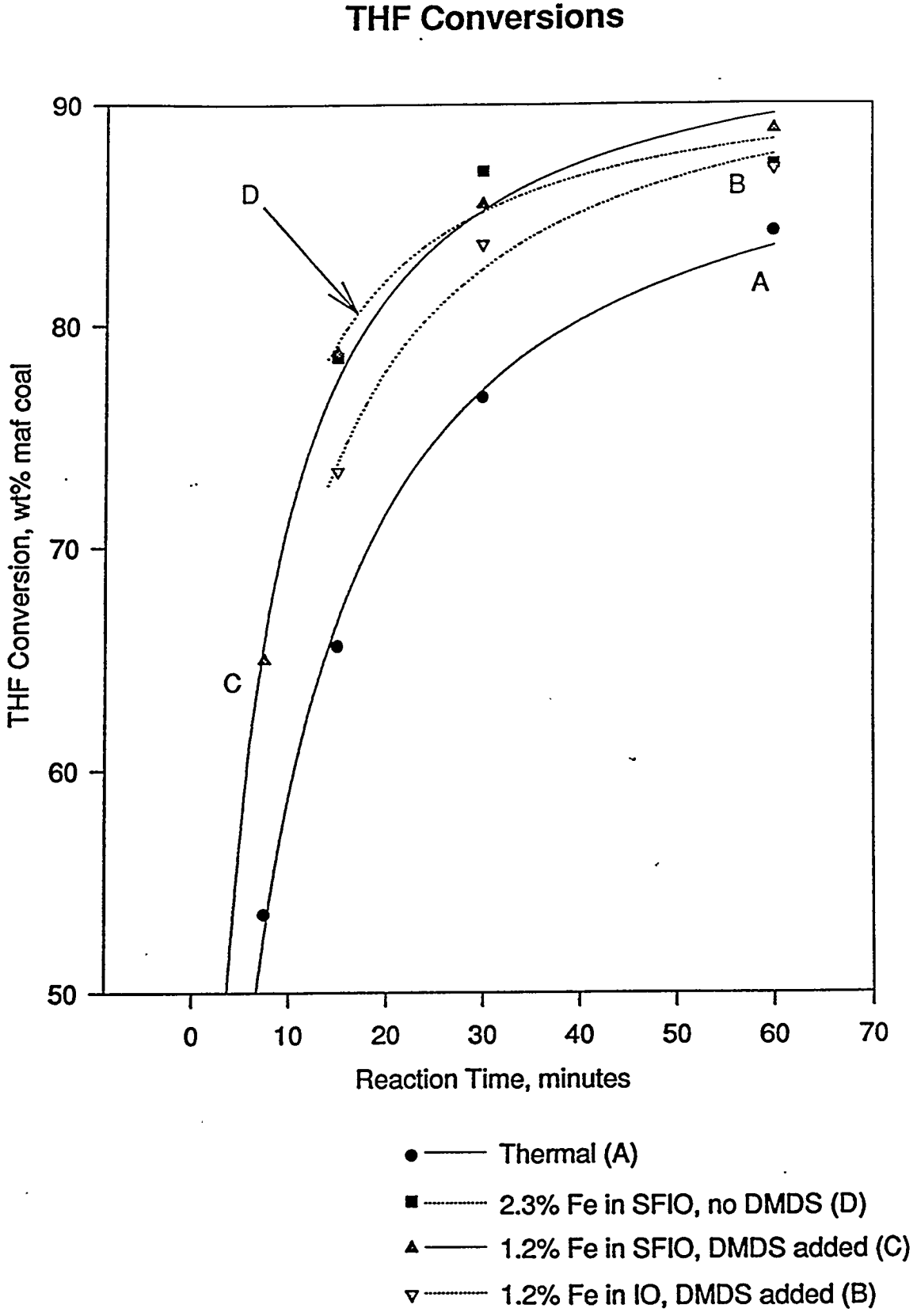


Figure 6-1. THF conversions of Black Thunder coal in tetralin as a function of time at 415°C for four different catalyst systems. 6.89 MPa cold hydrogen pressure.

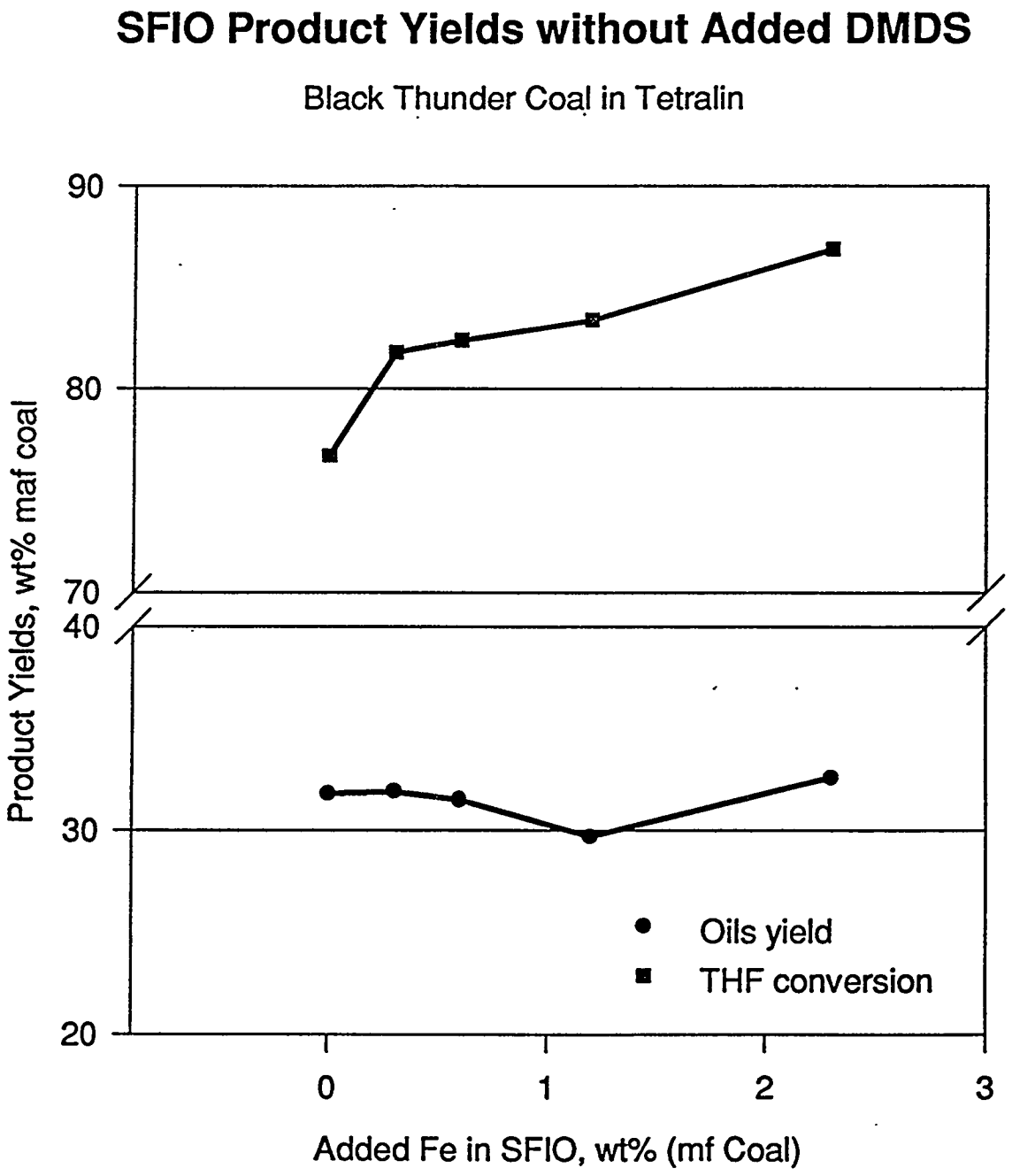


Figure 6-2. THF conversions and Oils yields for Black Thunder coal at different concentrations of added SFIO. 30 minute reactions at 415°C, with no sulfur added. 6.89 MPa cold hydrogen pressure.

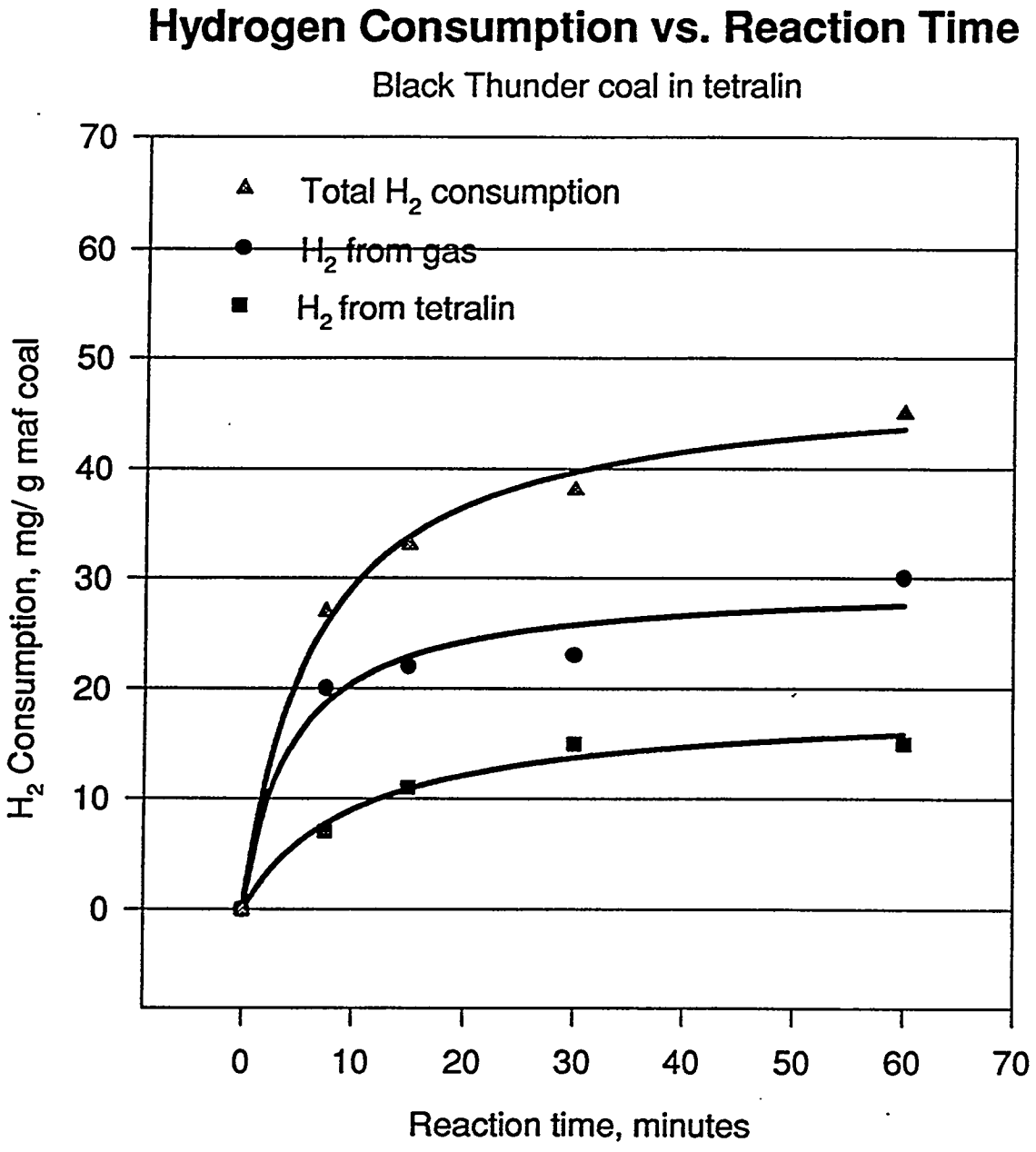


Figure 6-3. Hydrogen consumption during Black Thunder coal liquefaction experiments in tetralin at 415°C as a function of time. No catalyst or DMDS added (A). 6.89 MPa cold hydrogen pressure.

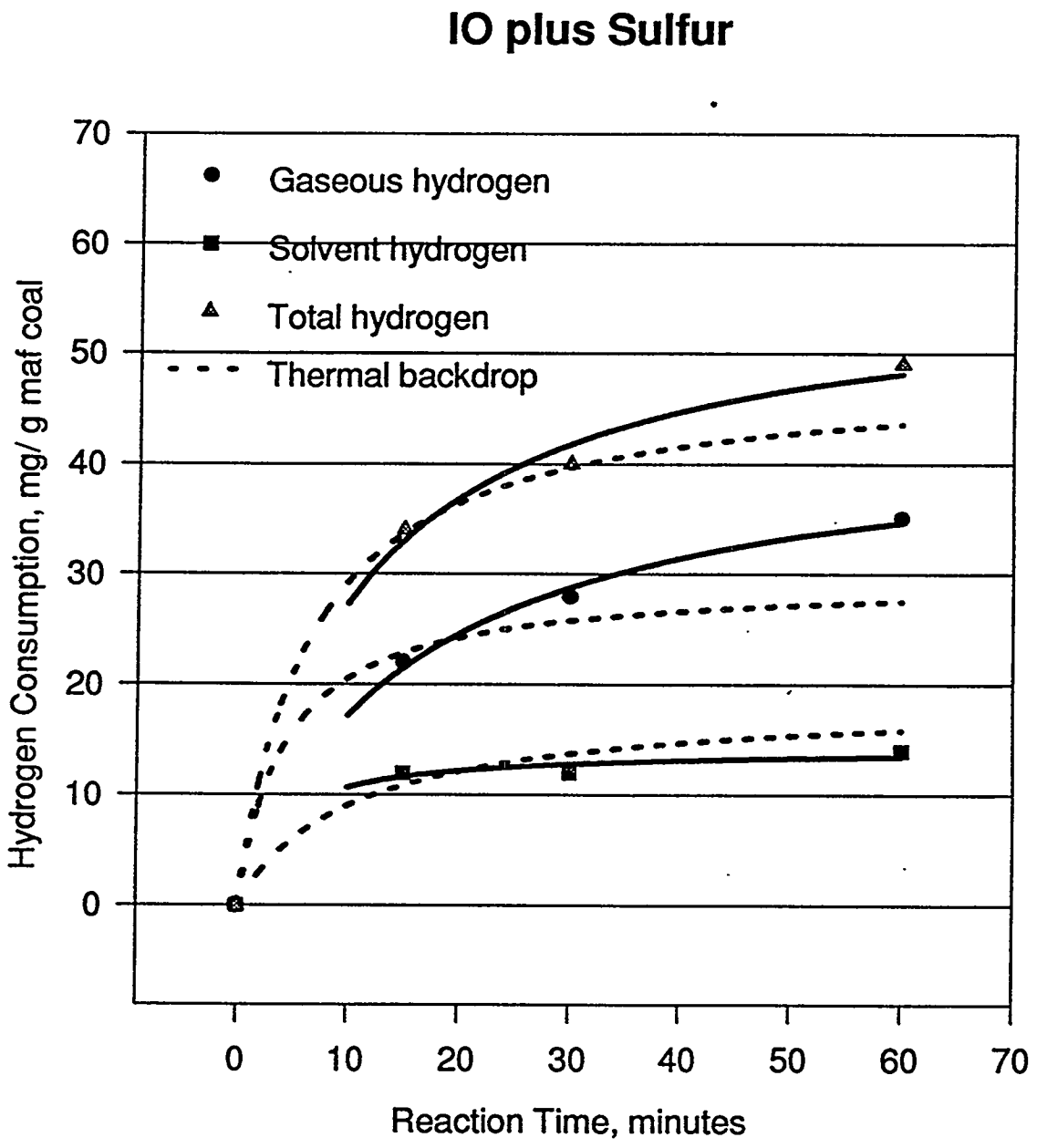


Figure 6-4. Hydrogen consumption during Black Thunder coal liquefaction experiments in tetralin at 415°C as a function of time. 1.2 wt% Fe in IO with 3.0 mS/mFe added (B). 6.89 MPa cold hydrogen pressure.

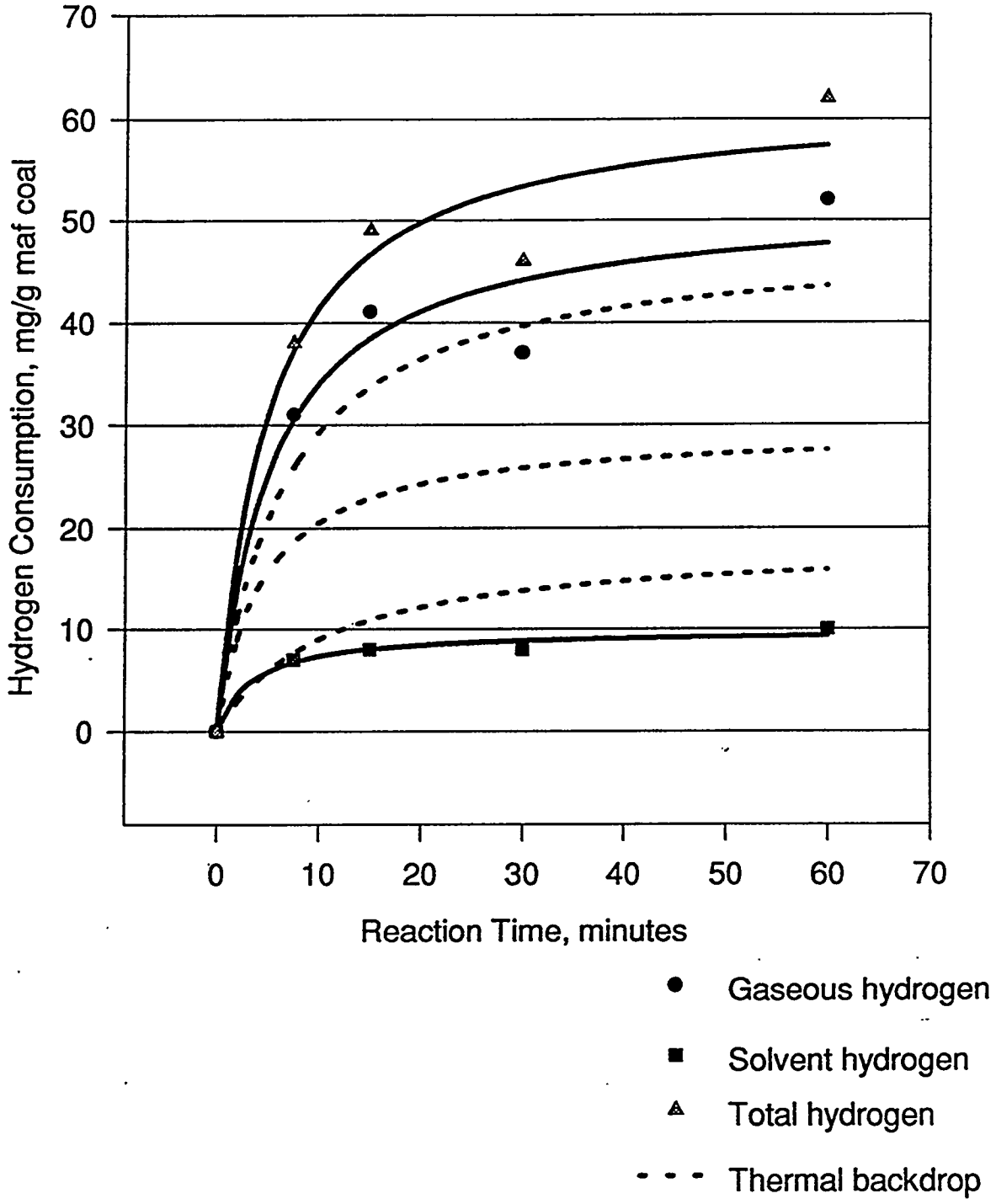


Figure 6-5. Hydrogen consumption during Black Thunder coal liquefaction experiments in tetralin at 415°C as a function of time. 1.2 wt% Fe in SFIO with 3.0 mS/mFe added (C). 6.89 MPa cold hydrogen pressure.

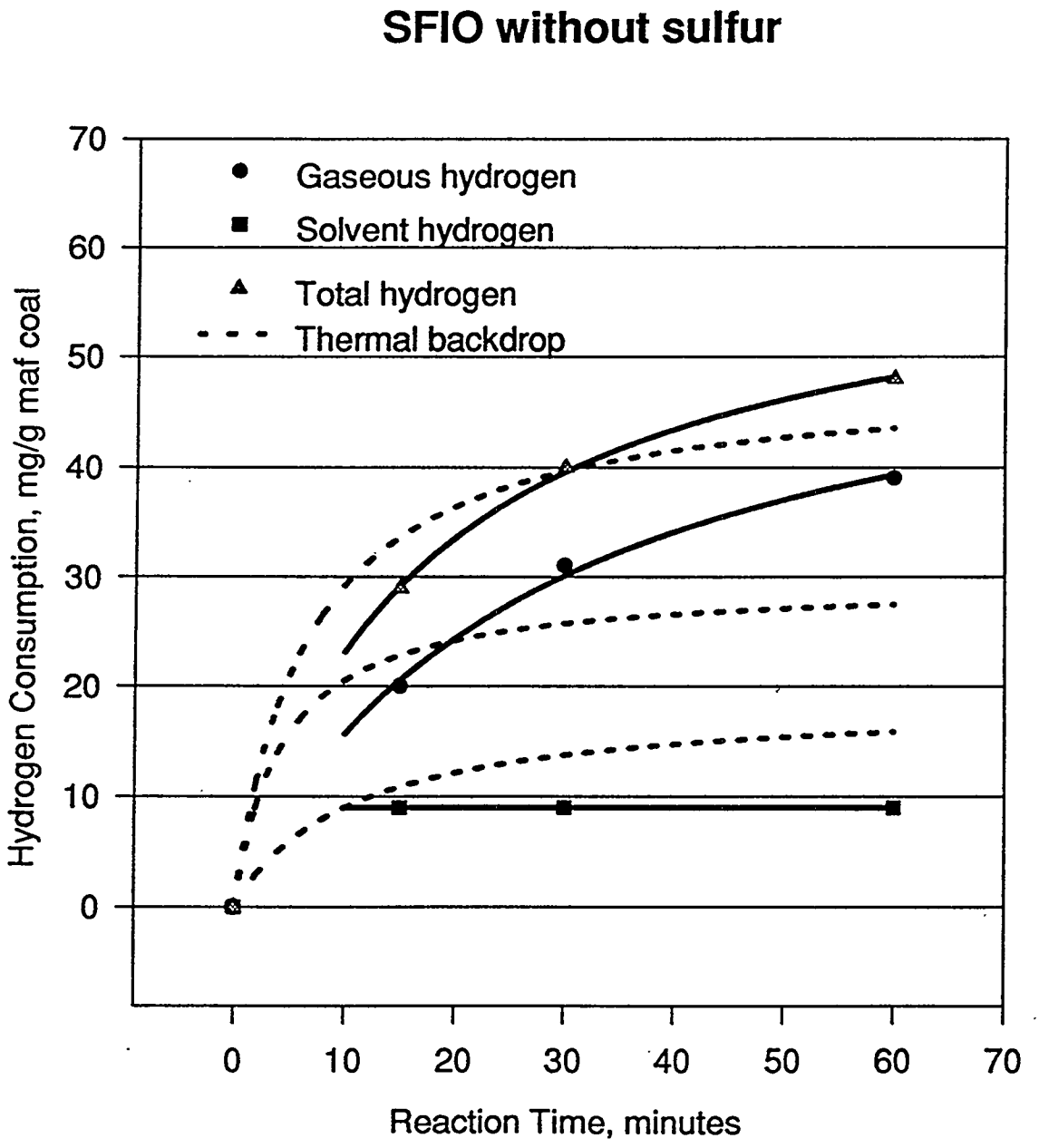


Figure 6-6. Hydrogen consumption during Black Thunder coal liquefaction experiments in tetralin at 415°C as a function of time. 2.3 wt% Fe in SFIO added, but no DMDS (D). 6.89 MPa cold hydrogen pressure.

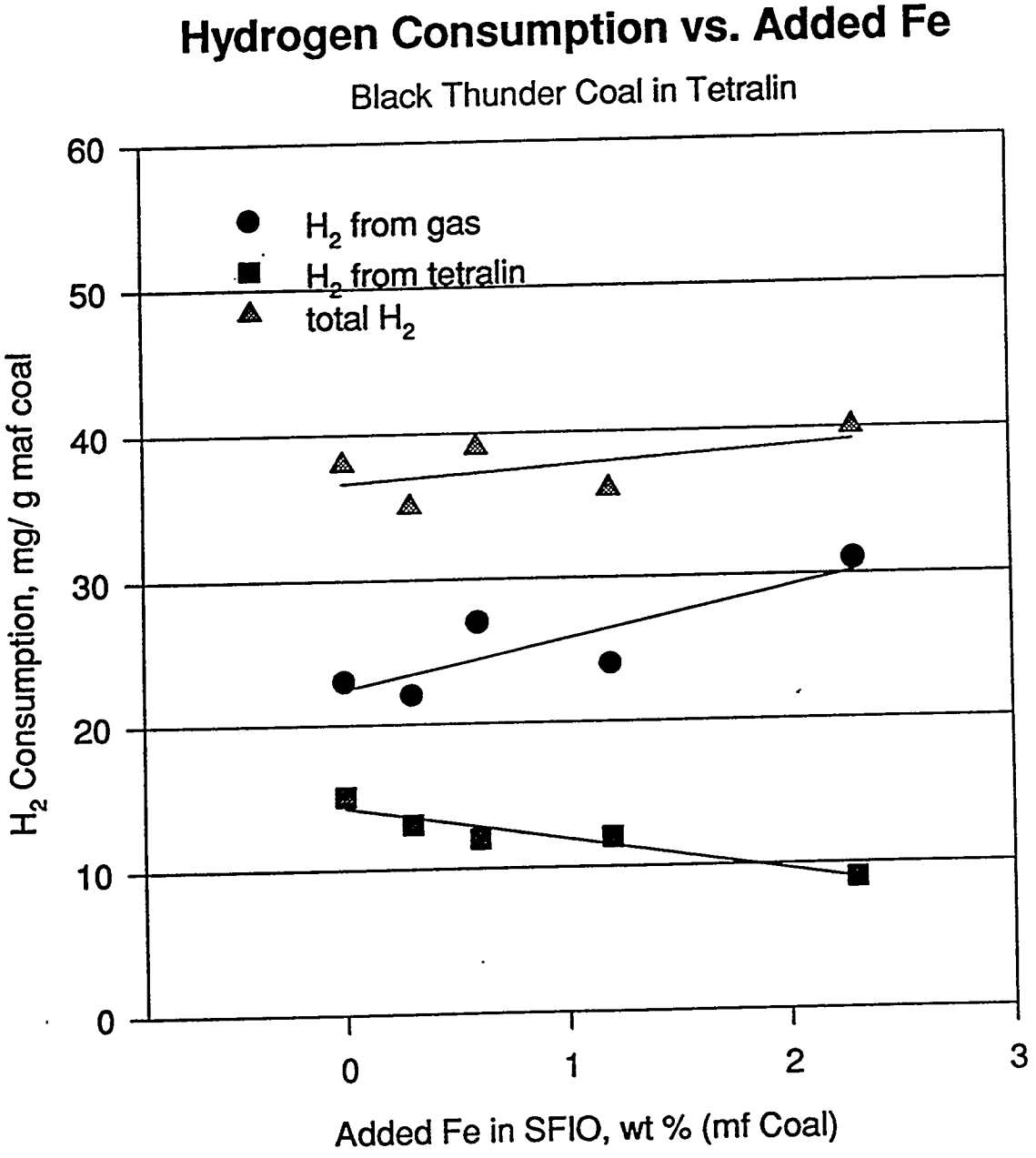


Figure 6-7. Hydrogen consumption during 30 minute Black Thunder coal liquefaction experiments in tetralin at 415°C as a function of added SFIO concentration, with no added DMDS (D). 6.89 MPa cold hydrogen pressure.

Chapter 7

Process Simulation Testing Program

Introduction

During the third phase of this contract a program was outlined to evaluate the effect of integrating several individual steps on overall process performance. Because of the presence of significant concentrations of molybdenum in the ashy resid in the Wilsonville Run 262E solvent, which had been selected as the process solvent for evaluation earlier in the program, it was desired that comparisons be made in both Mo-containing and Mo-free full range process solvent. At the same time, the effects of coal cleaning using oil agglomeration and modifying the solvent by solvent dewaxing and solvent hydrotreating were evaluated.

The individual steps involved in the evaluation are described below. Black Thunder coal was used throughout this study. The solvents that were selected were the full-range reconstituted Mo-containing V-131B from Run 262E and a Mo-free V131B made up of 1050 °F$^+$ bottoms from Run 258K V-131B and the V-1074 distillate from Run 262E. The steps were:

- Dewaxing of the distillate recycle solvent stream to remove the paraffinic fraction by treating either the entire distillate recycle stream (100% case) or a portion of the stream (25% slipstream case).
- Preparing the 25% slipstream distillate by blending 37.5 wt% V-1074 from Run 262E and 62.5 wt% -5 °C acetone dewaxed V-1074 from Run 262E.
- Hydrotreating the 25% slipstream and 100% dewaxed distillate streams in a downflow fixed bed reactor.
- Agglomerating the coal using both the 25% and 100% dewaxed-hydrotreated distillate streams.
- Liquefying the as-received coal and the agglomerated coal using two different Mo-promoted hematite particulate catalysts. Catalyst P-1 consisted of ~1% nickel, ~1 % molybdenum on sulfated hematite while P-2 was ~10%

molybdenum on sulfated hematite.

- Liquefying two different Mo-Fe impregnated coals that had been prepared by the incipient wetness (IW) technique.
- Liquefying two oil-agglomerated, Mo-Fe impregnated coals.

A summary of the experimental format is shown in Table 7-1.

Experimental Outline

A description of the experiments in this series follows:

1. Liquefaction was performed on as-received coal in a solvent comprising Run 262E V-1074 distillate and Run 258K V-131B 1050 $°F^+$ bottoms.
2. Liquefaction was performed on as-received coal in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 $°F^+$ bottoms.
3. In this experiment, the coal was oil-agglomerated using hydrotreated dewaxed Run 262E V-1074 distillate and then liquefied in hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 $°F^+$ bottoms.
4. Liquefaction was performed on as-received coal in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 $°F^+$ bottoms with a particulate 1 wt% Mo/1 wt% Ni on sulfated-hematite catalyst added at a concentration of 1.0 wt% Fe_2O_3 on dry coal.
5. In this experiment, liquefaction was performed on as-received coal in a solvent comprising Run 262E V-1074 distillate and Run 258K V-131B 1050 $°F^+$ bottoms to which was added a particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe_2O_3 on dry coal.
6. This experiment was performed on as-received coal in the 25% slipstream distillate and Run 258K V-131B 1050 $°F^+$ bottoms to which was added a particulate 9 wt% Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe_2O_3 on dry coal.
7. In this experiment, as-received coal was liquefied in a solvent comprising a hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 $°F^+$ bottoms to which was added a particulate 9 wt % Mo on sulfated-hematite catalyst at a concentration of 1.0 wt% Fe_2O_3 on dry coal.
8. In this experiment, as-received coal was oil-agglomerated using hydrotreated dewaxed Run 262E V-1074 distillate and liquefied in hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 $°F^+$ bottoms to which was added a particulate 9 wt % Mo on sulfated-hematite at a concentration of 1.0 wt% Fe_2O_3 on dry coal.
9. In this experiment, an as-received coal impregnated with 500 ppm Mo/0.77 wt % Fe (dry basis) and dried to 5.4 wt % moisture was liquefied in a solvent comprising Run 262E V-1074 distillate and Run 258K V-131B 1050 $°F^+$ bottoms.
10. In this experiment, an as-received coal impregnated with 500 ppm Mo/0.77 wt % Fe (dry basis) and dried to 5.4 wt % moisture was liquefied in a solvent comprising hydrotreated

Table 7-1. Process Simulation Testing Results

Sample No.	Solvent[a]	Coal[b]	Oil Agglom.[c]	Resid[d]	Catalyst[e]	Resid Conv wt% af resid	THF Conv
1	V	AR	N	FM	N	12.9	93.7
2	D	AR	N	FM	N	12.7	97.7
3	D	AR	Y	FM	N	13.9	96.0
4	D	AR	N	FM	P1	21.3	104.9
5	V	AR	N	FM	P2	25.2	104.7
6	S	AR	N	FM	P2	22.3	107.1
7	D	AR	N	FM	P2	23.4	107.0
8	D	AR	Y	FM	P2	22.2	105.8
9	V	IW-1	N	FM	N	19.9	101.4
10	D	IW-1	N	FM	N	21.8	104.6
11	V	IW-1	Y	FM	N	17.9	106.0
12	S	IW-1	Y	FM	N	19.1	106.2
13	D	IW-1	Y	FM	N	22.5	106.4
14	D	IW-2	Y	FM	N	16.9	105.1
15	V	AR	N	M	P2	32.9	104.2
16	D	AR	N	M	P2	33.0	104.2
17	D	IW-1	Y	M	N	29.5	110.8
18	V	AR	N	M	B	31.7	n.a.
19	D	AR	N	M	B	32.8	110.8
A	K	AR	N	N	B	17.5	103.7
B1	K	IW-1	N	N	N	26.5	104.4
C	K	IW-2	N	N	N	24.2	103.5
D	V	IW-1	N	M	N	31.7	104.8
E	V	IW-2	N	M	N	29.8	104.4
F	K	AR	N	N	N	16.7	98.1

a. Distillate solvent:
- V = Run 262E V-1074;
- D = hydrotreated dewaxed V;
- S = hydrotreated blend of 25% dewaxed slipstream of V and 75% V.
- K = Run 258K V-131B

b. Coal: Wyodak Black Thunder coal used throughout;
- AR = as received;
- IW-1 = AR impregnated with 500 ppmw Mo/0.77 wt% Fe (dry basis);
- IW-2 = AR impregnated with 250 ppmw Mo/0.77 wt% Fe (dry basis).

c. Oil Agglomerated using specified distillate solvent;
- Y = yes;
- N = no.

d. Resid:
- M = 1050 °F$^+$ fraction of Run 262 V-131B, contains Mo;
- FM = Distillate bottoms of Run 258k V-131B, free of Mo.
- N = none since V-131B contains resid.

e. Catalyst:
- N = none;
- P1 = particulate 1 wt% Mo/1 wt% Ni on sulfated-hematite catalyst added at a concentration of 1.0 wt% Fe_2O_3 on dry coal;
- P2 = particulate 9 wt% Mo on sulfated-hematite catalyst at a conc of 1.0 wt% Fe_2O_3 on dry coal;
- B = 1.0 wt% Wilsonville iron oxide and 100 ppmw Mo as Molyvan L on dry coal, base case catalyst.

dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F$^+$ bottoms.

11. An oil agglomerated coal, prepared by agglomerating undried as-received coal, that was impregnated with 500 ppm Mo and 0.77 wt% Fe (dry basis), in Run 262E V-1074 distillate oil, was liquefied in a solvent comprising Run 262E V-1074 distillate and Run 258K V-131B 1050 °F$^+$ bottoms.
12. An oil agglomerated coal prepared by agglomerating undried as-received coal, that was impregnated with 500 ppm Mo and 0.77 wt% Fe (dry basis), in an oil comprising a hydrotreated 25% dewaxed slipstream distillate, was liquefied in a hydrotreated 25% dewaxed slipstream distillate and Run 258K V-131B 1050 °F$^+$ bottoms.
13. An oil agglomerated coal prepared by agglomerating undried as-received coal, that was impregnated with 500 ppm Mo and 0.77 wt% Fe (dry basis), in a hydrotreated dewaxed Run 262E V-1074 distillate oil, was liquefied in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F$^+$ bottoms.
14. An oil agglomerated coal prepared by agglomerating undried as-received coal, that was impregnated with 250 ppm Mo and 0.77 wt% Fe (dry basis), in a hydrotreated dewaxed Run 262E V-1074 distillate oil, was liquefied in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 258K V-131B 1050 °F$^+$ bottoms.

The following experiments were conducted in a simulated full-range solvent with Mo-containing ashy-resid using 1050 °F$^+$ bottoms from Run 262E.

15. In this experiment liquefaction was performed on as-received coal in a solvent comprising Run 262E V-1074 distillate and Run 262E V-131B 1050 °F$^+$ bottoms to which was added a particulate 9 wt % Mo on sulfated-hematite catalyst at a concentration of 1.0 wt % Fe_2O_3 on dry coal.
16. In this experiment as-received coal was liquefied in a solvent comprising a hydrotreated dewaxed Run 262E V-1074 distillate and Run 262E V-131B 1050 °F$^+$ bottoms to which was added a particulate 9 wt % Mo on sulfated-hematite catalyst at a concentration of 1.0 wt % Fe_2O_3 on dry coal.
17. An oil agglomerated coal prepared by agglomerating undried as-received coal, that was impregnated with 500 ppm Mo/0.77 wt% Fe (dry basis), in a hydrotreated dewaxed Run 262E V-1074 distillate oil, was liquefied in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 262E V-131B 1050 °F$^+$ bottoms.
18. In this experiment liquefaction was performed on as-received coal in a solvent comprising Run 262E V-1074 distillate and Run 262E V-131B 1050 °F$^+$ bottoms to which was added 100 ppm wt % Mo as Molyvan L and 1.0 wt % Fe_2O_3 as Wilsonville Iron Oxide (dry coal basis).
19. Liquefaction was performed on as-received coal in a solvent comprising hydrotreated dewaxed Run 262E V-1074 distillate and Run 262E V-131B 1050 °F$^+$ bottoms to which was added 100 ppm wt % Mo as Molyvan L and 1.0 wt % Fe_2O_3 as Wilsonville Iron Oxide (dry coal basis).

The liquefaction tests were performed at 440 °C in tubing bombs for periods of 5 minutes and 22 minutes. Products were analyzed by a workup procedure involving vacuum distillation to determine resid conversion to distillate product.

An additional sets of 7 experiments were performed as follows:

A. Liquefaction was performed on as-received coal in Run 258K V-131B containing 100 ppm wt % Mo as Molyvan L and 1.0 wt % Fe_2O_3 as Wilsonville Iron Oxide (dry coal basis).

B1. Liquefaction was performed on as-received coal impregnated with 500 ppm Mo and 0.77 wt % Fe (dry basis) and dried to 5.4 wt % moisture in Run 258K V-131B. Distillation was used in product workup.

B2. Same as B1 except that pentane separation of THF solubles was performed.

C. Liquefaction was performed on as-received coal that was impregnated with 250 ppm Mo and 0.77 wt% Fe (dry basis) in Run 258K V-131B.

D. Liquefaction was performed on as-received coal impregnated with 500 ppm Mo and 0.77 wt % Fe (dry basis) and dried to 5.4 wt % moisture in a solvent comprising Run 262E V-1074 distillate and Run 262E V-131B 1050 °F$^+$ bottoms.

E. Liquefaction was performed on as-received coal impregnated with 250 ppm Mo and 0.77 wt % Fe (dry basis) in a solvent comprising Run 262E V-1074 distillate and Run 262E V-131B 1050 °F$^+$ bottoms.

F. Liquefaction was performed on as-received coal in Run 258K V-131B solvent. Includes 4251-1, 4208-1, 4173-1.

Liquefaction Experimental Procedure

The reconstituted process solvents were prepared by hydrotreating and dewaxing of process oils from two different runs at Wilsonville. When a reconstituted Mo-free process recycle oil was used as the liquefaction solvent, the "topped" Run 258K V-131B material provided by CONSOL was used for the resid, and the appropriate distillate was added in the percentage (35.1%) that had been removed by topping. Topping of the recycle oil had been done at CONSOL by distilling at 320°C and 2 Torr. CONSOL's analysis reported the composition of the topped resid shown in Table 7-2. These ash numbers translate to 8.24% ash (SO_3-free) on a whole recycle oil basis.

When the Mo laden R-262E V-131B recycle solvent was used, which is normally a reconstituted material from three fractions, the distillate fraction was merely substituted with the replacement distillate. The data in Table 7-3 were used in the liquefaction yield calculations.

Impregnated Catalyst Testing Procedure

Testing of the Oil Agglomerated Coals. Adding the coal to the reactor and reconstituting the hydrogen donor solvent for experiments using the Oil Agglomerated coals required special materials accounting. First, to add the coal portion, the amount of Oil Agglomerated mixture that was necessary for the experiment was determined by holding the total amount of process recycle oil constant (5.439 g), maintaining a constant 2.33 solvent-to-coal ratio, and using the weight fraction of moisture free coal in each agglomerated sample from Table 7-4.

The process recycle oil portion was added to the reactor in three forms:

1. Distillate included with the Oil Agglomerated mix;
2. Topped V-131B from Run 258K;
3. Make-up distillate.

Table 7-2. Composition of Topped R-258K Recycle Oil.			
	Ultimate (as determined), %		Proximate (dry), %
C	76.99	Ash (as-is)	15.52
H	5.07	Ash (SO_3-free)	12.72
N	1.04		
Cl	.08		
S	1.21		

Table 7-3. Data used in material balance calculations.				
	Whole R-262E V131B	R-262E ashy resid	R-258K V-131B	Topped R-258K V-131B
SO_3^- free ash, wt % (as determined)	~8.2[a]	16.04	8.14	12.70 (8.24 when recombined)
1050 °F$^-$ distillate fraction (as-determined)	44.2	-	46.6	same as whole
IOM, wt % af	~14.0[a]	26.55	16.48	same as whole
a. Calculated for each experiment as a function of composition.				

Table 7-4. Analyses of the Oil Agglomerated coals.[a]					
Aggl. Run	Distillate	Moisture	SO_3-free ash	Distillate	mf Coal
B37	D3	5.22	3.58	21.62	73.16
B38	D3	4.63	2.02	24.49	70.88
B39	D1	16.78	3.28	22.26	60.96
B40	D2	9.37	3.34	24.41	66.22
B41	D3	5.29	3.74	24.15	70.56
A53	D3	7.58	3.61	26.78	65.64
a. Wt% sample as-determined, update provided by Gary Robbins on 3-9-94.					

Recycle oil with the oil agglomerated coal was added as described above. Recycle oil from topped Run 258K V-131B was held constant since the topped Run-258K V-131B material supplied by CONSOL always comprised 64.9% of the total process recycle oil added to the reactor from any of the three sources. Finally, make-up distillate was added, as appropriate, to complete the total amount of process recycle oil needed for each experiment.

Distillation. A modification of the previous distillation technique was evaluated and is included here. The new method (previously described as Method "B") allowed the THF conversion of the coal to be determined prior to distillation, without adverse impact on the distillation result. First, the products of reaction were analyzed by extracting the materials in a Soxhlet with THF, then rotary evaporating the extract to reduce the volume of remaining THF. The recovered THF materials were then transferred to a 2-neck, 100 ml round bottom flask and vacuum distilled to recover a distillate with an end-point atmospheric equivalent temperature of 1050 °F, using the correlation as published in ASTM D-1160. A standard actual end-point of 331 °C (628 °F) at 1 mm Hg thus calculated was used for each run. A thermocouple was used to control the flask temperature, while a mercury thermometer was used in the distillation head to determine the end-point temperature. Each piece of equipment used in the distillation was weighed both before and after the distillation, including the high-vacuum grease. The weight of resid remaining in the flask, on the distillation head and associated equipment was used to calculate the resid conversion, while the weight of distillate recovered was used to calculate the recovery, reported as percent, described below.

Recovery. Material balances for these distillations, namely, the recovery efficiency for each distillation was calculated as follows:

$$\text{Recovery (\%)} = \text{Materials}_{\text{recovered}} / \text{Materials}_{\text{charged}}$$
$$\text{Materials}_{\text{recovered}} = \text{Insols}_{\text{THF extraction}} + \text{Resid}_{\text{recovered}} + \text{Distillate}_{\text{recovered}}$$

The amount of material charged in each experiment was adjusted for the water and gases that were removed in the liquefaction step and would not be recovered in either the THF extraction or subsequent product distillation. Also, the hydrogen gas added in the liquefaction step was included in the materials charged. All of the oxygen in the coal ($\text{Oxygen}_{\text{coal}}$) was assumed to be removed as water. The recovery calculated in this manner ranged from 92.0% to 98.3%, and was typically 96%.

$$\text{Materials}_{\text{charged}} = \text{Coal}_{\text{charge}} + \text{Solvent}_{\text{charge}} + \text{Hydrogen}_{\text{added}} - \text{Water}_{\text{coal}} - \text{Gas}_{\text{yield}} - \text{Oxygen}_{\text{coal}}$$

Certain light boilers (e.g., C_3 to C_5) are not collected as gases or recovered as distillate, and are part of the missing 4%. In earlier calculations, the oxygen that was removed from the products and the missing light boilers were included in the "Oil" yield, which was determined by difference. However, the weights of these components were not used in calculating resid conversion which are calculated from the remaining heavy resid fraction. Therefore, these corrections do not affect the accuracy of this calculation. In the resid conversion value, a 1% actual loss of resid product in the course of the experiment would result in an additional 1½%

resid conversion. These data on sulfate impregnated coals were calculated assuming the sulfate added during the impregnation step remains with the extracted IOM.

Results

The individual THF and resid conversion values obtained from the 22 min runs at 440 °C are compiled in Table 7-1. Generally as resid conversion increased the THF conversion also increased.

Activity of Incipient Wetness Impregnated Coals - IW-1, which contains the 500 ppmw Mo, increased resid conversion by 9% (PST B1), and IW-2, with its lower Mo content, increased resid conversion by slightly less than 7% (PST C) compared with run A which contained Wilsonville iron oxide and 100 ppm Mo as Molyvan L. The comparable changes in THF conversion were very small. When these runs are compared with the Mo-free recomposited solvent in PST 1, the increases in resid and THF conversion for IW-1 (PST B1) was 13.6% and 10.7%, respectively, and for IW-2 (PST-C) was 11.3% and 9.7%, respectively. Additionally, two runs were made in Run 262E V-131B with its high Mo content showed that the IW-1 coal gave the same resid conversion (see PST D) as the base case catalysts (PST 18), while IW-2 gave about 2% less resid conversion (PST E) than the base case catalyst (PST 18).

Activity of Particulate Catalysts - The activity of the P-2 catalyst, which contained ~10% molybdenum on sulfated hematite, showed an increase in resid conversion of 12% in comparing PST 5 with PST 1. The corresponding increase in THF conversion was 11%. In this system the particulate catalyst has a sizable activity. A comparison of the P-1 catalyst, that consisted of ~1% nickel and ~1 % molybdenum on sulfated hematite, is available in the dewaxed and hydrotreated solvent. In PST 4 the resid conversion increased by 12.5% and THF conversion increased by 7.2% over PST 2. Both are major changes relative to the absence of the catalyst. Resid conversion with P2 in the Mo-containing resid, PST 15, was 1% higher than obtained with the base case catalyst in PST 18. The results with both the particulate catalyst and the impregnated catalysts in the Mo-containing resid ultimately led to an appreciation of the high level of activity of the recycled Mo compared to freshly added Mo.

Effect of topping and reconstituting the R-258 V-131B. The effect that topping and reconstituting the Mo-free process solvent had on resid and coal conversions is shown in Table 7-5. In Run 258K V-131B, run F, resid conversion was 16.7 wt % and THF conversion was 98.1. Merely changing the distillate fraction in run 1 decreased resid conversion by 3.8% and THF conversion by 4.4%. A comparison between run 9 and B1 shows a decrease of 6.6% resid conversion and 3% THF conversion. This is a significant negative impact on both types of conversion. It isn't clear at the present time as to why this decrease occurred. One possibility is the effect that mismatching the solvent had on the liquefaction reaction. The method that was used in topping the Run 258K V-131B and replacing with an equal amount of higher boiling material actually resulted in an increase in the boiling distribution of the distillate solvent. If the higher boiling material was a poorer donor in the reaction, this replacement may have affected the liquefaction result. Another possibility is that the change in calculated THF conversion could be a result of the assumption that the IOM content of the reconstituted process solvent is the same as before distillation. However, this would not affect the resid conversion numbers.

Table 7-5. Effect of Topping and Reconstituting the Solvent

Liquefaction environment	Run numbers	Δ resid conv, wt %[a]	Δ THF conv, wt %[b]
AR coal, no added metals	F vs PST 1	-3.8	-4.4
IW-1	PST 9 vs B1	-6.6	-3.0
Average effect		-8.5	-2.8

a. Δ resid conv = Change in resid conversion, wt % af resid.
b. Δ THF conv = Change in THF conversion, wt % maf coal.

Effect of dewaxing/hydrotreating - The effect of using dewaxed and hydrotreated distillate as a constituent in the liquefaction solvent is shown in Table 7-6. Using 100% dewaxed and hydrotreated distillate was measured for both IW-1 impregnated and P2 particulate catalysts. For IW-1, resid conversion in PST 10 improved by 1.9% and THF conversion by 3.2% over PST 9. P2 in PST 7 with the 100% dewaxed and hydrotreated solvent gave slightly less of an increase in THF conversion than IW-2 but showed a decrease in resid conversion of 1.8%.

Table 7-6. Effect of dewaxing/hydrotreating on liquefaction performance.

Liquefaction environment	PST numbers	Δ % resid[a] conversion	Δ % THF[b] conversion
IW-1 in low Mo (3 ppm)[c] background solvent	9, 10	+1.9	+3.2
P2 in low Mo (3 ppm)[c] background solvent with 100% dewaxed solvent	7, 5	-1.8	+2.3
P2 in low Mo (3 ppm)[c] background solvent with 25% slipstream dewaxed solvent	6, 5	-2.9	+2.4
Oil agglomerated IW-1 in low Mo (3 ppm)[c] solvent; 2 levels of dewaxing	11, 12, 13	+4.6	+0.4
As-received coal with base case catalyst levels in high Mo (350 ppm)[c] background solvent	18, 19	+1.1	n/a
Average effect		+0.6	+2.1

a. Resid conversion, wt % af resid.
b. THF conversion, wt% maf coal.
c. ppmw on an mf coal basis.

P2 in the 25% slipstream dewaxed and hydrotreated solvent in PST 6 gave nearly the same reduction in resid conversion (-2.9%) and essentially the same THF conversion as the 100% case. Liquefaction of the oil agglomerated coal in PST 11, 12, and 13 was quite different, with a large impact (+4.6%) on resid conversion and very little effect (+0.4%) on THF conversion. The effect of the 100% dewaxed and hydrotreated distillate in the presence of the Mo-containing resid was an increase in resid conversion of 1.1%. A comparison of THF conversion is not available. The absence of any significant difference here suggests that the hydrotreated solvent does not significantly impact on the activity of the apparently very active recycle Mo contained in the Run 262E resid.

Effect of Oil Agglomeration - The impact of oil agglomeration on liquefaction is summarized in Table 7-7. Liquefaction of the oil agglomerated coal in the 100% dewaxed and hydrotreated solvent in PST 3 gave an increase in resid conversion of 1.2% and a decrease in THF

conversion of 1.7% relative to PST 2. Compared to comparable results in the presence of non-oil-agglomerated coal, in the presence of either the impregnated IW-1 (PST 9 and 10) or particulate P2 (PST 8) catalysts the resid conversions ranged from a decrease of 2% to an increase of 0.7% while the THF conversions ranged from a decrease of 1.2% up to an increase of 4.6%. Overall it appears that oil agglomeration of the coal does not affect either resid conversion or THF conversion regardless if catalyst is present of not.

Table 7-7. Effect of oil agglomeration on liquefaction performance.

Liquefaction environment	PST numbers	Δ % resid[a] conversion	Δ % THF[b] conversion
Low Mo (3 ppm)[c] background solvent, with DEW/HT distillate. No added catalysts.	2,3	+1.2	-1.7
P2 in a low Mo (3 ppm)[c] background solvent, with DEW/HT distillate.	8, 7	-1.2	-1.2
IW-1 in a low Mo (3 ppm)[c] background solvent, with AR distillate.	9,11	-2.0	+4.6
IW-1 in a low Mo (3 ppm)[c] background solvent, with DEW/HT distillate.	10,13	+0.7	+1.8
Average effect		-0.3	+0.9

a. Resid conversion, wt % af resid.
b. THF conversion, wt% maf coal.
c. ppmw on an mf coal basis.

Conclusions

Addition of catalyst had the biggest effect on resid conversion and THF conversion than any of the other parameters that was tested in this parametric evaluation. The 500 ppmw Mo impregnated coal (IW-1) and the P2 10% Mo on sulfated hematite, both when added with the coal to an Fe and ashy-resid-containing recycle solvent, gave an increase in resid conversion of at least 12% and an increase in THF conversion of 11%. This increment is far greater than observed by addition of 100 ppmw Mo as Molyvan L. The results from having Mo in the ashy-resid fraction of the solvent has led to an appreciation of the high level of activity of the

recycled Mo compared to freshly added Mo.

Topping and reconstituting the solvent had a negative impact on the results. In this series of experiments, the original Run 258K V-131B was topped by vacuum distillation. The bottoms were then combined with an equal weight of V-1074 from Run 262E to give the final reconstituted solvent. The effect of merely topping and reconstituting this solvent resulted in a decrease in resid conversion of 3.8% and a decrease in THF conversion of 4.4%. When an impregnated catalyst was present, comparable decreases of 6.6% in resid conversion and 3% in THF conversion were observed. It isn't clear at the present time why this decrease occurred.

The effect of using dewaxed and hydrotreated distillate as a constituent in the liquefaction solvent had relatively little impact on liquefaction performance. The range that was observed using both the impregnated and particulate catalysts was between a decrease in resid from 2.9% up to a gain of 4.6% for an average increase of 0.6%. THF conversion ranged up to a maximum of 3.2% for an average increase of 2.1%. Interestingly the biggest decrease in resid conversion was for the case in which the 25% slipstream sample was tested. Oil agglomerated coal also had little impact on liquefaction. Compared to non-oil-agglomerated coal, the change in resid conversions ranged from a decrease of 2% to an increase of 0.7% while the THF conversions ranged from a decrease of 1.2% up to an increase of 4.6%. Overall, the change is quite small. The change due to catalyst had the biggest effect on the liquefaction with the other variations having little effect.

Chapter 8
Chemical Pretreatment of Coal :
Background and Review

Introduction

Currently, the common approach to coal liquefaction is to thermally process the coal at temperatures in excess of 425 °C at high hydrogen partial pressures. These conditions overall favor thermolysis and hydrogenolysis over hydrogenation giving rise to higher distillate yields. However, under these aggressive processing conditions that enhance bond breaking reactions, competing retrogressive reactions also occur that lead to more refractory residual products and excessive hydrocarbon gas make. By relaxing the severity of the process conditions, the undesirable crosslinking and condensation reactions may be minimized. However, it is generally believed that relaxing severity will substantially increase processing costs. An objective of this program has been to determine if the increased cost associated with milder initial coal treatment would be off-set by other substantial product yield, selectivity or process yield benefits. Several potential benefits that milder reaction conditions could achieve are:

(1) to reduce hydrocarbon gas make which would reduce hydrogen consumption resulting in major cost reductions due to the need for a smaller hydrogen production facility;

(2) to suppress the crosslinking and condensation reactions that occur during primary coal dissolution to give better selectivity for distillate product;

(3) to reduce the oxygen content in the raw coal to reduce the hydrogen consumed in converting it to water.

One approach toward achieving these goals will be discussed here. This involved pretreating the coal under mild conditions in order to make it more reactive and reduce the oxygen content. The reduced oxygen content will ultimately lead to reduced hydrogen consumption and a correspondingly smaller hydrogen plant. A more active residual material could improve the economics through reduction of reactor space, reduced catalyst requirement, and produce a better overall product selectivity.

In this program, the objective was to develop a pretreating methodology that could be coupled with existing liquefaction processing schemes. Particular attention was paid toward combining existing pretreatment techniques that occur under mild conditions with currently existing technology. The goal of the pretreatment process was to partially depolymerize the coal, eliminate oxygen and structurally modify the coal to:

(1) diminish the propensity for retrograde reactions during subsequent liquefaction;

(2) enhance liquefaction activity and/or selectivity toward higher quality products;

(3) produce cleaner downstream products;

(4) improve overall plant operability and process economics.

An overview of the relevant work in the literature is documented in the following discussion.

Background

The process of coal liquefaction involves the cleavage of bonds within the coal structure and the stabilization of the resulting fragments with hydrogen to progressively reduce molecular weight and ultimately convert the material to a soluble product. To attain this goal, the reverse crosslinking and condensation reactions that occur within the coal structure must be minimized since these reactions are prevalent in coal carbonization and lead to the formation of higher molecular weight refractory species. Solomon et al.[1] identified at least two distinct cross-linking events that occur when coals are heated. One applies primarily to low-rank coals and occurs at lower temperatures. This reaction involves cross-linking that occurs simultaneously with CO_2 and H_2O evolution[2] that correlates with the loss of carboxyl groups. A second type of cross-linking reaction is exhibited by higher rank coals and occurs at moderate temperatures simultaneously with methane formation. It follows that the initial bridge-breaking reactions correlate best with methane formation. For lignites, these cross-linking reactions begin at about 200 °C while the corresponding reactions for higher rank coals begin at temperatures above 400 °C.[1]

Pretreating coal prior to direct liquefaction has been shown to result in higher yields of product through a net reduction of crosslinking and condensation reactions. The methodology can vary

from treatment by demineralization,[3,4] solvent swelling,[5,6] alkylation,[7,8,9] dissolution with strong acids and bases,[10,11] catalytic reactions,[12] or by the presence of hydrogen.[13]

Role of Water

The beneficial effects of water in liquefaction, extraction and pyrolysis reactions with coal which have been observed can be, in part, attributed to a physical effect that the water has on the coal. However, some of the benefit is derived from the action of water as a reactant or co-reactant with the coal matrix. These effects have been observed not only in the generation of a material that can be separated from the coal itself but also influences the composition and reactivity of the residue that is produced. The triple-point or critical temperature, T_c, of water lies within the temperature regime of greatest interest to coal conversion, since it is within this temperature range that phase transitions within the coal structure can occur. Reactions that are conducted in this general temperature regime are complicated by the lack of an understanding of the concentrations of the various phases that are present, namely the amount of gas, liquid, and solid that co-exist at these conditions. Regardless, there has been considerable interest in recent years in the effect of water on enhancing the performance of coal under a variety of process conditions[14,15]

For water the densities of the gas and liquid phases at the triple point, namely 374 °C (T_c) and 220 bar (3190 psi, 22 MPa), are both equal to 0.32 g/cc. Above 374 °C the liquid phase ceases to exist. From an examination of the steam tables it is clear that liquid density increases rapidly as the temperature drops below T_c such that for a 10 °C drop the density of the liquid phase increases to 0.54 g/cc.[16] With a further decrease in temperature the increase in density is much slower. A liquid phase can only exist when the reaction temperature is below the critical temperature and a sufficient amount of water is present to satisfy the density requirements of the system. It seems plausible that only under these conditions will the density of the liquid phase remain higher than the supercritical density of 0.32 g/cc.

Another aspect of operating in water at high temperature is the increased miscibility of some hydrocarbons, which under ambient conditions are nearly completely immiscible. Benzene and

naphthalene, which at ordinary temperatures are normally immiscible, become completely miscible at higher temperatures and pressures. For benzene and water the critical solution temperature, which is defined as the minimum temperature for mixing two substances in all proportions as a single phase liquid, is 297 °C. This miscibility occurs only at very high pressures, between 300 and 350 bar.[17] Naphthalene also behaves similarly except its miscibility occurs at much lower pressures. At pressures between about 150 up to 220 bar, the latter being the supercritical pressure of water, both naphthalene and water are miscible in all proportions at temperatures greater than about 320 °C.[18] The upper limit of this range, of course, is the critical temperature of the mixture, which is a function of the concentration of the respective components in the mixture. For this system, T_c values over most of the concentration range goes through a minimum at about 345 °C, versus the higher corresponding values for the pure components, namely, naphthalene of 475 °C and water of 374 °C.

Single ring compounds with methyl groups attached to these ring systems behave in a manner similar to benzene except miscibility occurs at both higher temperatures and higher pressures. Not only does the critical solution temperatures increase as branching occurs but the pressure window through which miscibility occurs narrows significantly. Presumably, a like pattern will occur in the naphthalene system where the very broad miscibility of naphthalene would be reduced through partial reductive saturation to form a single ring aromatic, tetralin, or by the addition of methyl groups. In any case, the favorable miscibility of naphthalene would probably disappear for the hydrocarbon component within coal liquid mixtures within the temperature range of interest for liquefaction. For coal and/or hydrocarbon-water systems of the type we are interested, very little is known regarding liquid phase miscibility at temperatures near the critical temperature of water.

Another aspect of these systems that will impact on phase phenomena is the polar aspects of these mixtures, namely the humic acids that are extracted from coals both under low temperature extraction conditions as well as higher temperature aqueous treatment conditions. Presumably, solubilities of phenolic compounds will increase quite significantly with temperature such that at higher temperatures their solubility in the aqueous phase will be quite significant.

In most of the liquefaction systems that have been piloted up to the present time, water concentrations do not approach values where a liquid phase would exist. In many of these studies, the water pressures were only a fraction of the pressure necessary to approach the requirements for forming a liquid phase. However, in the case of the data in the literature on the aqueous pretreatment of coal, the amount of water used in the treatment process was adequate to create a liquid phase. Those studies that provide the most basic of requirements for formation of a liquid phase are noted in Table 8.1. However, as already pointed out above, the impact of co-solubilities, ion effects, and other factors may alter the actual phases that are present in these systems. Unquestionably, the multi-component systems are undefined with regard to their phase behavior at the temperatures and pressures of interest in the present study.

The pressures that will be experienced in these systems above the critical temperature is entirely dependent on the amount of water in the system. Below the critical temperature, under all conditions, regardless of the amount of water in the reaction space, the pressure will not rise beyond 220 bars (3190 psi) at a gas phase density at or below 0.32 g/cc. Above this temperature, however, all the water will be in the gas phase, which, depending on the amount present, can result in a sizable pressure increase over a very narrow temperature range. In the absence of any liquid phase at temperatures approaching the critical temperature, any increase in temperature will result in a pressure increase but not with the dramatic impact of the corresponding increase referred to above when liquid is present. Therefore, in a closed system at temperatures above T_c, pressures can be controlled by regulating the amount of water injected in the system. It is this method that was used in developing much of the data on the effect of water on coal at or below T_c with water densities at or below those at the critical point.

Experimentally, two approaches have been used to control steam densities. The method most commonly used is addition of known amounts of water to a closed system coupled with temperature control. In other cases, steam under pressure has been passed over the coal at temperatures that were higher than the dew point of the steam. Using this method at the critical temperature of water, the pressure and density would be significantly below the pressures and densities at the critical point. Using either method provides the advantage of operating at high

water densities approaching those that would be applied in supercritical extraction. Under these conditions the fluid can act as a much stronger solvent when brought into contact with either solids or liquids because of its significantly higher solvation capability. For coals, such a high solvation reaction may play a major role in reducing competing retrograde condensation reactions that lead to low conversions and charring.

Hydrothermal Treatment of Coal

Water is known to participate as a reactant in the thermolytic chemistry of model compounds. Under conditions where bond scission of organic moieties takes place, ionic pathways are likely involved. Dibenzyl ether, which decomposes at 374 °C in water, does so by both a pyrolytic and hydrolytic pathway.[19] In a study of the hydrothermal chemistry of a number of various ethers and esters at 250 °C, ionic mechanisms provided a pathway for C-O bond cleavage.[20] At higher temperatures, radical pathways became favored.

The removal of nitrogen from both quinoline and isoquinoline was observed in the presence of water at temperatures of 400 and 500 °C at water densities from 0.17 to 0.25 g/cc.[21] Denitrification up to 70% was observed in the absence of any catalyst addition. In the presence of zinc chloride conversions increased quite significantly. Most recently, it was suggested that in the presence of water at high temperature the hydrolysis of model compounds representative of coal proceeds through a transition state that is more polar than the reactants.[22]

Aqueous treatment of coal near the critical temperature causes significant changes in the coal structure which influence the conversion to liquid products. Results summarizing results from a number of studies on the hydrothermal conversion of a variety of coals at high temperature are presented in Table 8-1. The effect of using supercritical water on the extraction of coal and related substances has been demonstrated by Modell and co-workers.[23] They found that glucose, cellulose, and maple sawdust as well as coal reacted with supercritical steam at 374 °C and 22.3 MPa operating pressure. Although char is the chief product when these substances were pyrolyzed, no char was found when hydrothermally treated at the supercritical temperature. The presence of the supercritical water appears to prevent the formation of condensation products by

keeping the reactive intermediates in a highly solvated and dispersed state. At temperatures from 250-450 °C a range of different coals has been found to partially convert to liquid products. Bienkowski et al. found that up to 40% of a Wyodak coal was extracted when 750 psig (5.1 MPa) steam was passed over coal at 400 °C resulting in the formation of a mixture of gaseous and liquid products.[24] Under these conditions, the water densities varied up to 0.077 g/cc, which is well below the 0.32 g/cc density of water at the critical point.

In work done in water at its critical point (374 °C, 22.4 MPa, 0.32 g/cc), Deshpande, et al., found higher extraction yields than under subcritical conditions.[25] THF soluble yields for German brown coal up to 36% were obtained while even higher yields were obtained with Bruceton bituminous coal (50% THF solubles). In a subsequent publication, they reported even high THF solubles (58%) from the Bruceton coal at 380 °C and 30 MPa.[26] An experimental apparatus was used in these studies in which coal was injected directly into an autoclave containing preheated supercritical water rather than being mixed with water before heating. Using this technique smaller quantities of THF-insoluble char were observed. They concluded that injecting ambient coal into supercritical water allowed extraction of reactive intermediates before retrogressive reactions could take place. In general, these results are directionally in agreement with the results of Modell, et al., who reported higher yields of hydrocarbon gases and liquids with minimal char formation in reactions run at the critical point.[27]

Graff and Brandes reported that Illinois #6 coal treated for 30 minutes in a fixed-bed configuration with 260 °C flowing steam over a temperature range from 320 to 360 °C lost about 7% of its weight in the treatment period with total yields of up to 30% being obtained when subsequently extracted with pyridine.[28] The pretreated coal had a reduced oxygen content,[29] exhibited reduced hydrogen bonding, an increased pore volume,[30] and had twice as many hydroxyl groups as the starting coal.[31] The presence of steam inhibited the retrograde reactions of the phenolic groups that were formed.[30,32] The pretreated coal showed a two-fold increase in liquid yield and a 20% increase in total volatile yield when pyrolyzed at 740 °C. In the case where steam pretreatment had worked, Brandes and Graff[28,31] observed a morphological change

Table 8-1. Coal Conversion in High Temperature Water

COAL	Water Density g/cc	Temp, °C	Time, min	Conversion		Reactor Type	Reference
				Solvent	Wt%		
Supercritical Treatment							
Brown	0.32	375	15	THF	36	Injection at temp, batch	Deshpande
Bituminous	0.32	375	<60	THF	50	Injection at temp, batch	Deshpande
Bituminous	0.32	374	60	None	28 g+1	Batch Autoclave	Modell
Bruceton	0.32	380	60	THF	58	Injection at temp, batch	Towne
Powhaten	0.32	380	60	THF	21	Injection at temp, batch	Towne
Illinois #6	0.32	380	60	THF	29	Injection at temp, batch	Towne
Illinois #6	0.1-0.56	380-400	15-240	none	55	Fixed bed, flowing steam	Swanson
Illinois #6	0.25	400	240	g + 1	54	H2/Mo-Sn, basket reactor	Barton
Illinois #6	0.14	400	120	THF	34	Basket reactor, flowing stm	Vasilakos
Wyodak	0.02-0.08	240/400	30/30	Toluene	40	Basket reactor, flowing stm	Bienkowski
Subcritical Treatment							
Illinois #6	0.02	320-350	30	Pyridine	30	260C flowing steam	Graff
Illinois #6	0.03	320	15	Water	7	Batch Autoclave	Khan
Illinois #6	0.03	345	15	THF	12	Batch Autoclave	Mapstone
Illinois #6	0.02	250	300			Batch Autoclave	Ross
Pittsburgh	0.03	345	15	THF	15	Batch Autoclave	Mapstone
ND Lignite	0.03	320	15	Water	17	Batch Autoclave	Khan
Wyodak	0.03	320	15	Water	10	Batch Autoclave	Khan
Wyodak	0.03	320	15	THF	15	Batch Autoclave	Mapstone

Abbreviations: THF = Tetrahydrofuran; g+1 = gases plus liquids.

as indicated by increased hydrophilicity and agglomeration in the coal structure in addition to chemical modifications. Chemical analyses determined that the pretreated coal had a lower oxygen content and hydrogen bonding, and higher hydrophilicity compared to untreated coal. Using a ^{13}C O-alklylation technique they were able to establish that steam treated coal contained twice as many hydroxyl groups than the raw coal. From this observation, they postulated that the steam reacted with the ether linkages in coal forming hydroxyl groups and in the process removed substantial and significant covalent crosslinking in the coal structure. This would not explain the corresponding sizable decrease in oxygen content that was observed.

Vasilakos et al. using a basket type reactor, which was in essence a compartmentalized batch type reactor located in an autoclave, extracted Illinois #6 coal with water at 400 °C at water densities of 0.15 g/cc and obtained extraction yields of up to 34%.[33] The level of solubility in water was higher than predicted from the solubility parameter suggested by Giddings et al.[34] In contrast, running the reaction in a conventional type autoclave without a basket reactor, but at the same temperature and water density, i.e., 400 °C and 0.1 g/cc, respectively, was reported by Ross, et al.,[35] to give only 7% toluene solubles from Illinois #6 coal.

Swanson, et al., obtained coal conversions for a lignite of up to 55% at temperatures as high as 440 °C and water densities as high as 0.56 g/cc when using a fixed bed reactor system. This yield was significantly higher than obtained by Graff and Brandes at subcritical temperatures when using Illinois #6 coal.[36] Swanson, et al found that the rate of water flow over the sample had an impact on the amount of material removed from the coal.

In general, most of the data taken at temperatures at or above the critical temperature of water gave higher yields of extracted product than at lower reaction temperatures. Khan, et al.,[29] pretreated several coals at 300 °C with approximately 280 °C steam in a batch system for 15 minutes and found 17% weight loss for lignite, 10% for Wyodak and 7% for Illinois #6. This includes both the material extracted into the aqueous phase as well as gaseous products from each of these coals. The steam treatment for a low-rank coal resulted in significant reductions in total oxygen concentration while the high rank coals were unchanged or had even a higher

oxygen content. The reduction in the oxygen content of the low-rank coal came from reductions in the methoxy, phenolic, and aliphatic carbonyl and carboxyl groups in the coal. Phenols were the major component found in the pretreatment water after the reaction. Contrary to Graff and Brandes's results they reported that the volatile yields in vacuum pyrolysis were not affected by steam pretreatment for the five coals that they investigated. However, they acknowledged that this conclusion was based heavily on only one of the five coals which had not been exposed to air after the treatment process.[a] Mapstone[37] found that steam treatment at 345 °C of Pittsburgh, Illinois #6 and Wyodak coals with 280-300 °C steam gave 15, 12, and 15 wt% THF solubles, respectively, which were higher than those obtained at lower temperatures.

The data on Illinois #6 also suggest that high volatile bituminous coals will behave favorably in this type of processing environment to give not only partial conversion to a hydrocarbon rich product but also a residue that retains the high heating properties of the original coal. The advantages of this type of processing have been pointed out by Barton[38] who showed how distillation in water at temperatures above the critical temperature could result in separation of converted product from the residue. Vasilakos, et al., pointed out that water will have a definite advantage over hydrocarbon solvents because of its higher solubility property plus lower heat content.

Ross and Hirschon[39] hydrothermally treated Illinois No.6 coal at 250 °C (@ 38 atm.) for 30 min followed by pyrolysis of the pretreated sample in a field ionization mass spectrometer (FIMS) chamber from 100-500 °C. They found that the total volatile yield for the pretreated coal was virtually identical with that of the raw coal, i.e. 23% and 22% of the treated sample and as-received coal, respectively. However, the differences in product make-up was significant. The pretreated sample showed a broad increase in lower molecular weight material and a decrease in higher weight tars compared to the raw coal. Their data also showed that the evolution of

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[a] Brandes and Graff have shown that the beneficial effect of steam treatment is lost when the pretreated samples are exposed to air.

the low molecular weight alkylbenzenes, alkylphenanthrenes, anthracenes, pyrenes and alkylnaphthalenes from the organic matrix occurred at a considerably lower temperature after the hydrothermal pretreatment. These results led them to conclude that the release of the low molecular weight material is not merely a release of trapped material but rather the pretreatment changes the coal structure in some manner such that the tar precursors generate additional lower weight material upon thermolysis. Though the mechanism remains unclear, recent work by Hoering[40] underscores the impact of hydrothermal treatment on the generation of petroleum products including long chain normal alkanes, aromatics and biomarkers from Messel shale, which had been preextracted. When D_2O was used, deuterium was heavily incorporated into the hydrocarbons.

Ross and Hirschon[39] also reported that the bulk sulfur content of the coal was reduced by about 60% during pretreatment with steam. This level of reduction was matched by the lowered ash levels. Similar findings were reported by Rozgony et al.[41] who found reductions of 39% in total sulphur and 31% in ash for a bituminous coal after hydrothermal treatment at 292 °C for 40 minutes.

The mechanism by which hydrothermal treatment of coal affects conversion is not clear. One possibility is that the coal structure is opened thereby increasing pore volume and subsequent conversion.[30] The swelling ratio of steam treated coal has been found to be two-fold greater than raw coal.[31] However, such factors are not certain since steam treatment has also been noted to cause agglomeration.[28,31,3] Serio et al. reported that the beneficial effect of steam treatment was negated and the liquefaction yields were reduced when the reactor containing the steam treated coal was not shaken. They contended that as a result of agglomeration the coal was more difficult to liquefy and, presumably in this case, mass transport limitation became a factor in the conversion process.

It has been noted in many studies that there is generally a greater impact of hydrothermal treatment on low-rank coals with high oxygen contents than high-rank coals.[37,29] The beneficial effect of hydrothermal treatment is a balance between bond breaking and cross-linking reactions.

On the one hand there is the partial removal of covalent crosslinking by steam involving the removal of ether type linkages, and on the other, there is the evolution of phenolic groups which are known to undergo self-coupling reactions. Studies have shown that various phenolic compounds can undergo rapid coupling reactions when H-donor solvents are absent.[42] Trewhella et al. (28) reported that the presence of hydrogen donors, such as tetralin, significantly reduced the polymerization of phenolic compounds to larger ring furans.[43]

Recently, Tse et al.[30] reported the coupling reactions of catechol and showed how these reactions can be modified by kaolin and water in the temperature range from 300-400 °C. Catechol underwent very little condensation reaction at 400 °C (75% unreacted) and even less at 350 °C (92% unreacted). However the reaction was greatly accelerated when kaolin was added. For example, after 3 hours at 350 °C a mixture of catechol and kaolin was found to contain 46% of the original catechol compared to 92% when kaolin was not present. The addition of water to the kaolin/catechol mixture resulted in inhibition of the coupling reaction and consequently 89% of the catechol was recovered. Similar results were reported for reactions carried out at 400 °C. From these results it was suggested that in the presence of water, crosslinking due to coupling reactions by phenolic groups would be greatly reduced leading to a larger yield and/or better quality product.

Bienkowski et al. have identified dihydroxyl aromatics in their toluene solubles after pretreating coal with steam at 200 °C followed by extraction with supercritical steam at 400 °C.[24] Although polyhydroxy aromatics are a basic unit of lignin structures and are presumed to persist in low-rank coal structures, they are not major constituents in coal liquefaction products. A background of 27 references are provided in this paper. Conversely, significant amounts of these compounds have been identified in rapid pyrolysis studies, of which 10 references are provided. The survival of the dihydroxyl aromatics suggested that steam is able to stabilize and extract reactive fragments from coal before they can undergo retrogressive reactions.

Reaction of Coal in Alkaline Solution

The effect of aqueous alkali on a range of different rank coals has been examined. For lower

rank coals, very large quantities can be dissolved in a manner similar to the reactions that occur for many natural products. At least 25% of a German Rhenish lignite can be converted to ether soluble material in a 5 N NaOH solution at 250 °C.[44] This reaction is not unlike reactions with other natural materials, such as wood, which can be converted to tar, gas and a residue when reacted with 5 N NaOH solution.[45]

It is well recognized that as the reaction temperature falls below 300 °C, there is no significant thermal degradation of the coal macromolecular structure. In effect, any application of a process that depends upon high thermal activity may become limited as the pretreatment conditions shift to the lower end of the temperature regime between 200 and 320 °C.

In this regard chemical techniques which have been used for coal structural studies and those that have been extended for use to solubilize coal at moderately low temperatures may find some application in this area, such as reactions with strong alkaline solutions. Fischer et al. showed that part of the coal can be rendered soluble simply by heating with NaOH and KOH at elevated temperatures.[46] Their results showed that the alkali-soluble products increased with temperature from 2.5% of the weight of coal at 250 °C to 21 % at 300 °C. In a study of the action of aqueous alkali on lignin they found that the methoxyl structure in lignin was stable at 200 °C in a 2.8% NaOH solution. However, hydrolysis of this structure was almost complete at 300 °C. In a similar study Kasehagen reacted a Pittsburgh seam coal with 1 N to 100% NaOH solution over the temperature range from 250-400 °C.[11] The results showed that the maximum yield of alkali-soluble products were obtained with a rather dilute alkaline solution (1 N-5 N) at temperatures of 325 and 350 °C. The relatively small yields of alkali degradation products and the large fraction of insoluble residue suggested the absence of significant hydrolysis of the C-O linkages under these conditions and may be a reflection upon the rank of the coal. However, exhaustive extraction of the residue with benzene in a Soxhlet produced significant benzene-soluble material equivalent to 27% of the carbon in the coal compared to 6 to 8% yield in the raw coal. This indicated that some deep seated change in the coal structure had occurred, although the data did not allow firm mechanistic conclusions to be made. Comparable results were obtained on hydrolysis of a Wyoming coal with 5 N NaOH at 350 °C for 24 hours. A

residue was produced containing much less oxygen than the coal.[47] The soluble products included phenols (8%), fatty acids (13%) and hydrocarbons (16%) in addition to 28% insoluble residue.

Earlier work by Withrow and Pew found that KOH in ethylene glycol monomethyl ether was a better solvent than aqueous alkaline solution.[48] Further, it is well known that alcohols are much better swelling agents than water. Brooks and Sternhell[49] found that treatment of brown and subbituminous coals with alcoholic alkali at about 190 °C for 12 hours, followed by acidification, produced materials which were almost entirely soluble in alcohol or pyridine. Analyses of the reaction products showed a marked increase in hydrogen and in some cases a decrease in oxygen. However, the content of reactive oxygen functional groups, which were primarily phenolic and carboxyl groups, remained virtually unchanged. They concluded that the reaction is not simply hydrolysis since no new functional groups were formed. Camier and Siemons[50] suggested that alkali digestion of low-rank coal at mild temperatures is a physico-chemical phenomenon in which the Na^+ ion diffuses into the pore structure of the coal and ion-exchanges with the hydrogen of the oxygen functional groups, i.e. carboxylic and phenolic groups. An electrical double layer would initially form between closely orientated carboxylic and phenolic groups which would lead to electrostatic repulsion and separation of the coal into smaller fragments. The ion-exchange mechanism is dependent on the pH of the solution used; at pH 7-8, the carboxylic acid functions would exchange with the Na^+ ions followed by exchange of the less accessible phenolic functions at pH >8.

Others have investigated the reaction of coal with alcohol-alkali mixtures at much higher temperatures.[51] Ross and Blessing reported that a 'beneficiated' Illinois No.6 coal (PSOC-26) was converted to a fully pyridine-soluble product with H/C ratios from 0.88 to 1.13, relative to the starting coal of 0.79, when treated with isopropyl alcohol in the presence of either the alkoxide or KOH at 335 °C for 90 min.[52] A higher pyridine yield was obtained by Makabe et al. for the reaction of Taiheiyo coal with either ethanol or methanol in the presence of NaOH and KOH at 350 °C.[53] They reported a good correlation between the ethanol extract and hydrogen absorbed into the coal, which corresponds to the difference between hydrogen

produced in the blank test and hydrogen from the reaction. In agreement with Makabe's work, Ross and Blessing reported that the product yield and elemental analysis of the pyridine solubles derived from the alcohol-alkali run were similar to that of a run with tetralin at 335 °C.

The mechanism for conversion under the alcohol-alkali system at high temperatures (>300 °C) most certainly includes a hydrogenation step, but other reactions such as hydrolysis has been suggested as important. Ross and Blessing suggested that the mechanism of conversion at 335 °C involved an initial hydrogenation of anthracene-like structures in the coal, followed by thermolysis of the dihydro-intermediate. On the other hand, Makabe et al. suggested hydrolysis as the main reaction for low-rank coals, in which ether linkages are split, followed by hydrogen transfer from the alcohol.[54,53]

The reaction of alkali with subbituminous coals results in at least partial solubilization of the coal, especially at elevated temperatures, through cleavage of carbon-oxygen bonds. Because so much alkali is necessary to effect this reaction, recovering the solubilized product requires a significant amount of acid to free the acidic components.

Hydrothermal Treatment with CO

When carbon monoxide has been used in conjunction with alkali, less base is required to cause significant change in the structure of the coal than necessary for caustic solubilization. The use of CO in coal liquefaction was first reported by Fischer et al in 1921.[55] In the mid 1960s there was renewed interest in the use of CO as a reducing gas in direct liquefaction, with much of the work being carried out by Appell and coworkers. This work led to the COSTEAM process which was developed at the Grand Forks Energy Technology Center.[56] A considerable amount of work was done to understand this reaction and to develop this process. This hydroconversion process is centered around feeding CO to coal slurries containing water in which hydrogen is formed through the water-gas shift reaction, which is the reaction between water and CO to form H_2 and CO_2.

Most of the early work on liquefaction in the presence of CO was done at temperatures above

the critical temperature of water and was promoted by the presence of base, especially for low rank coals.[57,58,59,60] It has since been found to apply to bituminous coal, lignite, peat, dry leaves and pine needles where conversions increase with increasing H/C and O/C ratios of the starting materials.[61] Since then temperatures below the critical temperature of water have been studied. At these temperatures the conversions are generally higher than in hydrogen donor solvents alone.[62] But first, the water-gas-shift reaction will be discussed because of its importance in this process.

Water-Gas-Shift Reaction. The reaction of CO and water occurs quite readily in the presence of a catalyst at temperatures well below the critical temperature of water.[63] However, in the absence of a catalyst, temperatures of 400 °C or higher are needed to get appreciable conversion of the CO.[64] The water-gas-shift reaction will unquestionably occur in aqueous alkaline systems.[65] However, in some of the studies done on the water-gas-shift reaction in this system, this reaction has been incorrectly equated with CO reacting with the alkaline media. As King et al. reported, CO will react quantitatively with $NaOH/H_2O$ at approximately 100 °C to produce formate.[66] By contrast, conversion of CO to H_2 and CO_2 occurs only at temperatures of about 180 °C, where over a 2.5 hour period ~4% of the starting CO was converted to H_2 and CO_2.[67] Elliott, et al.,[68] reported the reaction of CO at 300 °C in the presence of various alkali metal salts in which up to ~90% was consumed. They followed the disappearance of CO into the aqueous system as a function of time but did not report yields of CO_2 and H_2. Even in the absence of any alkali metal salt, they found that a sizable quantity of the CO disappeared over a 1 hour period. Schuchardt and Sousa did a similar study over a wider temperature range using sodium hydroxide, sodium carbonate and sodium formate. They provided data on the resulting gas phase product and the composition of the aqueous phase.[69] Assimilation of CO into the aqueous phase was predominant at temperatures below 300 °C with negligible formation of H_2 at either 200 or 250 °C. Using their data, we calculated that the production of H_2, as a function of the amount of $CO+CO_2$ in the gaseous phase, was between 4 to 7% at 300 °C and 21 to 28% at 350 °C for all three of these salts. Although the authors concluded a significantly lower activity for NaOH, their data show similar $H_2/CO+CO_2$ ratios for all three salts suggesting they are essentially equivalent. Interestingly, the composition of the aqueous phase, which was

determined after evaporating off the water, appeared to be quite similar regardless of the starting salts. They report that when Na_2CO_3 was used, CO displaced the CO_3^{2-} ion quite readily to form formate, even at 200 °C where the water-gas-shift reaction does not occur. Starting with HCOONa, which has been projected to be the active intermediate in these systems, they found that approximately the same concentration of CO_3^{-2} was obtained at 350 °C as with both NaOH and Na_2CO_3. The carbonate exchange appears to occur only under conditions where the shift reaction becomes substantial.

The role of either base or the role of various salts in the water-gas-shift reaction is still not well defined. From the information that has been developed thus far in these systems, it appears that the salts that have been used react to form an ionic salt media whose composition is determined by equilibrium considerations. The composition of this incipiently formed salt system is a function of temperature and the concentrations and partial pressures of CO, H_2, and CO_2. At temperatures around 300 °C, formate appears to exclusively form while at 340 °C, carbonate and bicarbonate ions are formed. Thereby, its role as a catalyst in the water-gas-shift reaction can be defined.

Hydrothermal Reaction of Coal in Presence of CO. The addition of an alkali metal hydroxide or carbonate has a significant effect on the liquefaction process because it catalyzes the water-gas-shift reaction.[70,71,58,59,61,72] Ross et al. calculated that the turnover number (molar ratio of H added to the coal divided by the quantity of base present in the reaction) for the reaction of an Illinois No.6, PSOC-26 coal in KOH is 80-90.[35] The addition of an organic solvent tended to slow down the water-gas-shift reaction but it did not necessarily lead to a decline in coal conversion. They also demonstrated that the initial pH of the water has a significant bearing on the conversion and the pH at which there is rapid conversion activity is dependent on the metal catalyst.[14] The performance of the catalyst seemed to be related to its high oxidation state.

Coal apparently provides some catalysis for the water-gas-shift reaction though it is still quite limited. Farnum, et al.[73] reported that at 300 °C about 6% CO_2 was produced via the water-gas-shift reaction when as-received Wyodak coal was treated with CO in a hydrocarbon solvent.

From this reaction, 20% of the oxygen in the coal was removed as CO_2 while another 16% was removed as water and CO. By using ^{13}CO, they showed that none of the starting CO was incorporated into the products other than CO_2. In a separate study, NMR was used to show that Martin Lake, Texas lignite heated with $^{13}CO/D_2O$ at 315 °C produced formate ion in the aqueous phase.[74] Most of the deuterium was transferred to the coal with only 10% being converted to D_2. MS analysis showed that the CO_2 contained 60% $^{12}CO_2$ from the coal, presumably formed via decarboxylation, and 40% $^{13}CO_2$ from CO, the product from the water-gas-shift reaction. Sulfur has also been used as a promoter for this reaction at temperatures below the critical temperature of water. Sofianos et al.,[75] observed ~15% CO conversion after 30 minutes at 350 °C in the presence of a Waterberg coal and a pyrite-H_2S catalyst.

Products From Hydrothermal Processing

The two main products from hydrothermal processing of coal in addition to a small amount of gaseous products are a hydrocarbon-rich, essentially ash free material and a solid, ash containing residue. Observations regarding the characteristics of the hydrocarbon-rich ash-free products have varied. In some cases the hydrocarbon product was separated from the ash containing material during the reaction while in others, the product from the reaction was separated using solvents to produce an ash-free hydrocarbon product. Towne et al. ran their reactions in a batch type reactor and a hydrocarbon-rich ash-free product was separated from the total residual product by solvent dissolution after the total product was brought back to room temperature. Bienkowski et al. ran their reactions in a flow-through basket reactor system in which the products were separated from the reactant and residual product while at high temperature. They found small amounts of ash in the hydrocarbon-rich extract which suggested that ash was being leached from the coal and carried over in the vapor phase. Mapstone ran the reactions in a conventional autoclave and subsequently separated the products using solvent separation techniques. Using Illinois #6 coal, he also found ash (< 1%) in the hydrocarbon-rich extract versus 19% ash in the starting coal.

Reports on the composition of the hydrocarbon-rich extract product has varied. Vasilakos et al., who collected the vapor phase product while at reaction conditions, observed that the extract

product was water white. Similar reactions run in supercritical toluene produced a vapor phase product from coal that was always black. Their results suggest the absence of entrained ash or insoluble organic matter in the overhead product. Bienkowski et al., observed that the extract was enriched in sulfur, nitrogen and oxygen with a major amount of phenolic material in both the water soluble and insoluble portions. The results of Mapstone found that THF extract was enriched in hydrogen but, rather than increased concentrations of nitrogen and sulfur, found much lower levels of nitrogen and sulfur than the starting coal.

For the residual product, Vasilakos et al. observed that this product from an Illinois #6 coal had lower volatiles than the feed coal while Swanson et al. found the 500 °C$^-$ volatile fraction present in raw lignite had been removed in the extraction process. They also found that the residual product contained lower hydrogen and a correspondingly lower H/C ratio, about the same amount of nitrogen, and 22% less sulfur. Ross, et al.,[76] found similar results for hydrogen with approximately 50% reduction in both sulfur and ash for the same coal. Vasilakos et al., found for Illinois #6 coal higher oxygen content, with the same heating value while Ross et al., found a reduced level of oxygen in the residual product. Khan et al. showed that even though steam treatment gave lower oxygen in low-rank residual product, for high rank coals oxygen concentration was either unchanged or increased. This contrasts with the results of Brandes and Graff[31] who found that pretreated Illinois #6 had lower oxygen content. The results of Mapstone confirm these latter results of lower oxygen in the residual product.

The solid product from treating a Wyoming subbituminous coal with CO/H_2O at 345 °C had a significantly higher THF solubility than the corresponding hydrothermal treatment.[77] Thermally treating the coal in decalin gave little increase in THF solubility over raw coal (see Table 8-2). Even higher solubilities were obtained in a stirred reactor by running for periods from 3 to 16 hours. At 16 hours, 92.5% of the dried and ash-free (daf) coal was soluble in THF, indicating significant structural changes in the coal. The resulting product has been reported to be substantially depolymerized and more reactive in addition to being more soluble than the starting coal.[77,78] It also was enriched in hydrogen and had reduced oxygen content. Conversion of the pretreated coal to distillate products has been reported to be more facile than the starting coal

in a hydrogen donor solvent.

Table 8-2. Pretreatment of Wyoming Subbituminous Coal at 345 °C for 2 Hours				
	Coal	Decalin/N_2	H_2O/N_2	H_2O/CO
THF Solubles, wt% daf coal	6	4	8	65
H/C Ratio	0.80	0.72	0.73	0.91
Oxygen, wt%	20	16	13	11

Lim showed that there is a significant increase in selectivity toward oil yields (methylene chloride/light petroleum solubles) when Australian brown coals were reacted with $CO/H_2O/NaAlO_2$ compared to reactions in SnO_2/H_2 or H_2/tetralin.[62] The oil/asphaltene ratio obtained in the CO/H_2O reaction is about twice that for the latter reactions. The oil fraction is found to be rich in phenolic compounds. Ross et al. found that the chemical composition of the benzene soluble fraction obtained from the reaction of Illinois No.6 coal with CO/H_2O/KOH at 400 °C was similar to that obtained from tetralin/H_2 at the same temperature.[14]

Mechanism

Proposals have been made as to how CO participates in the structural modification and liquefaction of coal. They generally involve formation of an active formate-type intermediate via the water-gas-shift reaction. Although the reaction of CO and water occurs quite readily in the presence of a catalyst at temperatures well below the critical temperature of water,[63] in the absence of a catalyst, temperatures of 400 °C or higher are needed to get appreciable shift of the CO.[64] Below the critical temperature of water, it appears the degree of the shift reaction to CO_2 and H_2 is limited, however the degree of formation of the formate intermediate would be extensive.[66] The relationship of the formation of the formate intermediate, its role in the shift reaction or its role as a H-donor in the conversion of the coal is not well understood. Unquestionably, the initial salt, its composition, its initial concentration, the temperature of the

reaction and the pressure of CO, H_2, and CO_2 in the reaction all impact on this reaction. Even though the shift reaction is limited at temperatures below the critical temperature of water, whether this affects the H-donor activity remains undefined.

The generally accepted mechanism by which coal reacts involves transfer of a hydride ion from a formate-type anion to the coal structure with subsequent transfer of a proton to provide a hydrogenated coal species.[64] With transfer of the hydride ion, CO_2 is released and reaction with water results in proton exchange and formation of OH^-. The individual steps in the reaction are written:

$$CO + OH^- \rightarrow HCO_2^-$$
$$HCO_2^- + [Coal] \rightarrow [Coal]H^- + CO_2$$
$$[Coal]H^- + H_2O \rightarrow [Coal]H_2 + OH^-$$

The overall reaction is written as follows:

$$H_2O + CO + [Coal] \rightarrow [Coal]H_2 + CO_2$$

It is generally assumed that hydrogen is incorporated into the aromatic structure forming hydroaromatic material.

More recently, an alternative route has been proposed which applies primarily to low-rank coals wherein hydrothermal reaction of the coal leads to depolymerization of the structure which is indicated by increased solubility.[78] The chemistry is believed to involve oxygen-containing constituents attached to aromatic ring systems. Overall, the CO-aqueous system promotes decarboxylation plus some ether and ester cleavage in the coal resulting in a decreased oxygen content and increased hydrogen concentration.

The role of formate as a H-donor has been extensively reviewed. Comparable reactions in which formate participates in catalytic transfer hydrogenation (CTH) are well known in synthetic

organic chemistry.[79] Formic acid and formate ion, in addition to numerous other H-donor compounds such as tetralin, dihydrophenanthrene, and others, have been used extensively as CTH-donors.[80] Many of these same materials have also been used as hydrogen transfer agents in coal liquefaction, but usually in the absence of CTH type catalysts. Both formic acid and its salts, as well as various substituted cyclohexenes, unsaturated monoterpenes, tetralin, ethers and alcohols have been widely used as hydrogen transfer agents in organic synthesis for reduction of various functional groups.[79] Virtually any compound having a low oxidation potential can serve as a useful H-donor.[81] A driving force in the use of any H-donor is the stabilization of the resulting products. In this regard, the driving force for formic acid as a H-donor is the large negative enthalpy of formation of CO_2.[80]

Olefins is an example of a typical functional group that is easily reduced by the CTH reaction under rather mild conditions in the presence of various nobel metal catalysts. High conversions have been attained in the presence of water at reaction temperatures up to 100 °C; in some cases only a trace of water was present.[82] Aromatic aldehydes and ketones can also be readily reduced to the corresponding $-CH_3$ or $-CH_2-$ analogs in quite high yields at mild conditions.[83,84] In the absence of a catalyst, much higher temperatures are required. Benzaldehyde at 250 °C and tetralone at 460 °C were ~75% converted to predominantly reduced products in the presence of aqueous sodium formate.[85,86] Under conditions where formate is produced, ~40% of acetophenone is converted in the presence of CO in aqueous Na_2CO_3 at 350 °C to give 1-phenylethanol along with very small amounts of ethylbenzene and styrene.[87]

In the CTH reaction with homogeneous type catalysts, metal complexes are involved in which the formate combines with the metal as a ligand.[88] Subsequent transfer of a hydride ion to the receptor molecule could occur via a stepwise route involving hydride transfer to the metal accompanied by dissociation of the donor and addition of the acceptor as a ligand. Subsequent hydride transfer to the acceptor molecule followed by dissociation and proton acceptance could lead to the resulting product. Correspondingly, complexing both the donor molecule and the acceptor could create a direct hydrogen transfer without the intermediacy of a hydride transfer to the metal. In both cases the final step would be proton transfer followed by hydrogen transfer

from water or other protic source. The release of CO_2 energetically promotes the hydride transfer freeing up the metal to complex with additional ligand. The hydride route is supported by the high degree of stereoselectivity that can be attained in these homogeneous CTH reactions.

With heterogeneous catalysts, the CTH reaction is less well understood.[80] In this case, because formic acid and formate can react by either of two competing pathways, deciding which is operating in the role of catalytic hydrogen transfer is not easily resolved. One route is via an ionic pathway similar to that discussed above for homogeneously catalyzed reactions in which formic acid would transfer a hydride ion followed by subsequent proton transfer. This sequence was described above. However, the alternative pathway involving the transfer of two hydrogen atoms could also be operating. Both routes feature the competitive reaction where an acceptor for the hydrogen is unnecessary since hydrogen donors can decompose directly to H_2.[89]

Because the coal treatment reaction occurs both at high temperature and in the absence of a conventional catalyst, it is not really possible to differentiate the reaction pathway. However, even at high temperatures under essentially thermal conditions, the efficiency of the coal for incorporating the hydrogen into the product relative to promoting the formation of H_2 via the shift reaction will undoubtedly provide information regarding the mechanism. At present, such information is not available.

The corresponding hydrothermal reaction that does not involve the formate intermediate was proposed to explain the extensive reaction of some aryl carboxylates and esters at elevated temperatures. It was observed that naphthoic acid, and to a lesser extent, its methyl ester, will completely decarboxylate in water at 343 °C in 2 hours.[90] In the absence of water, however, the extent of reaction is considerably less and the product distribution is changed. Under similar aqueous conditions at 250 °C, benzoic acid was completely stable.[85] Since decarboxylation with formation of CO_2 occurs with no net transfer of electrons, the presence of a H-donor is unnecessary to promote this reaction which proceeds quite easily under essentially thermal conditions. Whether the presence of formate will affect this reaction is not known. However, it is known that carboxyl groups in peptides are quite stable to low-temperature catalytic transfer

hydrogenation. In fact, this technique is used as a convenient and effective method for removing benzyl protective groups from carboxyl groups in amino acids and peptides.[80] Whether this relative inactivity will translate to activity that is not greatly affected at high temperature isn't known.

Ross et al. proposed a reaction scheme for the reaction of coal with CO/H_2O.[14] In this scheme, the route to coal conversion is seen as a parallel to the water-gas-shift reaction. The formate intermediate is the active reducing species. In this scheme, coal conversion is a consequence of the competition between bond cleavage/hydrogenation and retrograde reactions. The decomposition of the formate intermediate has a positive isotope effect so that by adding D_2O instead of H_2O, it was argued the relative concentration of the intermediate was increased giving rise to an overall improvement in conversion. However, recent work by Stray and Jackson showed that the isotope effect disappeared when the coal was washed with dilute acid to remove the soluble mineral and inorganic matter.[91] It was suggested that the isotope effect was a consequence of an interaction between the gas (hydrogen or deuterium) and the mineral and inorganic phases.

Although the precise mechanism by which coal conversion takes place is still unclear, Jackson et al. have shown that the kinetics of the coal conversion process relative to that of the water-gas-shift reaction is critical.[92] They have demonstrated that the coal fragmentation process has to be compatible with the water-gas-shift reaction in order to obtain good conversion yields . Stenberg et al. have also demonstrated similar concepts by 'slowing' the radical fragmentation process via a temperature programming technique to enhance the efficiency of the hydrogen donating media through the use of H_2S/H_2O with CO or H_2 in the presence of pyrrhotite.[93]

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Chapter 9

Hydrothermal Pretreatment of Low-Rank Coal

Introduction

The process of coal liquefaction involves the cleavage of bonds within the coal structure and the stabilization of the resulting fragments with hydrogen to progressively reduce molecular weight and ultimately to produce distillable liquid products. The attainment of this goal requires minimizing the crosslinking and condensation reactions that are important to coal carbonization and lead to the formation of high molecular weight refractory species. A considerable volume of literature exists in this area that includes a large volume of related work. This work was reviewed above. Pretreating coal prior to direct liquefaction by any number of methods has been shown to result in higher yields of product through a net reduction of retrograde reactions. These methods include treatment by demineralization, solvent swelling, alkylation, dissolution with strong acids and bases, catalytic reactions, or by reacting in the presence of hydrogen. Aqueous treatment at around the critical temperature of water, i.e. ~374°C, is known to cause significant changes to the coal structure which can enhance coal conversion under a variety of liquefaction process conditions. The pretreated coal had a reduced oxygen content, exhibited reduced hydrogen bonding, had an increased pore volume, and had twice as many hydroxyl groups as the starting coal. The presence of steam inhibited the retrograde reactions of the phenolic groups that were formed.

Generally, coal conversion in aqueous systems to which CO and base are added, is higher than in pure aqueous systems or in hydrogen donor solvents, especially for low rank coals. In the $CO/H_2O/NaOH$ system, CO was found to quantitatively react with the base at approximately 100 °C to produce formate. Some of the starting CO was converted to H_2 and CO_2 at 180 °C, whereas in the absence of base the water-gas-shift reaction was not observed. In these treatments with CO the WGS reaction is undoubtedly important but it has not been well defined. In the study reported here, the effect of aqueous CO pretreatment on subbituminous coals at temperatures around 300 °C has been investigated and the findings are consistent with recently reported results.[1] Substantial changes to the coal structure have been identified and the

liquefaction of the pretreated coal in a hydrogen donor solvent has been evaluated.

The Water-Gas-Shift Reaction in Absence of Coal

As already discussed in the review of the WGS reaction above, the quantitative reaction of CO with the base in the $CO/H_2O/NaOH$ system at 100 °C to produce formate is a known reaction. It is also known that in this system only very small amounts (~4%) of the starting CO has been observed to be converted to H_2 and CO_2 at 180 °C, this being over a 2.5 hour period. The corresponding reaction in the absence of base also was not observed. Some confusion over terminology appears in the literature with regard to observations concerning the WGS reaction. In the review above we speculated that salt composition is driven primarily by equilibrium factors that determines the composition of the aqueous media. That question will be further addressed in the discussion that follows. We also pointed out that even though apparent CO shift to H_2 and CO_2 is considerably less than the 90% conversions observed over CoMo/S after an hour at 240 °C, the comparisons have not been accurately made to provide a true measure of the catalytic effect of aqueous media for promoting this reaction.

The WGS reaction was experimentally measured in the absence of coal both in the presence and absence of NaOH over a temperature range from 250 to 350 °C under conditions where sufficient water was present to maintain an aqueous phase in the reactor. As technique developed, recoveries of the carbon oxides were quantitative as shown in Table 9-1. Under these reaction conditions the NaOH reacted with the CO to give formate:

$$CO + NaOH \rightleftarrows HCOONa$$

In this temperature range in the absence of NaOH, formation of the products from the WGS reaction, i.e. H_2 and CO_2, were very small. It appears that as the temperature increased, formation of H_2 and CO_2 increased, presumably through decomposition of the formate ion as follows:

$$HCOONa + H_2O \rightleftarrows CO_2 + H_2 + NaOH$$

The reverse reaction to reform CO and H_2 can also occur:

$$HCOONa + H_2O \rightleftarrows CO + H_2O + NaOH$$

As CO_2 is formed, the aqueous salt composition can change with the formation of the HCO_3^-

ion. Equilibrium considerations will then determine the ultimate salt composition. At lower temperatures formate appears to be the primary ion while as temperature increases, the bicarbonate concentration in the aqueous media appears to increase. These changes are reflected in the pH of the resulting aqueous media.

Table 9-1. Effect of Temperature on the WGS Reaction								
Temperature, °C	350	320	320	300	300	300	250	250
CO press, psig	800	800	800	800	800	800	800	800
NaOH Conc, mol/L	0.33	0.33	none	0.33	0.33	none	0.33	none
Reaction Time, min	60	60	60	120	60	60	60	60
CO_X recoveries, mol%	102	100	100	91	96	97	97	98
CO Conv, mole % (ex. aqueous CO_x)	34	27	1	19	15	1	5	1
CO Conv, mmol/mmol Na	8.5	6.8	-	4.8	3.8	-	1.2	-

The $CO/H_2O/NaOH$ system at 300 °C gives an aqueous media having a pH of 4.5 while the same mixture at 340 °C gives a higher pH of ~7. The higher pH obtained at 340 °C is consistent with increased formation of bicarbonate that has been previously observed at these higher temperatures. In both cases, the pH of these solutions resulting from thermally treating the $CO/H_2O/NaOH$ system are somewhat lower than observed with corresponding solutions of the pure salts. The effect of varying the ion ratio of $HCOO^-$ and HCO_3^- in solutions containing a total of 0.33 M ions is shown in Table 9-2.

The pH of HCOONa solution at a concentration which is equivalent to the amount of NaOH used in the shift experiments in Table 9-1, was 7.7 versus the 4.5 observed from thermally treating the $CO/H_2O/NaOH$ system at 300 °C. Likewise, the pH 7 observed at 340 °C for the thermally treated $CO/H_2O/NaOH$ system was lower than a solution containing only 25% HCO_3^-. In both cases, the lower pH suggests the presence of a buffered solution having a CO_x-ion-containing concentration in excess of the Na^+ concentration. In an experiment in which

^{14}CO was treated at 340 °C, an aqueous phase was obtained which had a $^{14}C/Na$ ratio of 1.09, which is consistent with free acid in the presence of the CO_x-containing the Na counterion. If the ion distribution were known, the degree of agreement between observed and calculated pH values could be determined. At any rate, at this time, this explanation is speculative since these solutions have undergone an extreme temperature change and my now have completely reached equilibrium at ambient temperature before pH measurements were taken which could have an effect on the kinds and concentrations of the ions that are present.

Table 9-2. pH of Formate-Bicarbonate Mixtures

HCOONa mol/L	$NaHCO_3$ mol/L	pH
0.33	0	7.8
0.25	0.08	8.2
0.16	0.16	8.2
0.08	0.25	8.2
0	0.33	8.3

In order to calculate CO_x recoveries the amount incorporated in the aqueous phase must be considered. The amount of carbon oxides that will be contained in the aqueous phase will vary depending on whether the carbon is present as CO or CO_2. Likewise, the pH of the resulting solution will be dependent upon the particular ions that are present and their concentrations. Because bicarbonate and formate, the two principal anions in the system, both have the same charge, the ion balance dictated by the cation concentration, assuming no buffering effect by free acid, will define the amount of CO_x that will be present in the aqueous phase. Because the pH of these solutions are quite low the concentration of free bicarbonate in these solutions will also be quite low. In the systems described in Table 9-1, the amount of total CO_x incorporated in the aqueous phase was approximately 5% of the total CO in the system. Total recoveries, which are the sum of gaseous CO and CO_2 plus the amount of formate and bicarbonate present in the aqueous solution, were experimentally found to be very close to 100%.

The values for CO conversion shown in Table 9-1 represent the amount of CO that was converted to gaseous CO_2 and ignores the amount of CO_x incorporated into the aqueous phase. The reason for reporting these values in this manner is that the shift reaction is more directly associated with the amount of CO_2 formation and not the amount of CO incorporated into the aqueous phase. If the composition of the aqueous phase had reached steady state, there would be no net CO assimilation into the aqueous phase, in which the amount of CO disappearance would be equivalent to the amount of shift reaction. Since all of the studies reported here were not run at steady state, this format provides a more direct measure of the degree of WGS conversion occurring in the system.

The data in Table 9-1 show that over the temperature range from 250 to 350 °C in the presence of NaOH, CO conversion increased steadily reaching 34% at the higher temperature. In the absence of the base in water only, conversion of CO over this entire temperature range was approximately 1 wt %. This indicates the maximum effect that the reactor can have on the reaction. Even at 350 °C, the catalytic effect of the reactor wall on the reaction was quite small and does not impact on the interpretation of the data. Hydrogen formation in most of these runs essentially agreed with the CO_2 yield, with some scatter in the data. It was obvious, however, the yield of H_2 was significantly higher in these runs than when coal was added to the reaction.

Hydrothermal Reaction of Coal

Heating Wyodak coal in a confined space in the absence of any added water can still be regarded as a hydrothermal treatment since sufficient moisture is present (~20%) in the coal to create a significant water partial pressure at this condition. In the experiments reported here, 2.5 g of as-received Wyodak coal from the Black Thunder mine was heated in a 25 ml reactor. In these cases without added water and based upon the reactor size, sufficient water was present in the as-received coal to generate a vapor density of 0.027 g/cc (50 atm). However, insufficient water was present to maintain an aqueous phase at reaction conditions. After heating the coal a solid material was recovered that typically accounted for over 90% of the charged material, on an maf coal basis. The texture of this material was coal-like and showed no physical evidence of agglomeration or charring. The solid material that is formed differs from

the starting coal in that it contains less oxygen than the starting material. CO_2 accounts for a sizable portion of the removed oxygen while water accounts for most of the remaining oxygen that was removed. Under the conditions that were investigated the amount of CO that is formed is very small, typically less than $\sim 1\%$.

This results from treating the coal over a range of temperatures is shown in Table 9-3. Heating at 300 to 340 °C for one hour produces between 4.1 and 4.7 wt% CO_2 which contains 16 to 18 wt % of the oxygen that was present in the coal. The H/C ratio in the sample treated at 340 °C (J286) decreased from an initial 0.80 in the starting coal to 0.73 in the product. The results were only affected very slightly when sufficient water was present in the reactor to give a liquid phase at reaction conditions. In this case, total oxygen rejection, the amount of oxygen eliminated as CO_2, and the resulting H/C ratios of the products changed with temperature but otherwise remained almost the same.

Addition of NaOH to the reaction mixture had an influence on oxygen elimination from the coal. Analysis of the solid products obtained at 340 °C (J285) indicated that oxygen elimination increased from 42 to 49% when NaOH was present. The solid product also had a higher H/C ratio when base was present suggesting that relatively less oxygen was lost as water. In fact, the presence of base (J285 vs J287) appeared to increase the selectivity for removal of oxygen as CO_2 while keeping the amount of water that was produced about the same. The constant level of water production both in the presence and absence of base plus the increasing amount of CO_2 elimination in the presence of base are shown in Table 9-4.

By conducting these hydrothermal treatments in the presence of hydrogen instead of in nitrogen does not appear to affect the amount of oxygen elimination or the selectivity of the reaction. However, it does appear to increase the hydrogen in the solid product. When coal was treated at 300 and 340 °C in hydrogen in the presence of a liquid phase but in the absence of base (J304, J260, J302), the CO_2 yields were very close to being the same. However, the highest H/C ratio observed in any of the solid products was obtained at 300 °C, which was equivalent to the H/C ratio in the starting coal. When NaOH was added (J258, J303) the CO_2 yields

Table 9-3. Oxygen Rejection from BT coal as CO_x Gases.									
Run No.	Reaction Conditions			% Wt. maf coal		Oxygen rejected as CO_2, wt %	Total Oxygen rejected, wt%	H/C	pH
	Base	g water/g maf coal	Temp (°C)	CO	CO_2				
J250	none	0.5	300	0.1	4.3	16	-	-	7
J328			320	0.1	4.1	16	-	-	
J256			330	0.1	4.7	18	-	-	
J286			340	0.1	4.7	18	32	0.73	
J329	none	3.3	300				21	0.76	
J249			320	0.1	5.2	20	-	0.71	7
J287			340	0.1	5.7	22	42	0.70	
J304	none	3.3, H2	300	0.1	2.7	10	24	0.80	
J260			330	0.2	4.6	18	-	-	
J302			340	0.2	6.6	25	-	-	
J251	NaOH	3.3	320	0.1	6.4	25	-	-	
J285			340	0.2	7.7	30	49	0.75	7
J258	NaOH	3.3, H2	330	0.2	5.8	22	40	0.78	8
J303			340	0.1	7.9	30	49	0.77	
Reaction Conditions: 2g maf coal, 3 ml. water/g maf coal, 800 psig N_2 unless otherwise noted, 1 hr. reaction time in 25 mL microreactors. Concentration of NaOH used = 4.4 wt % maf coal.									

Table 9-4. Oxygen elimination from coal by hydrothermal treatment at 340 °C				
	base	CO_2	H_2O	Total
J287	none	22	20	42
J285	0.33 M	30	19	49
J302 / H_2	none	25	-	-
J303 / H_2	0.33 M	30	19	49

increased slightly. At 330 °C, the CO_2 increased from 4.5 to 5.8% while at 340 °C the CO_2 yield increased from 6.6 to 7.9%. The H/C ratios in the products were 0.78 and 0.77, respectively, which were higher than observed in the absence of added hydrogen.

The final pH of the water solutions that were recovered were generally the same as those obtained in the study of the WGS reaction in the absence of coal. These values, as shown in Table 9-3, were not affected by temperature, presence of NaOH, or the effect of adding H_2 to the reaction mixture. In the absence of added NaOH, the pH was probably the result of the bicarbonate ion formed from the CO_2 product. In the presence of NaOH, the resulting pH is consistent with formation of $NaHCO_3$. Since the pH of a 0.33 M $NaHCO_3$ solution is 8.3, the slightly lower pH values observed in these experiments suggest that some buffering by the coal products probably was occurring, although the bicarbonate ion is definitely the dominating ion present in these solutions.

Solubility Characteristics of Products. The solid material recovered after heating as-received coal in a closed reactor in the absence of added water at temperatures between 300 and 340 °C accounted for 90 to 97 wt % of the starting coal, on an maf basis (see Table 9-5). The solubility of these solid products in THF reached a high of only ~6% at 330 °C (J256) and appeared to level out at 340 °C. Optical examination of these products indicated a more pronounced reaction had occurred relative to material collected at <300 °C, however, it was far less than for the CO pretreated coals that are discussed below.

The addition of sufficient water to the reaction mixture (2.5ml/g as-received coal) to create a liquid phase at reaction temperature caused a slight increase in the THF solubility of the product from 5-6% to 9-10%. At 340 °C, the solubility of the products doubled that of the corresponding dry reaction products (compare J286 with J287). However, THF solubility leveled out between 330 and 340 °C. The small positive effect of having an aqueous phase during reaction can perhaps be ascribed to better mixing and mass transfer in which close intimate contact between coal, coal fragments and water during hydrothermal treatment is

Table 9-5. Composition of Water-Insoluble Product from Hydrothermal Treatment of BT coal										
Run No.	Reaction Condition			% wt maf coal						
	Base	g water/g maf coal	Temp (°C)	THF Insols.	THF Sols.	PA+A	Humic acid	OGW	Water-insoluble Prod	H/C
J250	none	0.5	300	92	5	5	0	3	97	
J256			330	84	6	6	0	10	90	
J286			340	88	5	5	0	7	93	0.73
J329	none	3.3	300	91	4	4	0	5	95	0.76
J249			320	79	10	9	0	12	88	
J287			340	79	9	8	0	13	87	0.70
J304	none	3.3/H_2	300	86	9	8	0	6	94	0.80
J260			330	78	7	6	0	16	84	
J302			340	80	10	9	0	11	89	
J251	NaOH	3.3	320	75	14	8	4	13	83	
J285			340	74	13	8	4	14	82	0.75
J258	NaOH	3.3/H_2	330	78	18	13	4	5	91	
J303			340	70	13	11	1	18	81	0.77

Reaction Conditions: 2g maf coal, 3 ml. water/g maf coal, 800 psig N_2 unless noted otherwise, 1 hr. reaction time in 25 ml. micro-reactors. Concentration of NaOH was 4.4 wt% maf coal or 0.33 M soln.
Insols = THF Insolubles, Sols. =THF solubles, Rec.= Solids Recovery

important. The water phase may also solvate reactive fragments and help minimize retrogressive reaction at these temperatures. The effect is not found at lower temperatures (<300 °C) possibly due to slow reaction kinetics. Running the thermal treatments in the presence of H_2 had little effect on the amount of recovered water insoluble product or the THF solubility of the product. The hydrogen did not promote any noticeable liquefaction reaction since the PA+A product did not change, even at the highest temperature that was run.

Adding NaOH to the reactions decreased the amount of water insoluble product that was recovered to 82-83% (J251, J285). At the same time the THF solubility increased and between 3 and 4 wt % humic acid material, which was soluble in alkali and insoluble in acid, was produced. The THF solubility of the product increased from 9-10% to 13-14%, with the improvement being primarily to the production of more humic acid material. The THF solubility of the material at 340 °C was apparently not affected by the presence of H_2 (J303).

The conclusions that can be drawn from these data are that the CO_2 elimination during hydrothermal treatment of the coal increases with temperature and appears to be about equal to the amount of oxygen eliminated as water. The initial data appear to indicate that the addition of base increases the amount of oxygen that is eliminated with the increase being in the amount of CO_2 that is formed. When H_2 was present during the hydrothermal treatment, the degree and selectivity of oxygen elimination appeared to be unaffected, however the H/C ratio in the resulting solid product increased. The THF solubility of the resulting solid product appeared to increase with the presence of a liquid phase in the reaction system, although this affect could also be attributed to the higher steam pressure in the system. When base was present, the apparent increase in THF solubility was largely the result of alkaline soluble humic acid material. Whether the base promoted the formation of materials that would solubilize in the caustic solution or whether the presence of base merely solubilized the material that was formed independently of the presence of base isn't known from the data that has been developed.

Reaction of BT Coal in Tetralin

Unquestionably, these Wyodak coals undergo significant changes under hydrothermal reaction conditions at rather mild temperatures relative to liquefaction. Since it has been established in related low-temperature liquefaction studies that the evolution of CO_2 correlates with the decomposition of carboxyl groups in the coal structure,[2] several experiments were conducted at these low temperatures to determine the reactivity of these Wyodak coals in tetralin and hydrogen. Surygala et al.[3] found that CO_2 production reached a maximum of 4.7 wt % maf coal (23.5% of the oxygen in the coal) when brown coal was liquefied in hydrogenated anthracene oil with hydrogen in the absence of a catalyst at reaction temperatures from 200-450 °C. It has

also been shown by Redlich et al. that the relative yields of CO_2 and water can vary depending on hydrogen availability. In an inert decalin/N_2 atmosphere, repolymerization is significant resulting in higher CO_2 yield (between 0-2 wt % daf coal) and lower water yield (between 0-1% wt daf coal) compared to reactions in tetralin and H_2. This applies to a wide range of coals. In some cases the CO_2 yield was much higher than the carboxyl content of the coal suggesting that CO_2 was produced from a secondary source.

In the reaction of BT coal in tetralin at these milder conditions, experiments were performed by adding 4 grams tetralin into 25 mL microautoclaves along with 2.5 g of as received coal (~20% moisture). The reactors were charged with 800 psig of H_2 and heated in a fluidized sandbath at temperatures from 300 to 400 °C while shaking at a rate of 400 cycles per minute. At the end of the period, the reactor was rapidly quenched to room temperature, and the gaseous products vented into a collection vessel and analyzed by gas chromatography. The products were collected using either of two methods. In the first, the solid and liquid products were scrapped and washed from the reactor using pentane (~400 ml.) and the mixture was placed in a Soxhlet apparatus overnight. The pentane insolubles, which were essentially free of tetralin, were analyzed. High mass recovery(~95%) indicated negligible formation of pentane soluble products. In the second method, the products were scrapped and washed from the reactor with THF (~400 ml.) and extracted overnight in a Soxhlet apparatus. The THF -insolubles were collected, dried overnight in a vacuum at 40 °C and weighed. The THF solubles were concentrated by removing excess THF in a rotary evaporator. A 50:1 volume of excess pentane was added and the mixture placed in an ultrasonic bath for 3 min. The pentane insoluble material (PA+A) was filtered, dried, and recovered after evaporating the solvent. All of the unaccounted for organic matter, gases ($CO+CO_2$ and gaseous hydrocarbons) plus water are lumped together (OGW).

Table 9-6 shows the results from the reaction of BT coal with tetralin and H_2 at 300 and 340 °C for 60 min. Also included are the results from treating the coal in the absence of any added solvent. The results are surprisingly the same in the absence and presence of tetralin, the latter also in the presence of H_2. At 340 ° C, the total removal of oxygen as well as the amount

removed as CO_2 are nearly the same. The results at 300 °C are also quite similar as far as the oxygen elimination as CO_2. At both temperatures, the THF solubilities were quite different with a much larger yield of PA+A being formed in tetralin.

Comparable liquefaction at higher temperatures during liquefaction can be related to carboxyl content with these Wyodak coals. During liquefaction of Wyodak coal in a Wilsonville Run 263J process solvent with Fe_2O_3/Molyvan L catalyst at 415 °C for 15 min, all of the carboxyl groups in the coal, in which the carboxyl content was estimated to be between 5.5-6.5 wt % (maf basis),[4] can be accounted for in the CO_2 yield. In that run, approximately 5 wt % CO_2 and 15 wt % H_2O (maf) were produced. This represents 20% oxygen removal as CO_2 and 70% as water.

Also included in Table 9-6 are results on liquefaction in water with H_2 overpressure. Results differ somewhat with the tetralin runs, however the oxygen selectivity did change reflecting the positive impact of hydrothermal treatment. These results suggest that mild heat treatment will not suffice as a strategy to significantly reduce oxygen by increasing the CO_2 yield. It appears that the level of improved oxygen elimination in these cases will not likely have significant economic impact on the cost of producing coal liquids. Moreover, CO_2 production seems to be favored only under less than desirable reaction conditions. Conversely, in a good hydrogenation system, water production appears to be the dominant process. In this respect, the hydrothermal reaction process discussed above, provides a better alternative route to reject oxygen as CO_x.

Hydrothermal Reaction in Presence of CO

The effect of adding CO to the reaction mixture during the hydrothermal treatment of coal was examined over a range of conditions. Analysis of the gas phase recovered from these reactions was no longer straightforward because of the addition of CO. Because CO was converted in the competing WGS reaction, the amount of CO_2 formed from the coal could not be determined. However, it was clear that the presence of coal promoted the disappearance of CO (Table 9-7). In the absence of any added water at 300 °C, 8% of the CO was converted. This is a significant

Table 9-6. Oxygen Removal from BT Coal in Tetralin						
Run No.	J316	J250	J304	J300	J286	J302
Solvent	Tetralin	None	Water	Tetralin	None	Water
g Solvent/g maf coal	2.1	-	3.3	2.1	-	3.3
Temp °C	300	300	300	340	340	340
Reaction time, min	60	60	60	60	60	60
Gas	H_2	N_2	H_2	H_2	N_2	H_2
Pressure, psig	800	800	800	800	800	800
Product, wt% maf coal						
CO_2	3.2	4.3	2.7	5.3	4.7	6.6
CO	0.1	0.1	0.1	0.3	0.1	0.2
THF Insol	83	92	86	68	88	80
THF Soluble	14	5	9	28	5	10
PA+A	13	5	8	26	5	9
OGW	4	3	6	6	7	11
Water Insoluble	96	97	94	94	93	89
H/C Ratio	n.d.	n.d.	0.80	0.76	0.73	n.d.
Oxygen Rem as CO_2	12	16	10	20	18	25
Total Oxygen Removal	-	-	24	35	32	-

increase over the 1% observed in absence of coal. As temperature increased the conversion of CO also increased reaching 29% at 340 °C (J275). From the data shown in Table 9-7, adding sufficient water to create a liquid phase at reaction temperature did not appear to further increase CO conversion, at least to the degree observed merely by adding coal. These data indicate that adding NaOH to the coal further increases the WGS reaction, which is more clearly shown below.

Adding CO to coal, at a temperature of reaction between 300 and 340 °C, appeared to increase the magnitude of the THF soluble product quite dramatically as shown in Figure 9−1. At all temperatures the amount of THF soluble product was greater than obtained in the absence of

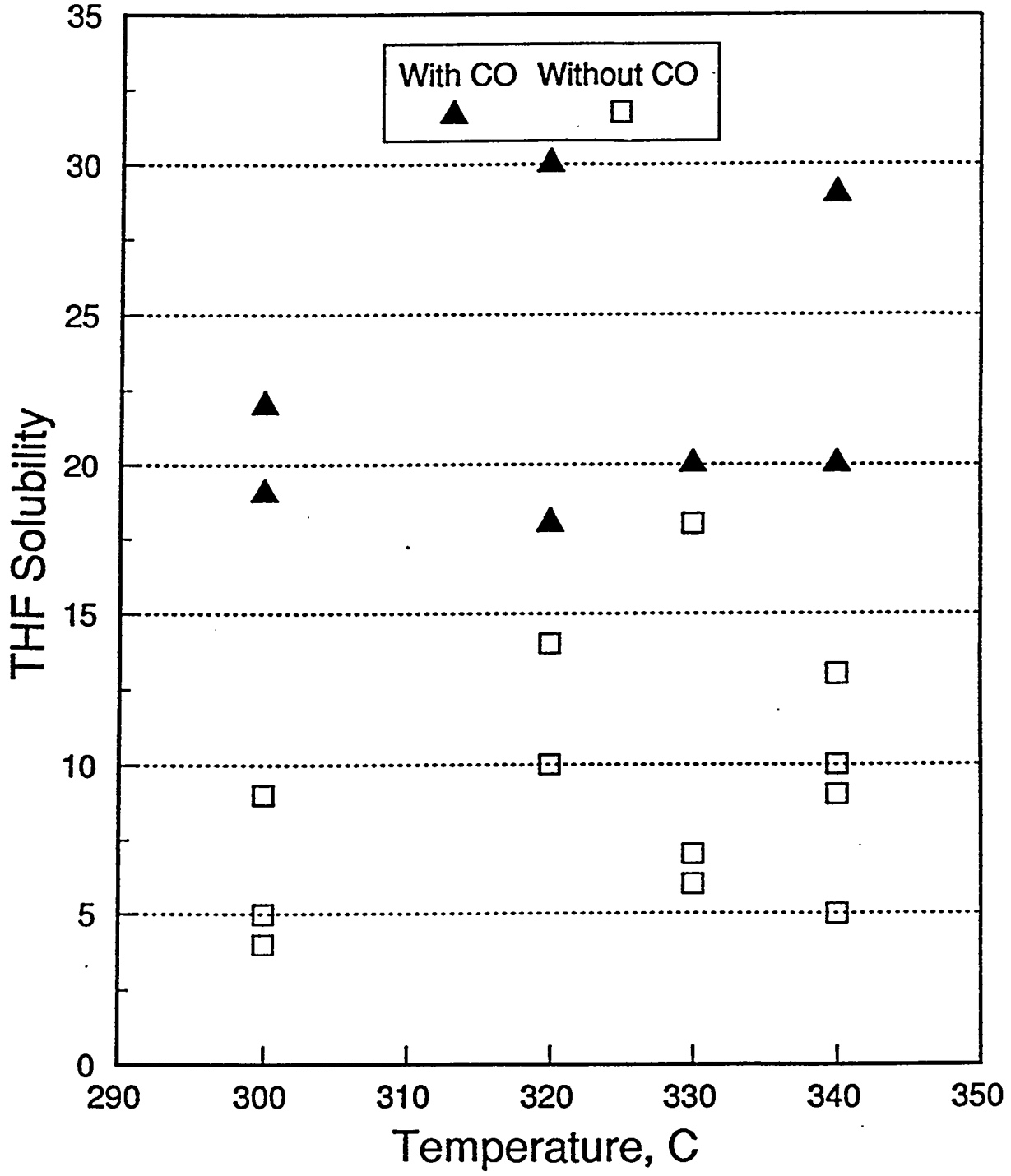
CO. Reactions containing NaOH are included in this data set as long as no CO was also added. Those data where both NaOH and CO were present are treated separately below. The oxygen and hydrogen contents of these materials in the presence of added CO all decreased relative to the starting coal, although the H/C ratio of the products were not significantly different than obtained in the absence of CO. Solids recovery varied depending on the degree of CO conversion, decreasing as CO conversion increased. These results clearly show the benefit of the presence of CO on the THF solubility of the solid product during the hydrothermal treatment.

When water was added to the reaction mixture to create a liquid phase at reaction temperature, the water insoluble product diminished and the THF soluble-pentane insoluble product increased from 22% at 300 °C to 29% at 340 °C. This was accompanied by a decrease in the amount of solid product recovered in the reaction. With added water there continued to be decreases in both the hydrogen and oxygen contents of the recovered products versus the starting coal.

Both NaOH and CO independently impact on the hydrothermal reaction of coal. In the absence of CO, NaOH promoted the removal of oxygen as CO_2 (Table 9-4) and CO, in the absence of NaOH, promoted an increase in THF solubility of the treated solid material. When both were present, their combined effect was even more pronounced than either alone, as shown by the data in Table 9-7. CO conversion in mmol/gram maf coal increased with temperature as the concentration of NaOH increased, as shown in Figure 9-2. At any particular temperature over the range shown in the figure, the presence of NaOH at a concentration of 0.9 mmol NaOH/g maf coal increased CO conversion by about 2 mmol CO per gram maf coal. At the lower NaOH loading of 0.06 mmol per gram maf coal the CO conversion was intermediate between these two level.

The level of CO conversion from the WGS reaction in the presence of the same concentration of NaOH but in the absence of coal was very close to that observed in the presence of the coal. In Figure 9-3 the effect of temperature on CO conversion as a function of the Na concentration in aqueous NaOH is shown both in the presence and absence of coal. Conversion at the higher

Figure 9-1
Effect of CO on THF Solubility of Coal
ex NaOH and CO Combinations



TH_v_COr

temperatures appeared to be slightly higher in the absence of coal, although the departure from the data was small.

When both CO and NaOH are present, the yield of water insoluble product does not appear to be significantly different from the reaction in the absence of NaOH. Figure 9-4 indicates that the yield of water insoluble product decreases with temperature dropping rapidly between 300 and 340 °C, but there is no significant difference between runs made in the presence or absence of NaOH. There is, however, little difference between yields at 250 °C and 300 °C. There is, however, a relationship between the solubility of the product and the concentration of NaOH in the reaction. In Figure 9-5 the THF solubility of the product over the entire temperature range obtained in 0.91 mmol NaOH/g maf coal was higher than obtained when no base was added. The corresponding results at the 0.06 mmol NaOH/g maf coal level was intermediate between these two plots.

The differences in hydrogen contents of the products are quite distinctive. In the presence of either CO or NaOH, the H/C ratios were lower than that of the starting coal, 0.80. When CO and NaOH were both present, the H/C ratios in the resulting products were higher than in the starting coal. Since H/C ratio appeared to follow THF solubility, a plot of H/C ratio versus temperature showed no overall relationship for all the data (Figure 9−6). However, the products obtained in the presence of 0.91 mmol NaOH/g maf coal were clearly higher than obtained when no CO was present or CO was present in the absence of any added Na. Since NaOH also promotes CO conversion as pointed out in Figure 9-2, the relationship between THF solubility and CO conversion was found to correlate quite well, as shown in Figure 9-7. The trend of higher H/C ratios observed in products having higher THF solubility suggested a relationship between CO conversion and THF solubility. A plot of H/C ratio in the solid product versus CO conversion is shown in Figure 9-8. This suggests a definite relationship between donor concentration in the aqueous phase and resulting hydrogen content in the final product.

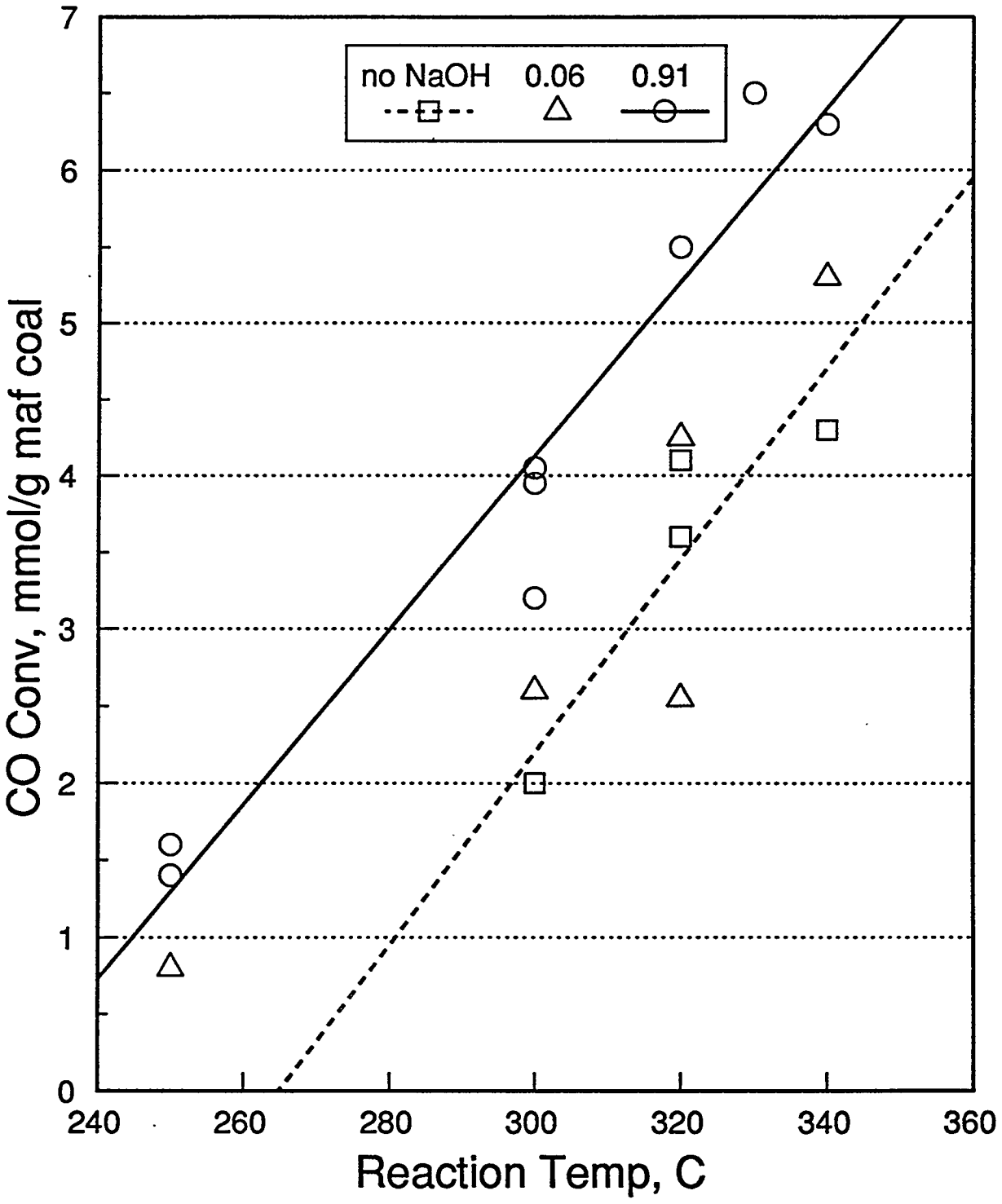
Removal of oxygen has the greatest impact on the process cost. Surprisingly, CO appears to

Table 9-7. Reactions of BT Coal with CO

Run No.	°C	Run conditions		% wt. maf coal basis									
		NaOH mmol/g maf coal	g water/ g maf coal	THF Insolubles	THF solubles	PA+A	Water Soluble	OGW	Recovery of Solids	H/C	Oxygen Removal	CO Conv %	CO Conv mmol/g maf coal
J237	300	none	0.5	76	19	18		6	94			8	2
J267	320				18	17		9	91	0.78	19	14	3.6
	330			73	20	18		9	91				
J275	340			71	20	18		11	89			16	4.3
J95	300	none	3.3	70	22	20		10	90	0.74	19	11	2.0
J268	320			61	30	27		12	88	0.79	37	21	4.1
J311	340			55	29	22		23	77				
J119	250	0.91	3.3	87	9	9		4	96	0.79	11	8	1.6
J238	300			66	28	26		8	92	0.86	19	20	4.0
J127	320			55	36	31		14	86	0.86	40	23	5.5
J270	330			49	40	32		18	81			31	6.5
J308	340			49	37	28		23	77	0.85	52	31	6.3
J138	250	0.06	3.3	94	2	2		4	96	0.75		4	0.8
B005	300			77	19	18		5	95			13	2.6
J236	320			63	27	24		13	87			22	4.2
J296	340			56	32	26		18	82			27	5.3
	310	0.52	3.3	63	28	25		12	88	0.90	32		

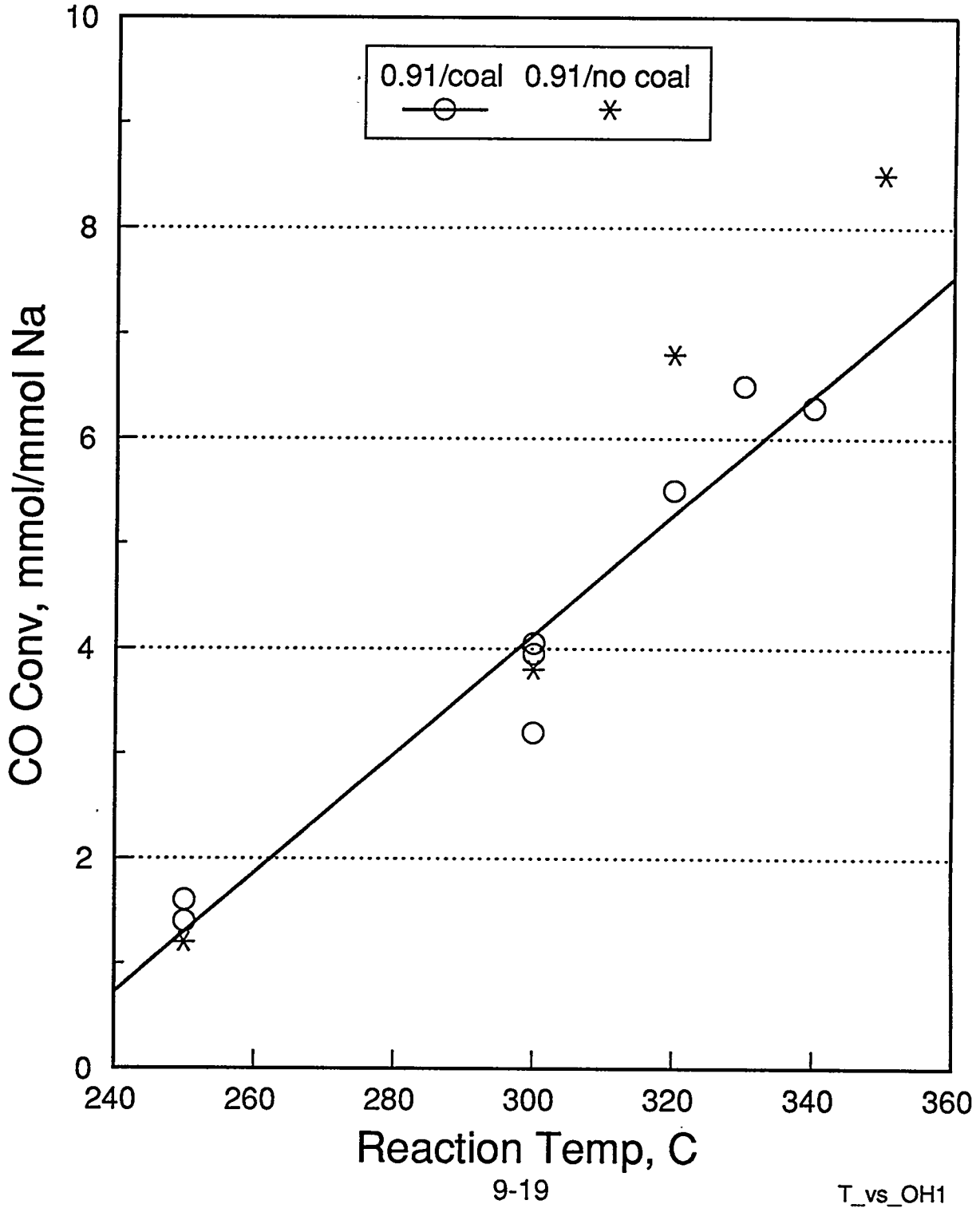
Reaction Conditions: 2g maf coal, 3 ml. water/g maf coal, 800 psig CO, 1 hr. reaction time in 25 ml. micro-reactors. N.A= not available

Figure 9-2
Effect of NaOH on CO Conversion



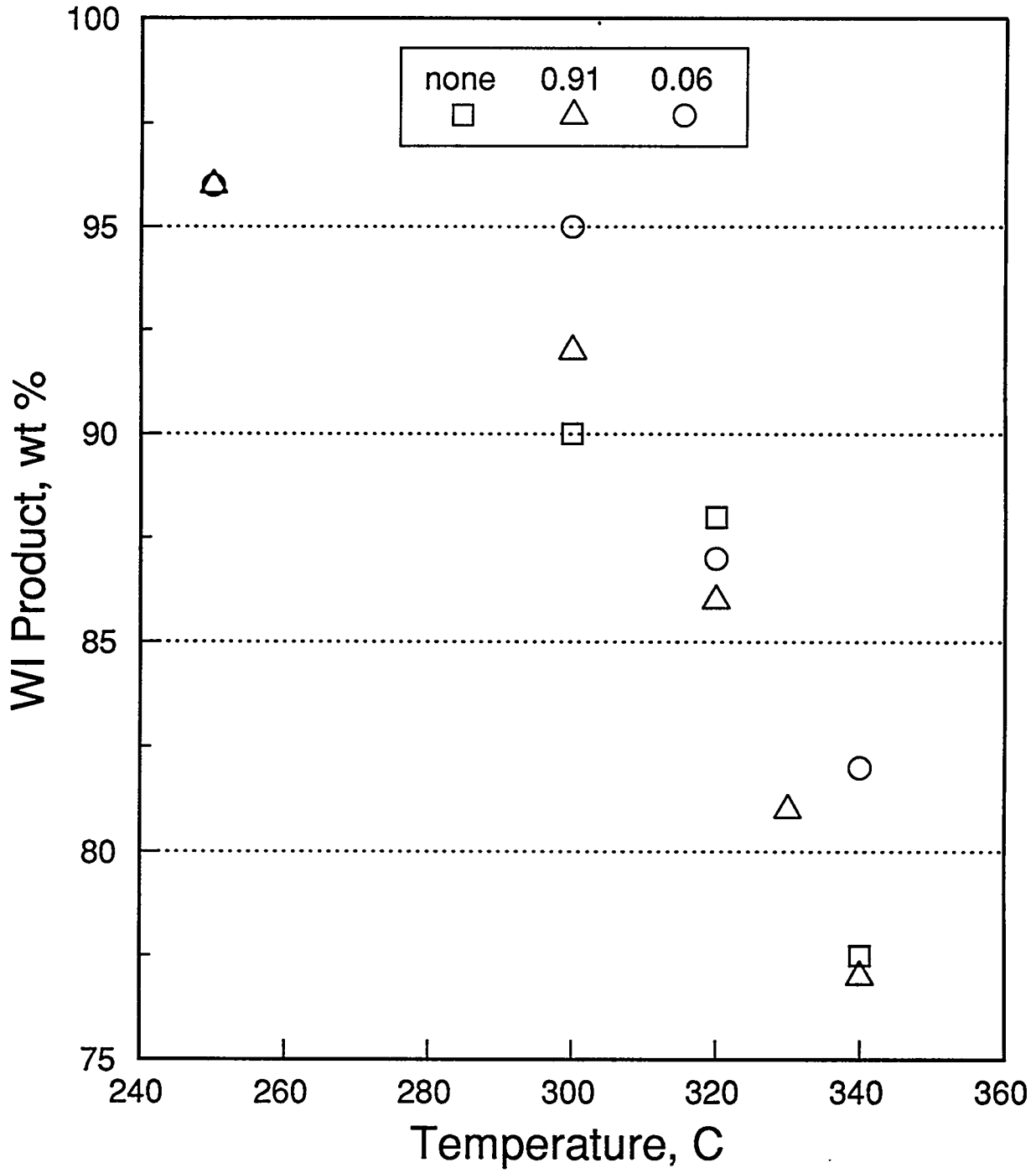
T_vs_OH

Figure 9-3
Effect of Coal on CO Conv with NaOH



T_vs_OH1

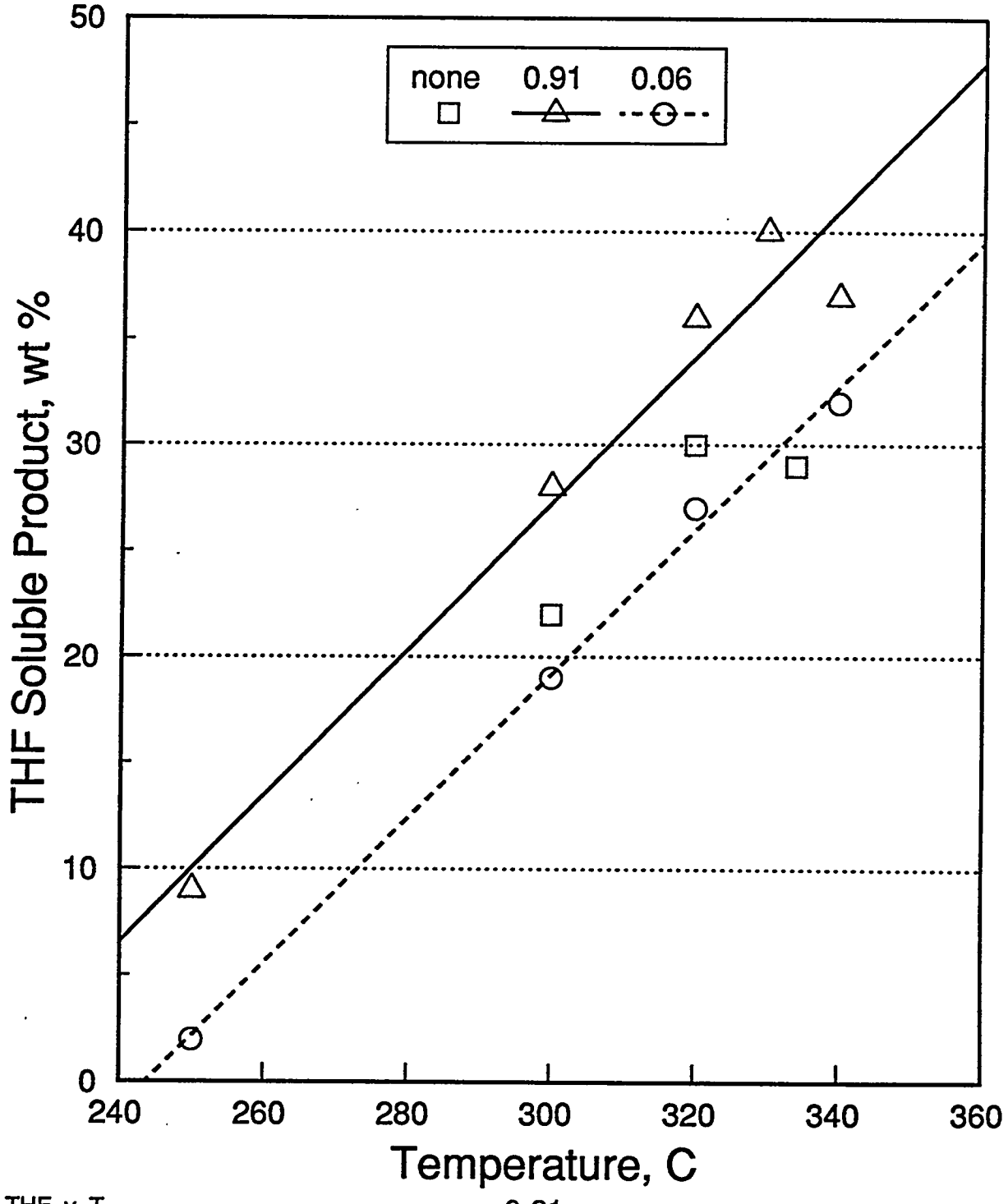
Figure 9-4
Effect of Temperature on Recovery of Water Insoluble Product



T_v_Sol

Figure 9-5

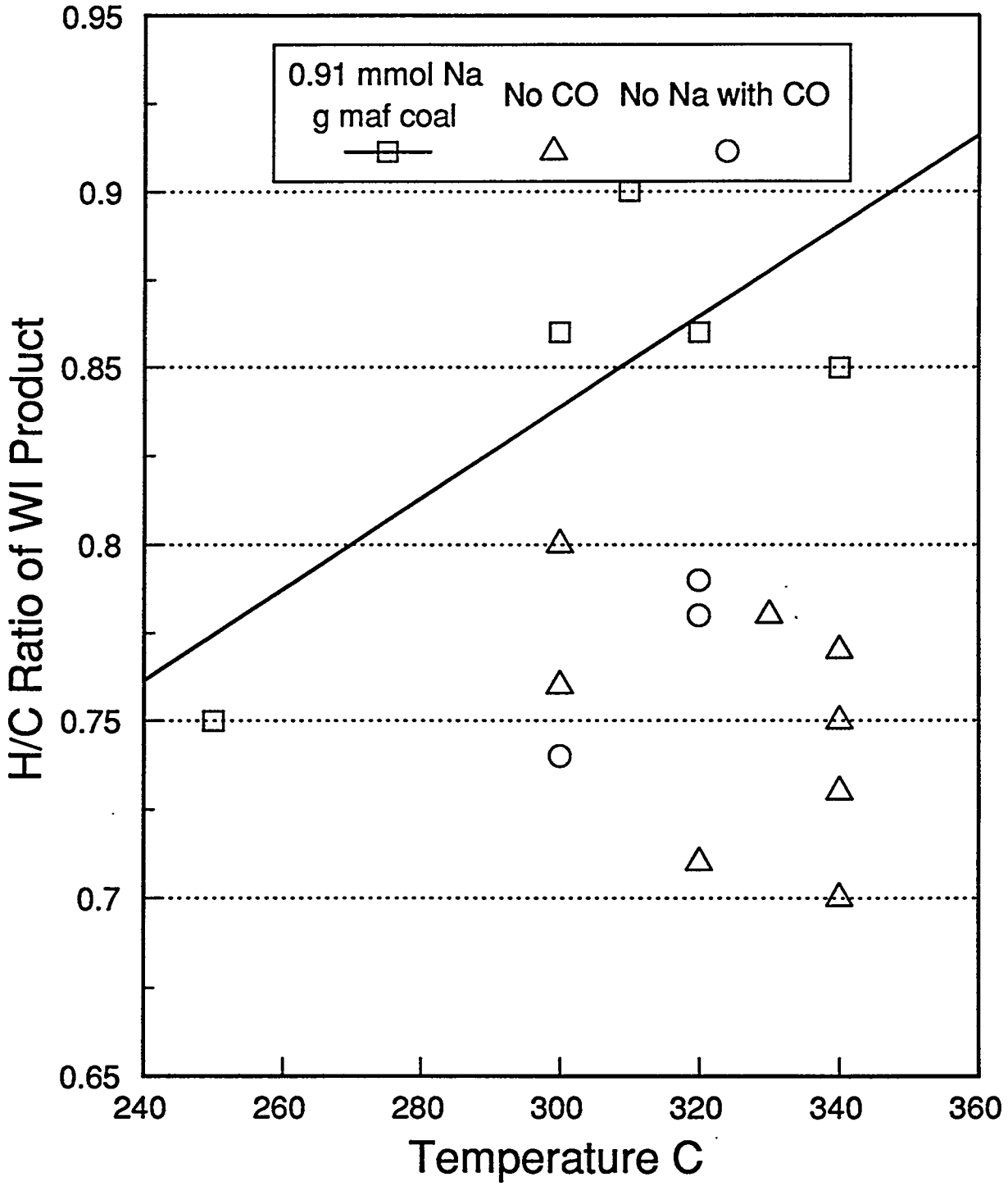
THF Soluble Product



THF_v_T

Figure 9-6

Combined Effect of NaOH and CO on H/C Ratio



hc_v_cop

have little effect on the amount of oxygen that is removed in this process. A plot of oxygen removal over a temperature range from 250 to 340 °C in Figure 9-9 where oxygen removal is plotted against temperature shows no effect of the presence of CO during the reaction. This suggests that elimination of oxygen from the coal structure occurs in a kinetically rapid step independent of the presence of CO. The reaction of the CO-donor acts subsequent to the kinetically slow oxygen elimination step. Whether the donor is involved in the fast step or acts completely independent of the oxygen elimination step isn't known, except that its activity results in a distinctly different product than obtained in its absence.

The effect of time on the reaction at 800 psig CO in the presence of 0.91 mmol NaOH/g maf coal over a span from 30 to 120 minutes is shown in Table 9-8. With increasing reaction time the THF solubility of the product increased from 20% to slightly less than 30%. CO conversion over the period increased slightly but appeared to level out at longer times. Overall, there doesn't appear to be a benefit from increasing the reaction period, nor does the option of decreasing reaction time to less than 60 minute appear feasible.

The effect of CO pressure in the experiments that were run in these microautoclaves was also examined. Data from experiments run at initial ambient CO pressures of 300 psig are compared with results obtained at 800 psig in Table 9-8. At the high NaOH concentration of 0.91 mmol NaOH/g maf coal, THF solubility appears to be favored at the higher CO pressure. In comparing runs at 300 °C, the THF solubles increases in going from low CO pressure at 300 psig (J111) to 800 psig (J238), namely 23 to 28%. At low CO pressure (300 psig), the THF solubles increase with increasing NaOH concentration going from 10% at 0.06 mmol NaOH/g maf coal (J113) to 11% at 0.44 mmol/g maf coal (unnumbered) to 23% at 0.91 mmol/g maf coal (J238). The same trend is observed at 250 °C at 300 psig CO except the magnitude of the solubilities are much lower (J125 vs J130).

Previously we had shown in Figure 9-7 that THF solubility is related to the amount of converted CO. The additional data taken at lower CO pressures and at longer reaction times, that are shown in Table 9-8, were incorporated into the earlier correlation and plotted in Figure 9-10.

This plot further reinforces the correlation between THF solubility and CO conversion, especially at the lower CO conversion levels.

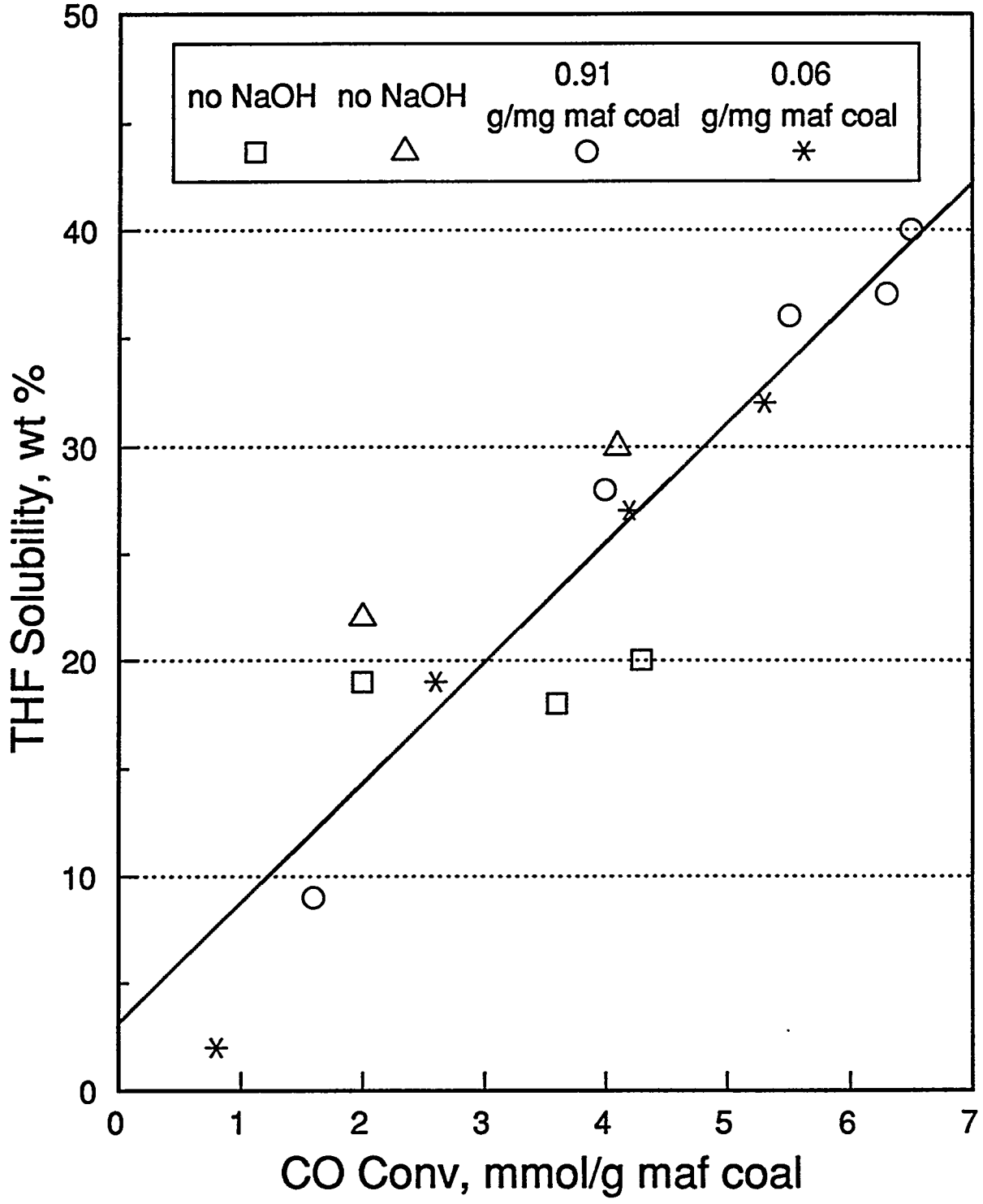
In these reactions of CO in the presence of coal, the amount of H_2 recovered is only a small fraction of that theoretically generated. The fate of this unrecovered hydrogen is consistent with it being incorporated into the reacting coal material. It is estimated that up to 85% of the hydrogen generated from the WGS reaction is taken up by the coal. A plot of the THF solubility of the recovered products versus hydrogen that was missing in the reaction is shown in Figure 9-11. A strong correlation exists between the missing hydrogen, which is presumably absorbed by the product, and THF solubility of the recovered pretreated material.

The conclusions that can be drawn from these data obtained in the presence of CO indicates that the magnitude of the oxygen elimination from the coal is unaffected by the presence of CO. The THF solubility dramatically increases in the presence of CO over the entire temperature range as shown in Figure 9-1. The addition of NaOH to the reaction in the presence of CO caused a further increase in THF soluble products of about 8% at all temperatures, as shown in Figure 9-5. The increase in THF solubility correlates with the increase in CO conversion, as shown in Figure 9-10. The increase in hydrogen content of the product can be related to the deficiency in recovered hydrogen in the product gas. This is attributed to the transfer of hydrogen to the product through the intermediacy of the formate ion that acts as a H-donor in the reaction. Although CO does not affect the final oxygen content in the product, it does significantly affect the quality of the final product with regard to its solubility and its behavior in the liquefaction reaction.

Clovis Point Wyodak Coal

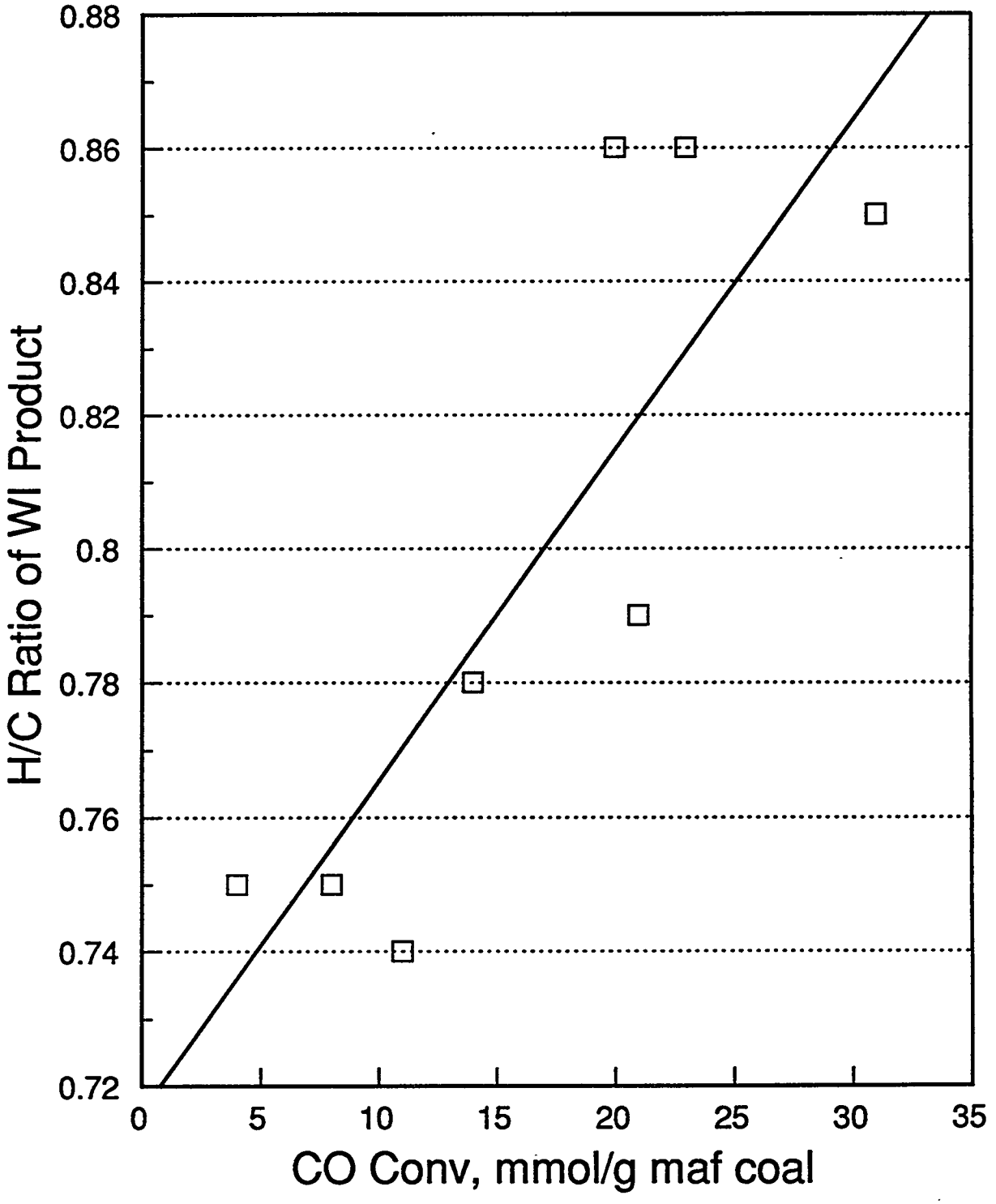
Prior to working with the Wyodak coal from the Black Thunder mine, a similar Wyodak coal from the Clovis Point mine was examined. Analysis of these two coals are shown in Table 9−9. Visual inspection of the products from the Clovis Point coal pretreatment with CO and water indicated that a significant transformation had occurred. The material acquired a brownish appearance, similar to that of brown coals, sprinkled with tiny bright orange specks.

Figure 9-7
THF Soluble Product vs CO Conversion



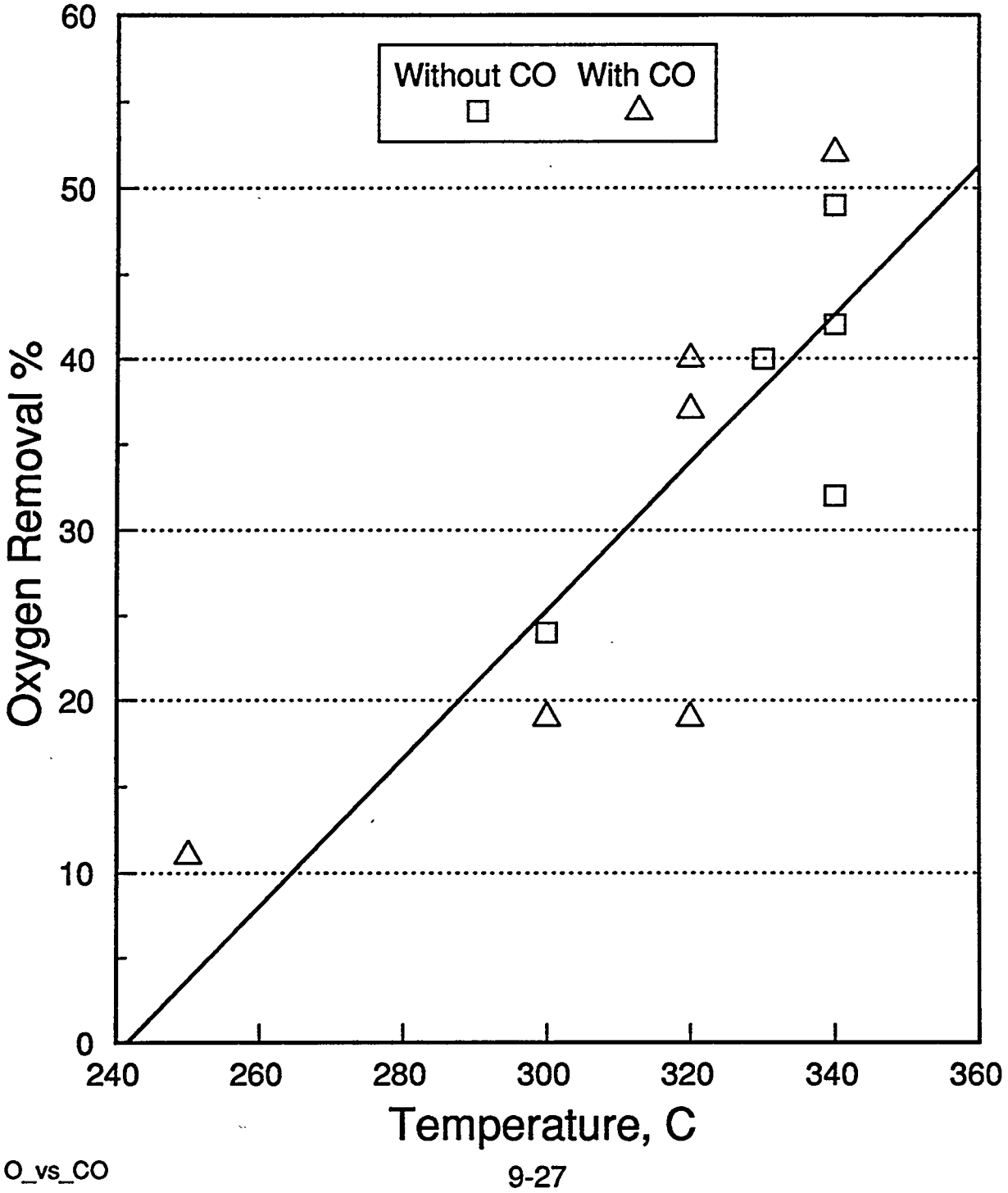
TH_v_CO

Figure 9-8
H/C Ratio vs CO Conv



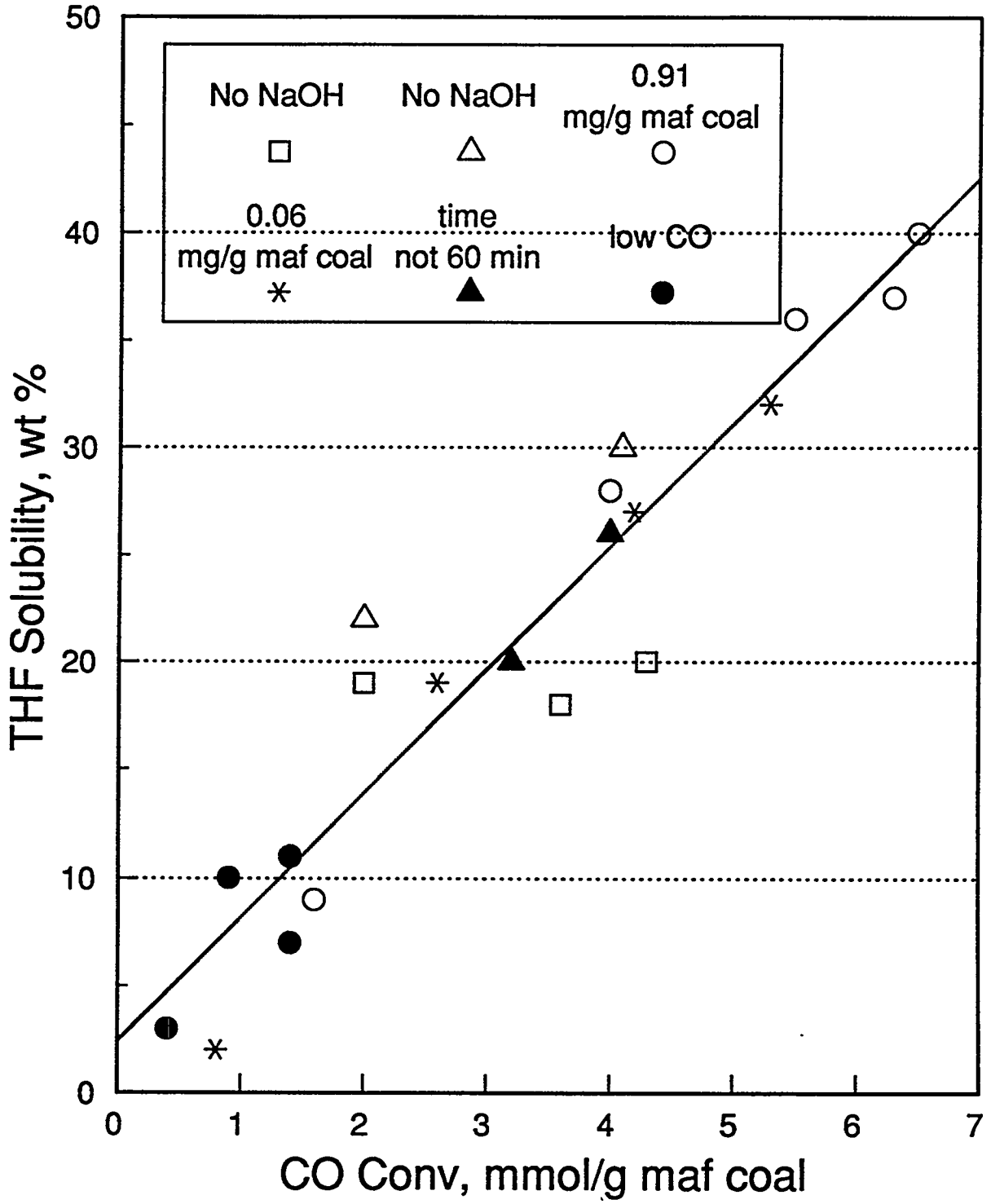
hc_v_co

Figure 9-9
Effect of CO on Oxygen Removal in Hydrothermal Threatment



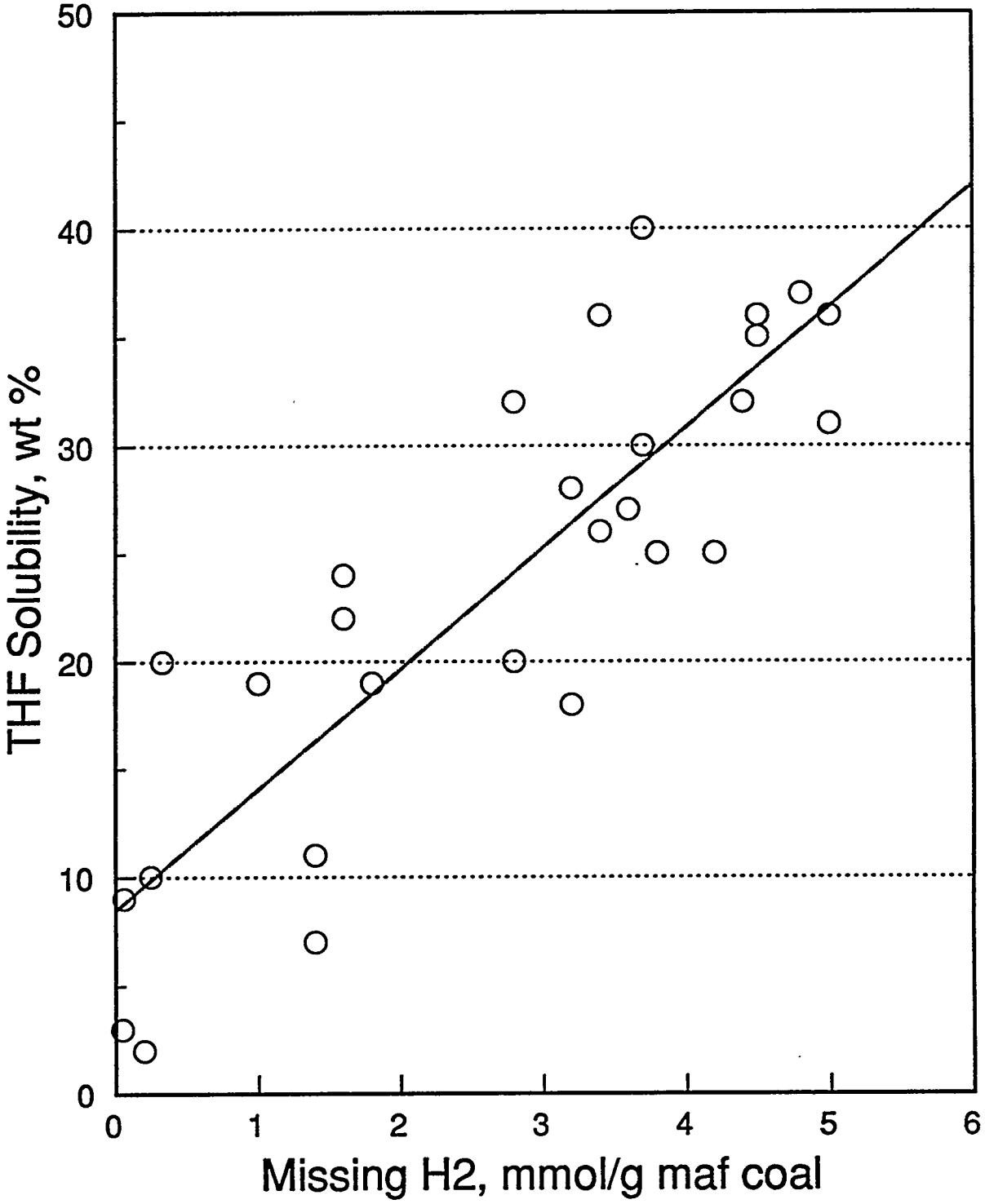
O_vs_CO

Figure 9-10
Effect of CO Conv on THF Solubility



TH_v_COq

Figure 9-11
THF Solubility of Product vs Missing H2



TH_v_h2m

Table 9-8. Reactions of BT Coal with CO

Run No.	°C	Run conditions				% wt. maf coal basis									
		NaOH mmol/g maf coal	g water/ g maf coal	CO psig	min	THF Insolubles	THF solubles	PA+ A	Water Soluble	OGW	Recovery of Solids	H/C	Oxygen Removal	CO Conv %	CO Conv mmol/ g maf coal
B058	300	0.91	3.3	800	30	73	20	18		9	91			16	3.2
J238					60	66	28	26		8	92	0.86	19	20	4.0
B056					90	64	26	23		13	87			23	4.0
J149					120							0.88	37		
J130	250	0.91	3.3	300	60	87	7	7		6	94	0.79	16	17	1.4
J111	300					74	23	18	4	4	96				
J125	250	0.06				95	3	3		2	98			4	0.4
J113	300					84	10	8	1	7	92			12	0.9
	275	0.44		550		86	11	11		3	97			10	1.4

Reaction Conditions: 2g maf coal, 3 ml. water/g maf coal, 1 hr. reaction time in 25 ml. micro-reactors. N.A= not available

Depending on the pretreatment reaction conditions, the physical characteristics of the solids range from being either soft and pliable to being highly friable. On heating to 60 °C, the solids turn black. In contrast, materials produced in the absence of CO, but in the presence of steam, were charred, granular, and very hard. None of the pretreated products consisted of the finely divided particles characteristic of the original coal. The appearance of the corresponding aqueous phases ranged from being lightly tinted to being quite dark, the latter indicating the presence of significant amounts of dissolved organic matter.

Table 9-9. Ultimate Analysis of Wyodak Coals

	Clovis Point	Black Thunder
Composition, wt% maf		
Carbon	71.0	73.9
Hydrogen	4.9	5.2
Nitrogen	1.3	1.3
Sulfur	1.1	0.6
Oxygen, by difference	21.7	19.0
Ash, wt% dry coal	6.94	6.12
H/C Ratio	0.83	0.84

The reaction products were recovered using water to remove the solid/liquid material from the reactor. The respective yields of materials soluble and insoluble in THF are shown in Table 9−10. The quantity of THF-soluble product that was soluble in pentane was so small in the high CO pressure runs that it could not be determined. At low CO pressures (Runs I, II and III), as well as in the absence of CO (Runs VII and VIII), regenerated humic acids and ether-extracted fulvic acids were recovered from the aqueous phase. The remaining unaccounted material in the mass balance, in addition to the pentane solubles, includes $CO+CO_2$ and water. Only trace quantities (<0.1 wt%) of hydrocarbon gases were detected.

Table 9-10. Pretreatment of Clovis Point Wyodak Coal[a]									
	V		IV	III	II	I	VI	VII	VIII
Temperature (°C)	300	300	300	300	300	300	300	300	300
Gas	CO	CO	CO	CO	CO	CO	CO	H2	N2
Gas Pressure (psig)	800	800	800	400	200	200	800	800	800
NaOH Conc. (Molar)	0.33	0.33	0.33	0.33	0.33	0.33	NIL	0.33	0.33
NaOH (mmol/g maf coal)	0.91	0.91	0.91	0.91	0.91	0.91	0	0.91	0.91
Water Added (ml.)	6	6	2	4	6	2	6	6	6
Reaction time, min	60	120	60	60	60	60	60	60	60
COX recov (% mole)	100	83	102	99	99	101	97	-	-
CO Conversion (mole % recov)	23	27	17	30	40	35	18	-	-
CO Input (mmol/g maf coal)	23	39	28	13	6	8	23	-	-
CO Converted (mmol/g maf coal)	5.3	5.7	4.7	3.9	2.4	2.6	4.1	-	-
H2 miss/H2 gen. (%)	77		84	88	82	61	79	-	-
H2 missing (mmol/g maf coal)	4.1		4.0	3.4	1.9	1.6	3.3		
Product Yield (maf coal)									
THF Solubility of WI	20	37	19	22	15	10	19	9	8
THF Insolubles	72	50	74	73	69	79	70	83	80
THF solubles (PA+A)	18	30	18	17	6	3	16	4	0
Oils+Gases+water	10	20	8	7	19	12	14	9	13
Water Insolubles	90	80	92	90	75	82	86	87	80
Humic Acids	0	15	0	3	5	5	0	4	7
Ether Extract	0	0	0	0	1	1	0	0	0
Oxygen removed (by diff)	40	N.A.	40	34	37	36	48	43	44
H/C ratio (Water Insolubles)	0.92	0.97	0.85	0.83	0.75	0.75	0.8	0.78	0.72
Elemental Recovery									
Carbon	99	N.A.	101	101	92	93	96	101	97
Hydrogen	108	N.A.	103	99	83	84	92	95	81
Oxygen	60	N.A.	60	66	63	64	52	57	56

[a] 2 g dry Clovis Point Wyodak coal, 4.4 wt% NaOH on moisture and ash free (maf) coal; N.A. not available

The yield of water-insoluble products ranged from 75-92 wt% while the yield of water soluble products ranged up to 7 wt%. Elemental balances, based upon analyses of the water-insoluble products and humic acids, indicate that almost all of the carbon is contained in these fractions, especially at the higher CO pressures. The carbon which could not be accounted is primarily associated with the direct elimination of CO_2 from the coal,[30,5] and to a lesser extent the pentane solubles, and the ether extracts, which were formed at low CO pressures.

The atomic H/C ratios of both the water-insoluble and soluble products are shown in Table 9-11. Predictably, the H/C value for the THF solubles is significantly higher than for the THF insolubles. The H/C ratio of the water-insoluble product from Run III, i.e., 0.83, is equal to the value calculated from the elemental analyses of the THF-soluble and THF-insoluble fractions, whose H/C ratios are 0.94 and 0.80, respectively, which is consistent with the pentane solubles being a minor constituent of the water-insoluble product. As the CO pressure is increased, the corresponding H/C ratio of the water-insoluble product increases from 0.72 in steam with nitrogen overpressure (Run VIII) to approximately 0.92 at 800 psig CO (V). The increase in H/C ratio is consistent with the incorporation of hydrogen formed from reaction of CO with the aqueous phase.

The effect of reaction time on THF solubility of recovered products and CO conversion is shown in Table 9-10. Solubility is related to the amount of missing hydrogen. For CP coal, the CO conversion and THF solubility of the water-insoluble product for the 120 min experiment is 27 and 37 wt%, respectively, versus 23 and 20 wt% for the 60 min run. The H/C ratio is also higher after 120 min, being 0.97 for the 120 min run and 0.92 for 60 min reaction.

The carbon oxide recoveries related to the initial CO feed were typically in excess of 90%, and include unreacted CO, gaseous CO_2, CO_2 dissolved in the aqueous phase, and CO present as formate in the aqueous phase. Theoretically, the recovery would be in excess of 100% by an amount equivalent to the CO_2 derived directly from the coal. The amount is unknown in these experiments. A measured titer value of the aqueous phase corresponded to the theoretical

Table 9-11. Hydrogen/Carbon Ratio of Products				
	Gas	Pressure psig	Products	
			Humic Acids	Water-Insoluble
I	CO	200	N.D.[a]	0.75
II	CO	200	0.71	0.75
III	CO	400	[b]	0.83
IV	CO	800	[c]	0.85[d]
V	CO	800	[c]	0.92
VI	CO	800	[c]	0.80
VII	H_2	800	0.82	0.78
VIII	N_2	800	0.52	0.72

a. N.D. not determined
b. Insufficient sample (~4%) for analysis.
c. None formed.
d. Calculated from THF-soluble and THF-insoluble fractions.

amount of formate generated from the base. The increase in hydrogen content in the water-insoluble product of approximately 4-5 mg/g maf coal accounts for a major portion of hydrogen produced by the 15-25% CO conversions observed in these experiments.

Regenerated humic acids were formed only at low CO pressures, or in the absence of CO where the reaction was conducted in steam with either hydrogen or nitrogen overpressure. The analysis of this fraction from Runs II, VII, and VIII indicated some difference in their composition. The oxygen content fell between 16.1 and 21.0 wt% and the hydrogen concentrations were between 3.3 and 4.9 wt% (Table 9-12). Surprisingly, the oxygen content of these acid fractions was not enriched relative to the starting coal and cannot account for any of the (~40%) decrease in oxygen in the products. The highest yield of humic acids were obtained in the complete absence of added CO (Run VIII) and decreased steadily as CO pressure was increased. At 800 psig CO they are completely absent (Runs IV, V, VI in Table 9-10). Therefore, 'upgrading' of the coal

involves both hydrogenation, which is related to the reaction of CO with the aqueous phase, and the rejection of oxygen from the coal. The formation of humic acid material is related to the aqueous chemistry of alkali extraction under non-reducing conditions. [6]

Table 9-12. Elemental Analysis of Humic Acids, wt% maf coal			
	II	VII	VIII
Carbon	77.4	71.5	75.0
Hydrogen	4.6	4.9	3.3
Oxygen	16.1	21.0	17.5

In the absence of a salt, in Run VI, change has occurred in the structure of the treated coal as evidenced by the sizable increase in the THF solubility. However, unlike the products obtained in the presence of a sodium salt at high CO pressure, the H/C ratio of the water-insoluble product was lower as shown in Table 9-11. In fact, the H/C ratio of the resulting product appears to be intermediate between those obtained at 200 psig and 400 psig. Assuming that the formate ion ($HCOO^-$) is involved in the depolymerization step, its concentration would be considerably reduced, in the absence of an added salt, since dissolution of the CO in the aqueous phase to form formic acid would be extremely small under these conditions.[7] Although, cationic agents may not be necessary to initiate the CO-pretreatment reaction, the extent of reaction that the salts provide, as suggested by the increased H/C ratio and the characteristics of the product under optical microscopic examination, shows improvement relative to the products obtained in their absence, as previously suggested.

Solubility Characteristics - The degree of solubility of products arising from pretreatment can qualitatively be considered to reflect the degree of cross-linking. Both THF and pyridine extraction of the water-insoluble products show that the highest solubilities are observed in samples pretreated at high CO pressures. In each case the pyridine solubility is significantly higher than for THF (Table 9-13). The increase in solubility over that of the raw coal indicates

the degree to which the coal has been transformed. The lower solubilities of products prepared either at low CO pressure or in its absence suggest that coal depolymerization has not progressed as extensively. Since the pretreated product obtained in H_2 in the presence of steam has a lower H/C ratio than the starting coal, the incorporation of hydrogen into the CO-pretreated coal must come via *in-situ* hydrogen generation. The reason for the poorer results observed at low CO concentrations is yet to be clearly defined, although it is likely related to the lower concentration of the active *in-situ* hydrogen donor intermediate which is consistent with a reaction path in which the coal structure is stabilized and hydrogenated by the active intermediate.

Table 9-13. Solubility of Water-Insoluble Product

Sample	THF Solubles,[a] wt%	Pyridine Solubles,[b] wt%
Wyodak Clovis Point Coal	1	4
VIII	0	6
II	7	9
V	20-30	60

[a] Wt% water-insoluble product, maf basis.
[b] Weight % extracted from 1.0 g water-insoluble product with 300 ml of pyridine in Soxhlet apparatus for 18 hours, maf basis.

Effect of Salt

A number of other salts have been used over the years in the investigation of the reaction of CO with coals. This entire area was reviewed in the Chapter 8. In much of the earlier work on CO-promoted liquefaction, sodium carbonate, sodium formate and ammonium formate had been evaluated extensively at higher temperatures. We examined these salts as well as others under conditions consistent with the CO-pretreatment described above. Substituting other sodium salts for the NaOH in the presence of CO resulted in very similar yields of water-insoluble product, which had similar THF-solubility characteristics. Results from treatments made at 300 °C for several salts are shown in Table 9-14. Under the conditions where the reactor was initially charged with 800 psig CO, humic acids were absent, which was consistent with results from use of NaOH as the promoter. Recall that only at the lower pressures of CO were humic acid products observed. The products were apparently also unaffected by the initial pH values of the reaction mixtures, which were 13-14 for NaOH and Na_2CO_3 and about 8 for $NaHCO_3$.

In these runs with various salts the recovery of CO_x from these reactions were very close to 100%. Since these values were not corrected for the carbon oxides formed from the coal, actual CO_x recoveries were somewhat lower. The conversion of CO under these conditions, uncorrected for the CO_x formed from coal, were quite similar varying between 16 and 26%. Based on the 20% oxygen removed from coal at 300 °C in the hydrothermal experiments in the absence of CO, total CO_x recoveries should have been about 105%, suggesting that the results are somewhat on the low side. Since CO was consumed in driving the aqueous solution to a salt equilibrium, assumptions regarding the aqueous phase may be slightly low. Interestingly, the recovery in HCOONa, where the salt solution is already in equilibrium at 300 °C, recovery was 110%, which could have been the result of the lack of CO assimilation by the aqueous phase plus a slightly higher oxygen elimination as CO_x from the coal.

The THF solubilities of the water-insoluble product appears to correlate with the degree of CO conversion, as reported above. For each of the sodium salts, these values ranged from 20 to 30%, which were higher than for the other salts that were used. In the absence of sodium ions, as well as when NaCl was present, the THF solubility drops. In these runs in the presence of

Table 9-14. Effect of Salt on CO-Pretreatment of BT Coal									
	J95	J238	J93	J183/B62	J209	J208/290		J217	J211
Temperature (°C)	300	300	300	300	300	300	300	300	300
CO Pressure (psig)	800	800	800	800	800	800	none (N2)	800	800
Salt	none	NaOH	Na_2CO_3	$NaHCO_3$	NaCl	HCOONa	HCOOH	NH_4OH	NH_4NO_3
Conc. (Molar)	none	0.33	0.16	0.33	0.33	0.33	0.33	0.33	0.33
Water Added (ml.)	6	6	6	6	6	6	6	6	6
CO_X recovery (mole %)	97	100	99	101	97	110	-	99	99
CO Conv (on mole % recov)	10	20	17	26	16	25	-	19	20
CO Input (mmol)	39.4	39 .4	39.3	38.6	37.7	38.1	none	37.8	33.7
CO Converted (mmol)	3.9	7.9	6.7	8.1	6.0	10	-	7.2	6.7
CO Conv, mmol/g maf coal	2	4	4	4	3	5	-	4	4
H2 miss/H2 gen.(%)	84	86	82	78	51	85	-	20	42
H2 missing, mmol	3.3	6.8	5.6	7.6	3.1	8.5	-	1.4	2.8
Product Yield (maf coal)									
THF Solubility of WI	22	28	32	25	24	25	9	17	10
THF Insolubles	70	66	63	64	68	60	83	79	79
THF solubles (PA+A)	20	26	30	21	22	20	9	16	9
Oils+Gases+water	10	8	7	14	10	20	8	5	12
Water Insolubles	90	92	92	85	90	80	92	95	88
Oxygen removed (by diff)	19	19	19		26	28	22		
H/C ratio (Water Insols)	0.74	0.86	0.80		0.82	0.81	0.80		

the ammonium hydroxide or nitrate or in the presence of NaCl, the CO conversion appeared to be largely unchanged. However, the THF solubility of the product dropped. Even though the CO conversions were similar to the others, note that the amounts of missing H_2 from these runs were significantly less than for the other runs. The values for missing hydrogen ranged from 20 to 51%, whereas for the other runs the values were consistently around 80%. The results in the presence of NaCl, where the formation of the corresponding formate was expected to be quite low, as well as the missing H_2 was lower, the THF solubility was higher than expected.

This leads us to suspect that intermediacy of a formate complex may be promoted by the presence of this salt even though conventional formate is not observed.

A separate run in the presence of formic acid without added CO being present gave exceptionally low THF solubility of the water-insoluble product. Here the amount of oil+gas+water was nearly the same as for the other runs, but the quality of the product was obviously lower than for the CO promoted runs. This is likely the result of the absence of sufficient CO pressure during the course of the reaction to promote driving the HCOOH to the CO_2 with the opportunity of the complex to act as a H-donor in the process. The reverse decomposition of the HCOOH to CO and water would become far more dominant in the absence of sufficient CO to promote the forward reaction.

A subsequent series of runs shown in Table 9-15 were made at higher temperatures than the set reported above. In these cases the CO_x recoveries were somewhat higher. For this series of 7 runs, the average recovery was 106%. This may have resulted from one of several possibilities: improved technique that developed during the course of the study, higher elimination of oxygen from the coal as CO_x, or less assimilation of CO into the aqueous phase. The THF solubility of the water-insoluble product based on feed coal increased for both the NaOH and HCOONa, which were the same as for KOH. Overall, the amount of recovered water-insoluble product decreased as temperature increased. This was the same result as observed for NaOH above.

The results with ammonium hydroxide are surprising. At 300 °C, the amount of THF insolubles are significantly lower than observed with the sodium salts, whereas at the higher temperatures the THF solubilities fell into line with the other data. This occurs even though it is known that the ammonium salts are quite unstable under these conditions, presumably decomposing to ammonia and CO.

With these other salts, the relationship of THF solubility of the water-insoluble products directly correlate with CO conversion as shown in Figure 9-12. The plot of these data show a

Table 9-15. Effect of Salts at Higher Temperature on CO-Pretreatment of BT Coal					
	J317/322	J295/ 308	J318	J288	J289
Temperature (C)	340	340	340	320	320
Gas	CO	CO	CO	CO	CO
Pressure (psig)	800	800	800	800	800
Salt	KOH	NaOH	NH_4OH	NH_4OH	HCOONa
Conc. (Molar)	0.33	0.33	0.33	0.33	0.33
Water Added (ml.)	6	6	6	6	6
CO_x recoveries (% mole)	107	111	101	110	102
CO conversion (% mole recovery)	41	31	30	26	31
CO Input (mmol)	39.5	42	39.2	39.2	42
CO Converted (mmol)	16	13	12	10	13
CO Conv, mmol/g maf coal	8	7	6	5	7
H2 miss/H2 gen.(%)	61	74	80	98	69
H2 missing, mmol	10	9.6	9.5	10	9
Product Yield (maf coal)					
THF Solubility of WI	36	36	35	31	36
THF Insolubles	42	48	45	54	48
THF Solubles (PA+A)	23	27	24	24	27
Oils+Gases+Water	35	25	32	22	25
Water Insolubles	65	75	69	78	75

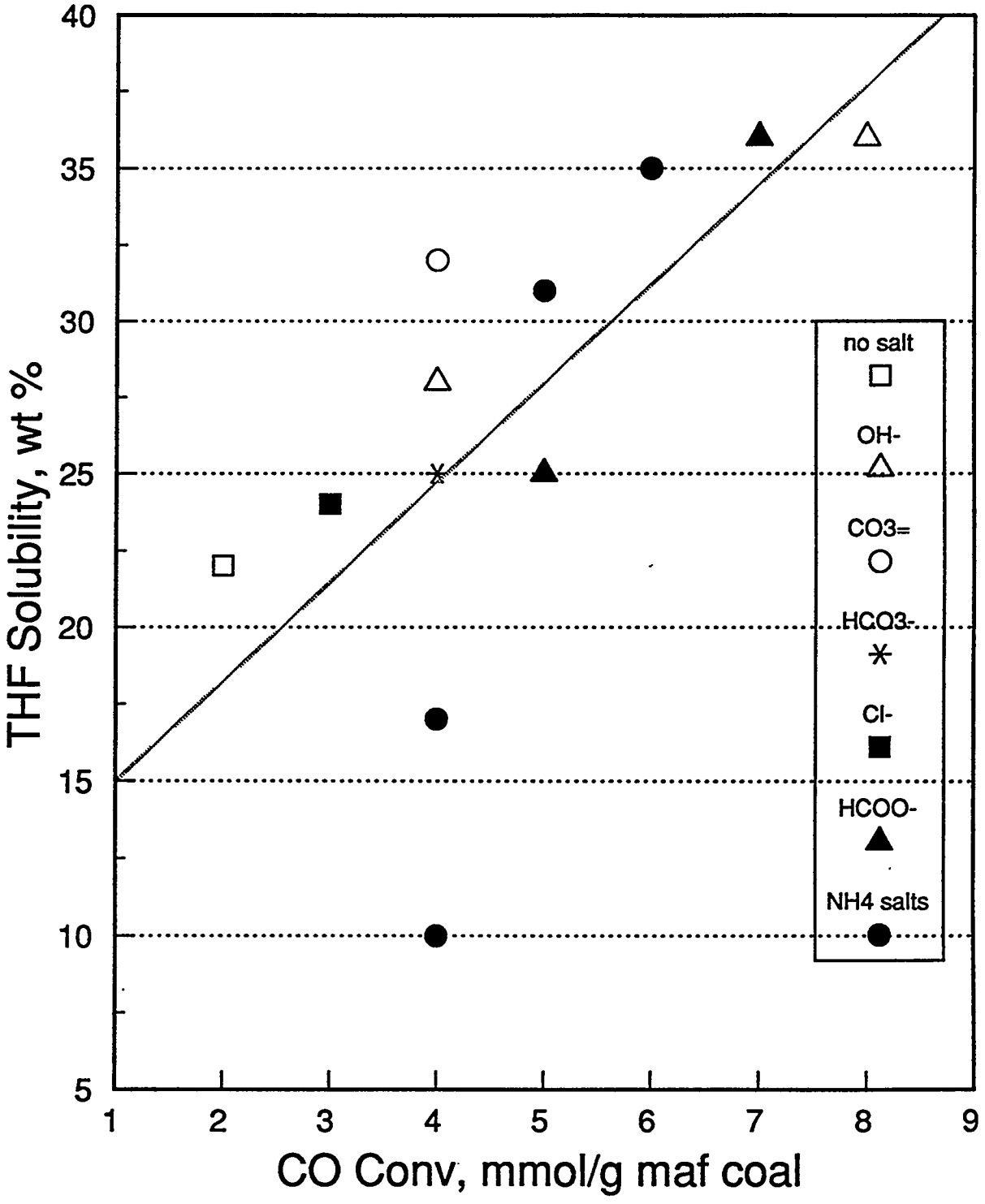
correlation similar to that observed for the data presented previously with NaOH, except that the NH_4OH and NH_4NO_3 taken at 300 °C depart quite dramatically from the line. From the data presented in Table 9-14 for these particular points, it appears that the missing hydrogen is much lower for the ammonium salts than for the other data presented in the table. This corresponds to a gaseous product that has a significantly higher H_2 concentration than observed in the other runs. Although the elemental analysis of the water-insoluble product from these runs was not determined, it would be expected that the H/C ratio would be lower than for those runs having higher missing hydrogen. Combining these results with those presented earlier shows a good correlation between THF solubility and CO conversion, as shown in Figure 9-13.

Scale-up Experiments

Several scale up runs were made to examine the effect of CO pretreatment on larger quantities of Black Thunder coal. Both NaOH and Na_2CO_3 were examined in a cold-charged 1-liter stirred autoclave reactor and a second series was run in a 300 mL stirred autoclave. Both reactors were equipped with a gas-circulating pitched blade stirrer.

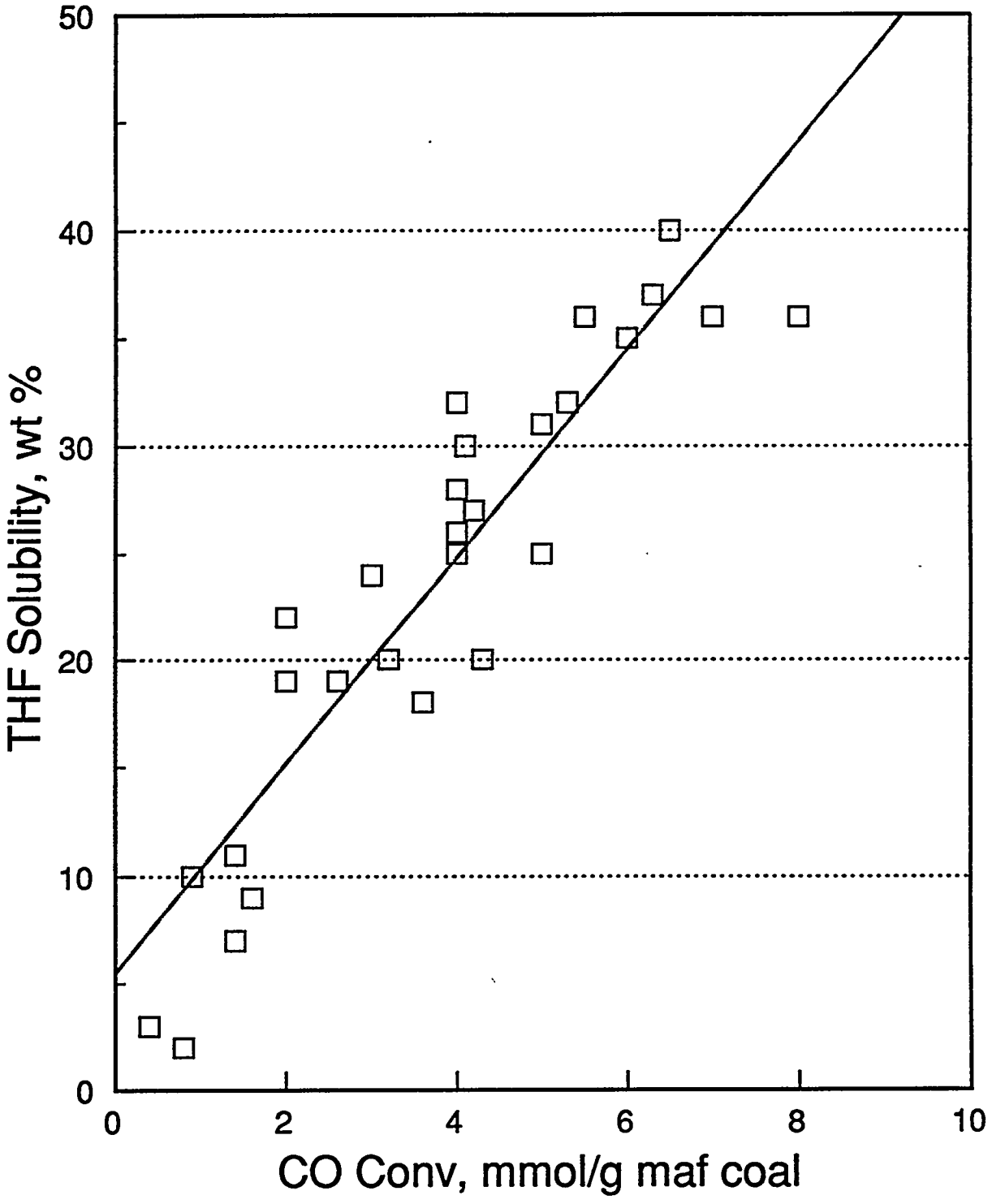
1-Liter Autoclave Reactor. The experimental procedure used with this reactor is described here in which approximately 80 gram samples of treated product was produced. The major portion of this material was subsequently used in oil agglomeration tests at CONSOL. In these runs, the reactor was initially charged with 70 ml water, purged three times with CO and pressurized with CO to 800 psig. While stirring at 400 rpm, the sealed reactor was heated to 300 °C where the total pressure was ~2800 psig. A slurry of 150 grams of as-received Black Thunder coal (23 wt % moisture) in 200 ml of either 0.38 M NaOH or 0.19 M Na_2CO_3 was prepared in a beaker. This was equivalent to 2.7 wt% NaOH or 3.7 wt% Na_2CO_3 on maf coal. The coal slurries were then transferred into the slurry holding tank which took about 2-3 minutes. The coal slurries were then forced into the reactor under a N_2 pressure head of 3200 psig. This 'hot-charging' technique avoided a long heat-up time which had been shown previously to have a detrimental effect on coal hydrogenation in the CO-H_2O system.[8] The internal reactor temperature dropped to 200 °C within seconds but recovered back to a lineout temperature of 310 ± 5 °C within 8.5 minutes. Heating was continued for one hour after which the gases were

Figure 9-12
Effect of Salt on THF Solubility



TH_v_COt

Figure 9-13
THF Solubility of Product vs CO Conversion



TH_v_COz

vented off slowly. The reactor cooled to ~100 °C in about 45 min to one hour. An additional 1-2 hours was necessary to cool to room temperature.

The products were washed from the reactor using distilled water. A total mass balance was not obtained since the quantity of gases, water and water soluble organic product were not measured in these experiments. However, coal conversion based solely on the solid water-insoluble product and corrected for the coal recovered from the charging tank are reported. Table 9-16 shows that the yields of water insoluble products recovered from the Na_2CO_3 experiment and a comparable NaOH experiment are ~85 wt% maf coal. This corresponds to a greater than 90% carbon recovery in both cases. The hydrogen recovery was 98 and 90%, respectively. The oxygen recovery for the NaOH generated product is higher than that of the Na_2CO_3 sample (59 vs 53%). The atomic H/C ratio of the NaOH and Na_2CO_3 generated H_2O-insoluble products was 0.90 and 0.84, respectively, compared to 0.85 for the raw coal. These numbers are very similar to those obtained from the micro-autoclave reactions.

The water-insoluble product produced from the reaction of Black Thunder coal was extracted both with pyridine and THF. The results, presented in Table 9-17, indicate a much higher solubility in pyridine than in THF. It was noted earlier that small samples of the NaOH generated material when place in 50 mL vials with pyridine appeared to swell and completely dissolved at room temperature. It was not clear, however, whether the resulting mixture was a true solution. It was also noted that after extracting for 12 hours in a Soxhlet that both thimbles became blocked. However, none of the solid material was lost from the thimble. The material in the thimbles resembled a gel. The material generated with NaOH in the 1−liter autoclave was 60 wt % soluble in pyridine which was identical to that obtained from Clovis Point coal in a microautoclave. The pyridine solubles from the microautoclave reaction were 30 wt % higher than the THF solubles yield. The Na_2CO_3 generated material had a lower pyridine solubility than that obtained from the NaOH experiment (ca. 56 vs 60%). However, the difference between the pyridine and THF extract yields obtained from the 1-liter reaction with Na_2CO_3 is less 16 wt %.

Table 9-16. Product Yields and Elemental Recovery		
	NaOH	Na_2CO_3
Coal Charge, g	110.35	111.37
Unreacted Coal, g	16.34	15.10
Water Insoluble Product, g	80.9	81.0
Water Insoluble Products, wt%[a]	86.0	84.1
Elemental Recovery in Water Insoluble Product, wt% maf coal[b]		
Carbon	91.8	90.3
Hydrogen	97.5	89.8
Nitrogen	84.7	83.2
Sulfur	61.6	70.0
Oxygen	58.9	53.3
H/C Ratio of WI Product	0.90	0.84

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

Table 9-17. THF and Pyridine Extraction of CO-Pretreated Products		
	THF Solubles[a]	Pyridine Solubles[a]
Microautoclave Experiments		
NaOH (0.35 M)[b]	30	60
Na_2CO_3[d]	37	n.d.[c]
1-Liter Stirred Autoclave		
NaOH (0.35 M)[d]	N.A.	60
Na_2CO_3[d]	39	56

a. Wt% maf basis
b. Clovis Point Wyodak subbituminous coal.
c. n.d. Not determined
d. Black Thunder Wyodak subbituminous coal.

Elemental analysis of the various solubility fractions shown in Table 9-18 indicate a significant decrease in the oxygen content of these fractions with more oxygen being present in the pyridine insoluble fraction and more hydrogen being in the pyridine soluble fraction. The H/C ratios of the pyridine solubles were noticeably higher than for the insolubles. The H/C ratio of the pyridine soluble products are higher than for the coal while the reverse is true for the pyridine insoluble products.

Table 9-18. Characterization of Water Insoluble Product from CO-Pretreated Coal[a]

	Na_2CO_3		NaOH		Coal
	Pyridine Insoluble	Pyridine Soluble	Pyridine Insoluble	Pyridine Soluble	
Yield	44	56	40	60	
Elemental Analysis					
Carbon	77.8	80.6	78.9	80.7	73.9
Hydrogen	5.0	5.7	5.2	6.0	5.2
Nitrogen	2.1	2.2	2.0	2.1	1.3
Sulfur	0.6	0.4	0.7	0.4	0.6
Oxygen	14.5	11.1	13.2	11.5	19.0
H/C mol ratio	0.77	0.85	0.78	0.89	0.84

a. Wt% maf coal

300 mL Autoclave Runs These runs were made at a much later date than the earlier 1-liter reactor runs described above. In this reactor, there was no cold charge feature; rather the material was heated in the reactor to reaction temperature. In a typical experiment, approximately 50 g of as-received BT coal containing approximately 20% moisture was charged into the reactor together with 4.2 g NaOH in 75 ml. of distilled and de-ionized water. The reactor was sealed, leak tested and pressurized with CO to 1000 psig. In the case where no base was used, 40 ml water was added. The heat-up time from ambient to reaction time at 340 °C

takes approximately 3.5 hr. The reaction was allowed to proceed at this temperature for an additional hour. The reactor was then quenched to ambient temperature within 1.5 hr. A gas sample was collected and analyzed by G.C and the solid products were collected and washed with distilled and de-ionized water and dried at 40 °C in a vacuum oven (see Table 9-19).

Table 9-19. Gas Products (mol %)

	$NaOH/CO/H_2O$	CO/H_2O
Gaseous Product		
Hydrogen, mol %	32.4	8.3
CO, mol %	7.0	52
CO_2, mol %	61.0	34.4
HC, mol %	<0.5	<0.5
Water-Insoluble Prod, wt% maf	81	85
Humic acids + ether solubles	1.3	n.d.

Initial solubility tests of the treated products obtained from the reaction of BT coal with CO, H_2O and NaOH at 340 °C were carried out with a Soxhlet extractor at the reflux temperature of the solvents. 5.0 g of material was extracted with 500 mL of solvent. However, it became apparent that the Soxhlet extraction technique is slow since colored material continued to exude from the thimble after a week of continuous extraction. In order to decrease the extraction time, the amount of material being extracted was scaled down to approximately 0.5 g. In addition, the treated product was also extracted using a sonication/vacuum filtration technique in which the material to be extracted was placed in 200 mL of pyridine or THF in a beaker. The mixture was ultrasonicated for 10 min and filtered under vacuum at ambient temperature. Filtration was usually rapid (within minutes). The insoluble organic material was collected, dried and weighed to determine solubility in the solvent.

The results presented in Table 9-20 indicate that considerably higher pyridine and THF

solubilities were obtained by the ultrasonication technique compared to Soxhlet extraction. For the reactions run with CO, H_2O and NaOH, pyridine and THF solubilities reached 94 and 78 wt % (maf product basis), respectively. The pyridine and THF solubilities of the product produced in the absence of added NaOH was significantly lower. In fact, during vacuum filtration of the pyridine extracts from the NaOH-free run, the filter paper became clogged within minutes and a reliable result could not be obtained by the ultrasonication technique. During Soxhlet extraction of NaOH-free product, the thimble filters also became clogged which resulted in a lower pyridine solubility than THF solubility (see Table 9-20). This behavior underscores the different properties of the materials generated under different reaction conditions.

Table 9-20. Solubility of Treated Product (maf basis)

Product	Ultrasonic/Filtration		Soxhlet Extraction	
	THF	Pyridine (RT)	THF	Pyridine
w/ NaOH[a]	78	94	55	88
w/o NaOH[b]	N.A.	N.A.	54	50

a BT coal, 1000 psig CO cold, 4.2 g NaOH, 75 mL H_2O, 340 °C, 300 mL reactor.
b BT coal, 1000 psig CO cold, 40 mL H_2O, 340 °C, 300 mL reactor.

The chemical compositions of the solvent fractions from the CO-treatment are shown in Table 9−21. Based upon the 82.3 wt % water-insoluble product plus humic acids, the ash content in the water-insoluble product was too high, i.e. observed 6.5% on feed based on the elemental analysis in Table 9-21 vs 5.5% in starting coal. Regardless, there is a dramatic decrease in the oxygen content both in the presence and absence of NaOH. The concentration of oxygen fell from 18.0% in the parent coal to 4.7% in the water-insoluble product. Without NaOH, the oxygen content decreased to 5.2%. These values represent ~75% oxygen removal in these reactions. Additionally, an increase in the hydrogen content of the material is observed when the material is generated in the presence of NaOH. This product has a H/C ratio of 0.88 which is higher than in the starting coal (0.80). In contrast, the H/C ratio of the product

generated in the absence of base is essentially the same as that of the starting coal.

Table 9-21. Products from Hydrothermal Treatment of BT Coal

	BT Coal	R#1-300			R#2-300
CO, psig cold	-	1000			1000
Base	-	NaOH			none
Temp, °C	-	340			340
	-	Water-Insoluble	Pyridine Soluble	Pyridine Insoluble	Water-Insoluble
Carbon	70.3	79.5	85.2	40.5	81.0
Hydrogen	4.7	5.8	6.9	2.0	5.3
Nitrogen	1.0	1.7	1.5	1.5	1.7
Sulfur	0.5	0.4	0.3	0.3	0.4
Oxygen	17.9	4.7	6.1	16.9	5.2
Ash, SO_3-free	5.5	8.0	-	38.9	6.3
H/C	0.80	0.88	0.97	0.59	0.79

An elemental balance was calculated around the pretreatment reaction that was performed in the 300 mL autoclave in the presence of NaOH. As noted above, the composition of the water-insoluble product shown in Table 9-21 had an ash concentration that was higher than in the coal. In calculating the elemental balance the ash concentration was corrected to a level consistent with the ash in the starting coal and the remaining elements were adjusted to account for this correction, assuming the total WI product was the sum of the WI product plus the humic acids and ether extracted product which total 82.3 wt %. The results of this adjustment to the WI product is shown in Table 9-22. Since the gas analysis showed that HC gases were quite small (see Table 9-19) the other products would be water, CO and CO_2. Assuming that the carbon formed CO_2, which is consistent with our previously discussed results, the CO_2 yield based on forcing the carbon balance would be approximately 14%. Using these assumptions, a total of 97% of the starting material would be accounted for in these two products. Of the 78% of the

oxygen that was not present in the WI product, most of it was present in the CO_2 (60% of the original oxygen). If the remaining 18% of the original oxygen was removed as water, the equivalent hydrogen consumed to form water would be 0.42 wt % of ash-free coal. The total forced mass balance is off by the amount of excess nitrogen, the deficiency in sulfur, and the hydrogen incorporated into the WI product and into the water.

Table 9-22. Elemental Balance for NaOH-Treatment Run in 300 mL Reactor

	Coal	WI-Insol	CO_2	H_2O	Total
Carbon	70.32	66.3	4.0		70.3
Hydrogen	4.68	4.83		0.42	5.25
Nitrogen	1.04	1.42			1.42
Oxygen	17.92	3.92	10.67	3.33	17.92
Sulfur	0.5	0.33			0.33
Ash	5.54	5.54			5.54
Total	100.00	82.3	14.67	3.75	100.72

From this calculation, the total hydrogen consumed in the reaction was approximately 0.6 wt % of the starting dry coal. The same calculation was performed on the reaction in the 300 mL autoclave in the absence of NaOH (see Table 9-23). In this case, the WI product was much more deficient in hydrogen relative to the product from the reaction in the presence of NaOH. Again forcing a carbon balance with CO_2 resulted in a much smaller value for the amount of CO_2 that would be produced. The corresponding amount of water necessary to balance the oxygen was much higher. A total of 75% of the oxygen in the coal was removed broken down as 23% CO_2 and 52% as water. The addition of hydrogen from the WGS reaction was 1.0 wt % on feed coal which accounted for 85% of the hydrogen incorporated into the water. The remaining hydrogen came from the decrease in hydrogen in the WI product.

Table 9-23. Elemental Balance for 300 mL Reactor Run without NaOH					
	Coal	WI-Insol	CO_2	H_2O	Total
Carbon	70.32	68.76	1.56		70.32
Hydrogen	4.68	4.50		1.17	5.67
Nitrogen	1.04	1.44			1.44
Oxygen	17.92	4.41	4.16	9.35	17.92
Sulfur	0.5	0.34			0.34
Ash	5.54	5.54			5.54
Total	100.00	85.00	5.72	10.52	101.23

Even with the significant number of assumptions made in making these forced elemental balances, directionally the enhanced removal of oxygen as CO_2 is apparent. Likewise, the lower hydrogen content in the WI product from the non-NaOH treated product is offset by a slight increase in the recovered solid product. To adequately evaluate these two approaches from an economic standpoint requires some additional confidence in the experimental observations that have been made, especially with regard to the compositions of the WI products. Unquestionably, the apparent agreement of the forced balance in the case where NaOH was used with the elimination of mostly CO_2 indicates that the target of removing oxygen with carbon as opposed to as water can be achieved from a process standpoint.

The elemental analyses of the pyridine soluble and insoluble materials from the NaOH run are shown in Table 9-21. As expected, the hydrogen concentrations in the soluble fraction are considerably higher than in the starting coal, whereas the concentration in the insoluble fraction is very much less than in the coal. The H/C ratio in the pyridine-soluble product was the highest observed during the course of this study, i.e. 0.97. As expected, the oxygen concentration is very high in the insoluble fraction. Somewhat surprising, however, is the oxygen concentration in the pyridine soluble material which was higher than in the starting coal. Based upon the time and methods involved in handling these materials, this material appears to

have taken up a significant amount of oxygen. Due to this extreme sensitivity to oxygen exposure, these materials must be handled with extreme care.

Heating Values of CO-Treated Products. Heating value and elemental composition of fossil fuels and coal derived material are useful parameters for gauging the quality of the fuel substances. A well known formula, developed by Boie and used by Ringen and co-workers[9] for the calculation of heating values for coal and coal derived substances has the form:

$$H_g(cal/g) = 8400C + 27765H + 1500N - 2500S - 26500$$

where H_g is the gross heating value and C, H, N, S and O are the normalized weight fractions of these elements in the sample. Multiplication by the factor 1.8 converts the results to units of Btu/lb.

	CO/NaOH Soln	CO/H_2O	BT Coal
Heating Value, Btu/lb maf	16,400	16,000	12,900

The heating values for the water-insoluble materials presented in Table 9-21 that were generated from the stirred autoclave are significantly higher by up to 26% as compared to the original coal.

Summary. Reacting BT coal with CO and H_2O in the presence and absence of a base at 340 °C in a 300 mL stirred autoclave produced a material which has a very low oxygen content. Oxygen removal is in excess of 75% whether with base or without. Addition of base gave a material which was highly soluble in both pyridine (95%) and THF (78%), although in the absence of base, solubility is significantly lower. In addition, the material generated in both cases has a significantly higher heating value than the starting coal. A forced material balance based upon the absence of any significant hydrocarbons in the gaseous product provides insight into the probable reaction pathways for removal of oxygen. In the presence of base, a large part of the oxygen leaves as CO_2 while in the absence of base the water pathway is far more

dominant. In both cases, the significant removal of oxygen can have a large economic impact on processing costs for low rank coals.

Characterization of Water-Insoluble Product

Analysis of the infrared spectra of the acid-washed water-insoluble product suggests that partial decarboxylation of the coal occurs during pretreatment (Figure 9-14). The intensity of the carbonyl absorption peak at 1703 cm^{-1} relative to that of the aromatic stretching peak at 1600 cm^{-1} is reduced in the pretreated products compared to the raw coal. This is consistent with the elemental analyses which indicate that ~40% of the coal oxygen is removed. The volatility of the water insoluble product is greater than the coal itself as shown by TGA (Figure 9-15). Samples prepared with NaOH and Na_2CO_3 both show greater loss in weight than the raw coal. Since higher volatility would correspond to the presence of smaller molecules or weakened bonds, it can be concluded that pretreatment results in molecular weight reduction.

Morphology of Pretreated Coals - Wyodak coals are composed predominantly of huminite and displays features such as remnant woody cell structures and layering (Figure 9-16a). There were only minor changes in morphology for coals treated in the absence of CO, i.e., in steam with nitrogen or hydrogen overpressure (Figure 9-16b). The particles retained their angular shapes, similar to those of the original coal, but became ragged indicating that some disintegration had occurred. In addition, some particles retained the botanical structures and layering features found in the original coal. Coal treated at 200 psig CO in aqueous NaOH had similar morphology, except that the coal particles had developed rounded edges indicative that some flow had taken place. Treatment at 400 psig CO led to more extensive reaction of the huminite macerals (Figure 9-16c). A preponderance of large, rounded, porous particles were formed and there was no evidence of the botanical structures and layering features found in the original coal. Finally, at 800 psig CO, the huminite structure was completely altered and the particles were agglomerated forming large, coherent, porous masses (Figure 9-16d). Some of the pores appeared to be filled with a solid, homogeneous bitumen-like material that exhibits a low reflectance and is fluorescent under ultraviolet irradiation. Such optical properties are displayed by hydrogen-rich liptinite macerals in coal and kerogen. Under the pretreatment conditions, the liptinite and, particularly, the inertinite macerals were relatively unaffected.

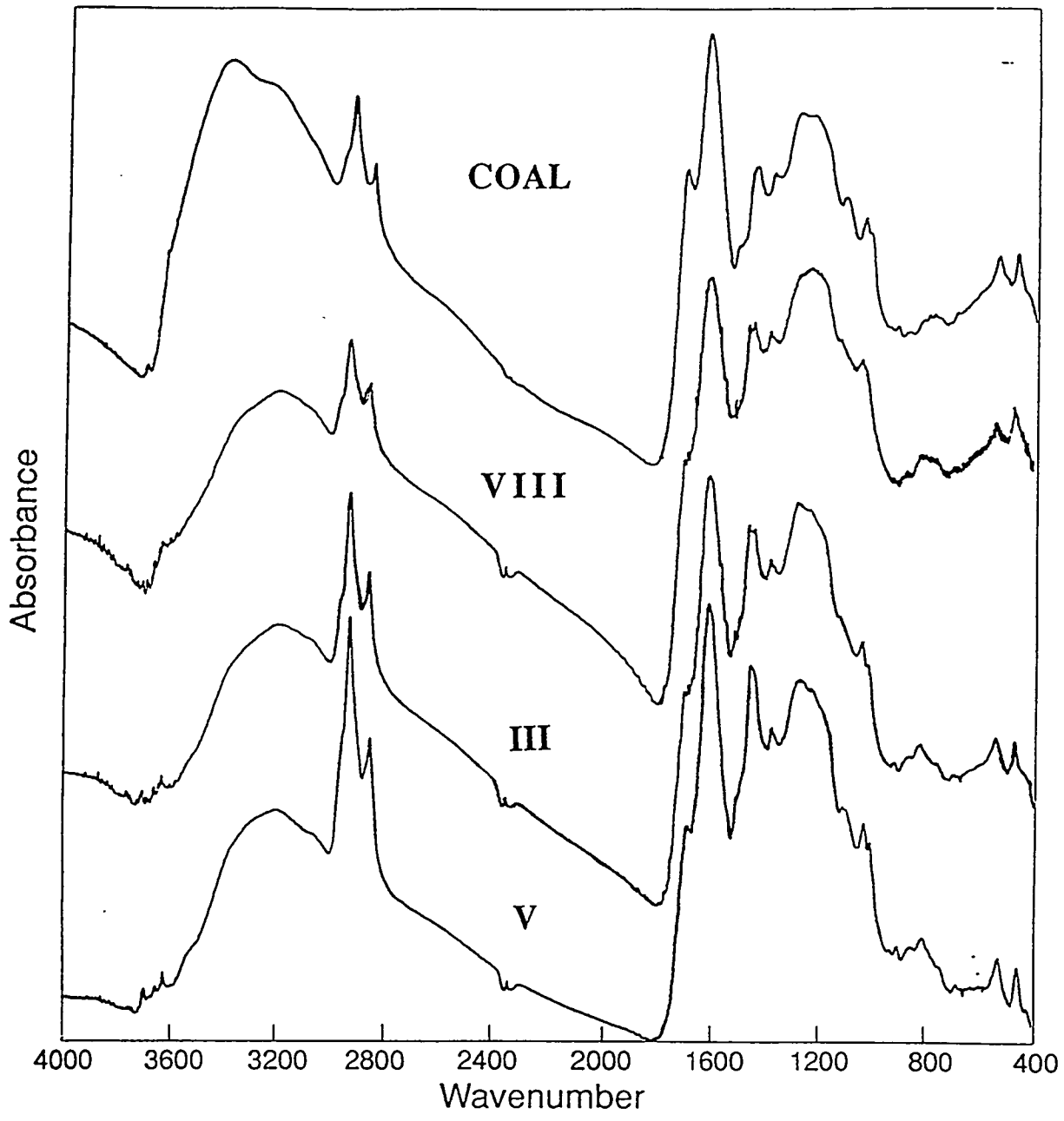


Figure 9-14. Infrared spectra of acid-washed-insoluble product

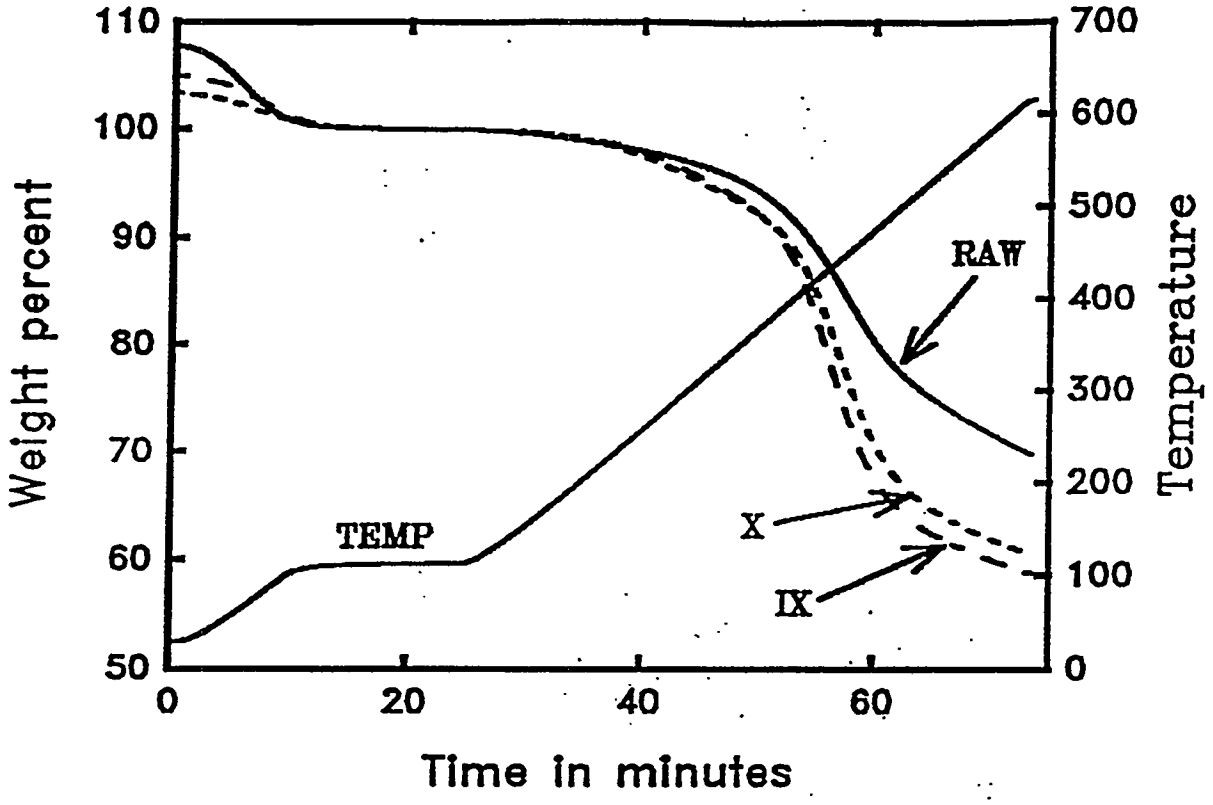


Figure 9-15. TGA of water-insoluble product

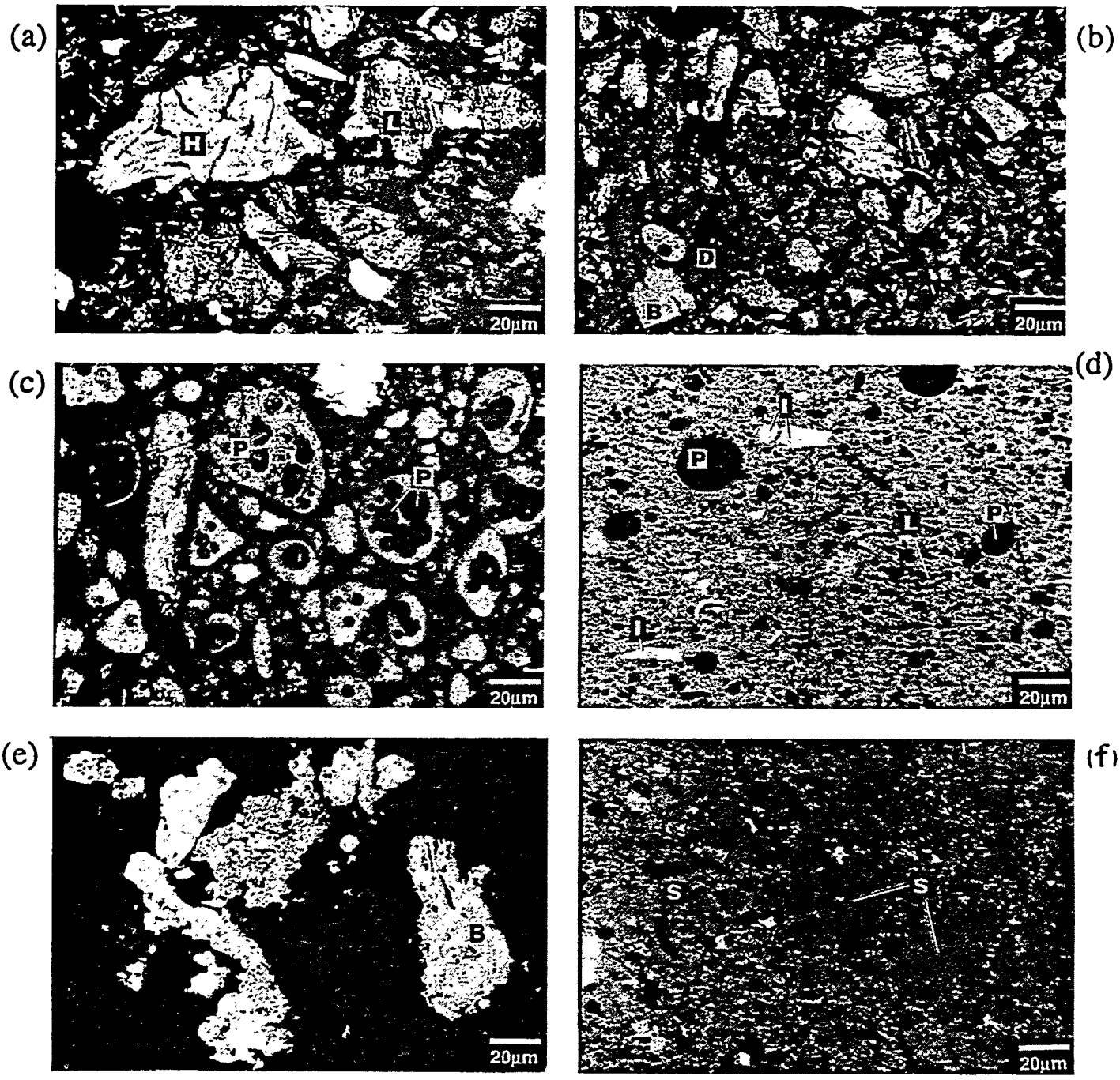


Figure 9-16. All photomicrographs obtained in reflected white light at a magnification of 625X.

(a) Subbituminous coal with huminite (H) and liptinite (L) macerals indicated. Note the botanical structures in the larger huminite particle. Dark gray background is epoxy resin.

(b) Coal treated with 5.62 MPa nitrogen. Many coal particles retain distinct, angular outlines, occasionally observed with botanical structures (B), whereas others appear partially disintegrated (D).

(c) Coal treated with 2.86 MPa CO. Note rounded particles, often containing large pores (P).

(d) Coal treated with 5.62 MPa CO. Majority of coal has melted and agglomerated forming larger masses with numerous pores (P). Liptinite (L) and inertinite (I) macerals are essentially intact.

(e) Coal treated with 5.62 MPa CO without added base. Coal particle outlines are rounded, indicative of partial melting, although botonical (B) and layering features are still observed.

(f) Coal treated with 5.62 MPa CO with $NaHCO_3$. Note areas with "smooth" (S) microtexture within material exhibiting a porous, specular appearance.

In the absence of NaOH, there was less transformation of the coal particles (Figure 9-16e). The particles become rounded losing their angular shapes, but occasionally exhibit some botanical structural and layering features. Likewise, at 250 °C, no indication of reaction occurred since no significant structural changes were observed accompanied by only a slight increase in (9%) THF solubility. The 250 °C product, which retained the original coal microstructure, comprised angular particles, similar in appearance to the residue produced at 300 °C in steam with nitrogen overpressure.

The effect of using Na_2CO_3 as a promoter was similar to that described with NaOH. However, with $NaHCO_3$, the extent of flow and agglomeration was more varied; some areas were completely agglomerated, while others showed evidence of flow and were only loosely agglomerated (Figure 9-16f). The loosely agglomerated areas had a smooth microtexture which presumably was due to the partial liquefaction of huminite, and was similar in appearance to the 400 psig CO treated residue (Figure 9-16c). Other areas were porous-looking, similar to the high pressure CO reaction product (Figure 9-16d).

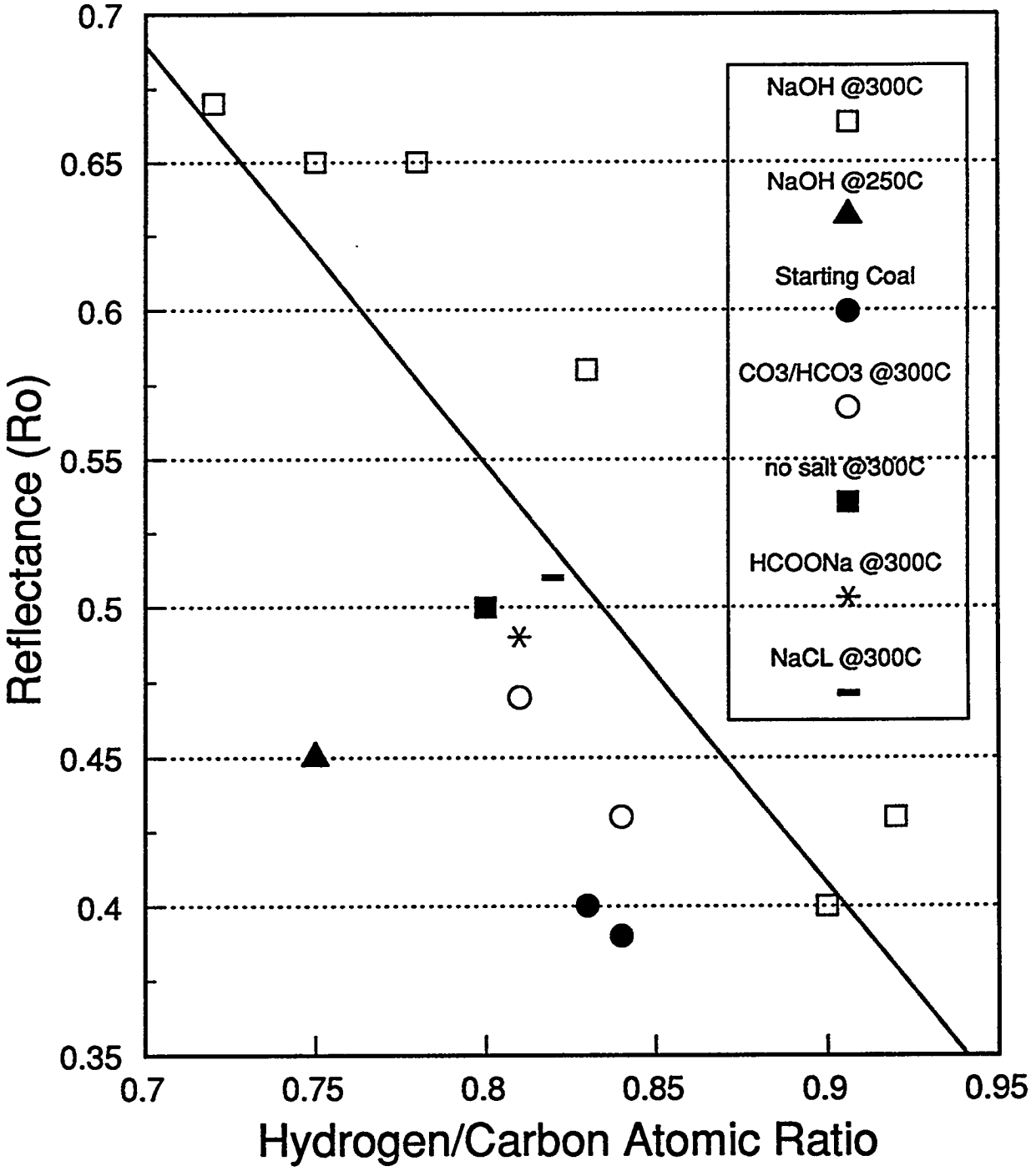
The mean reflectance measured for each of the samples appears to be dependent on the degree of pretreatment (see Table 9-24). Coals treated in the absence of CO or at low CO pressures have the highest reflectance while those treated at high CO pressures have the lowest values. Relatedly, the hydrogen to carbon atomic ratios (H/C) show a linear inverse correlation with their reflectance values (Figure 9-17). Not unexpectedly, the sample prepared at 250 °C deviates the most from this correlation since it had not converted. Since all of these samples have similar oxygen contents, this would not seem to be a factor in determining reflectance. The correlation is directionally in agreement with previous studies on coal liquefaction residues that showed that more effective liquefaction occurs in residues with low reflectance.[11]

The results of staining experiments indicate that all of the pretreated coal samples contain fewer carboxylic acid groups relative to the original coal. In contrast to the raw coal, which was intensely stained by the dye Safranin-O, all of the pretreated samples were only lightly stained. The staining arises from the reaction of the cationic dye with the oxygen-rich,

Table 9-24. Reflectance Data							
	Aqueous Pretreatment Conditions					R_o%[b]	H/C, atomic ratio[c]
	Coal[a]	Gas	Pressure, psig	Temperature °C	Base		
	BT	-	-	-	-	0.39	0.84
	BT	N_2	800	300	NaCl	0.67	n.d.[d]
	BT	N_2	800	300	NaOH	0.65	n.d.
VII	BT	H_2	800	300	NaOH	0.65	0.78
	BT	CO	800	300	NH_4OH	0.56	n.d.
	BT	CO	800	300	HCOOH	0.53	n.d.
	BT	CO	800	300	NaCl	0.51	0.82
	BT	CO	800	300	HCOONa	0.49	0.81
XIII	BT	CO	800	300	$NaHCO_3$	0.48	n.d.
XIV	BT	CO	800	250	NaOH	0.45	0.75
XII	BT	CO	800	310	Na_2CO_3	0.43	0.84
XV	BT	CO	800	310	NaOH	0.40	0.90
VIII	CP	N_2	800	300	NaOH	0.67	0.72
I	CP	CO	200	300	NaOH	0.65	0.75
III	CP	CO	400	300	NaOH	0.58	0.83
VI	CP	CO	800	300	none	0.50	0.80
XI	CP	CO	800	300	$NaHCO_3$	0.47	0.81
V	CP	CO	800	300	NaOH	0.43	0.92
	CP	-	-	-	-	0.40	0.83

a. BT = Black Thunder Wyodak coal; CP = Clovis Point Wyodak coal.
b. R_o is huminite reflectance in immersion oil.
c. Water-insoluble product.
d. n.a. - not determined

Figure 9-17
Reflectance vs H/C Ratio of CO-Pretreated Coals



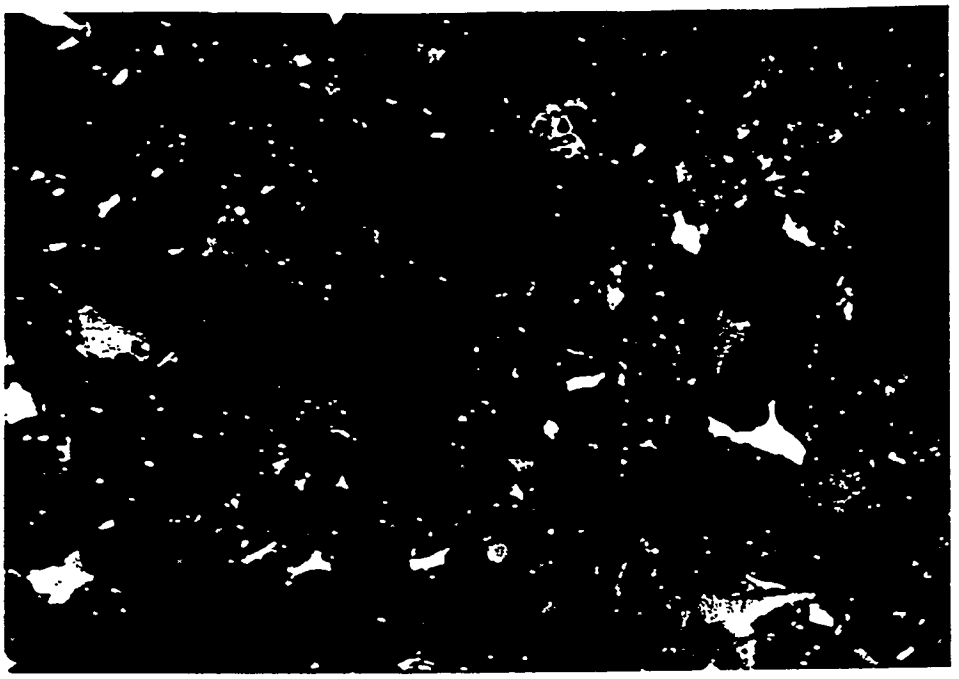
REFL-4

carboxylic acid groups in the huminite macerals while the liptinite and inertinite macerals, which are largely unreactive to the pretreatment, are unaffected by the dye. The uniform staining in these samples is directionally in agreement with their rather uniform oxygen content.

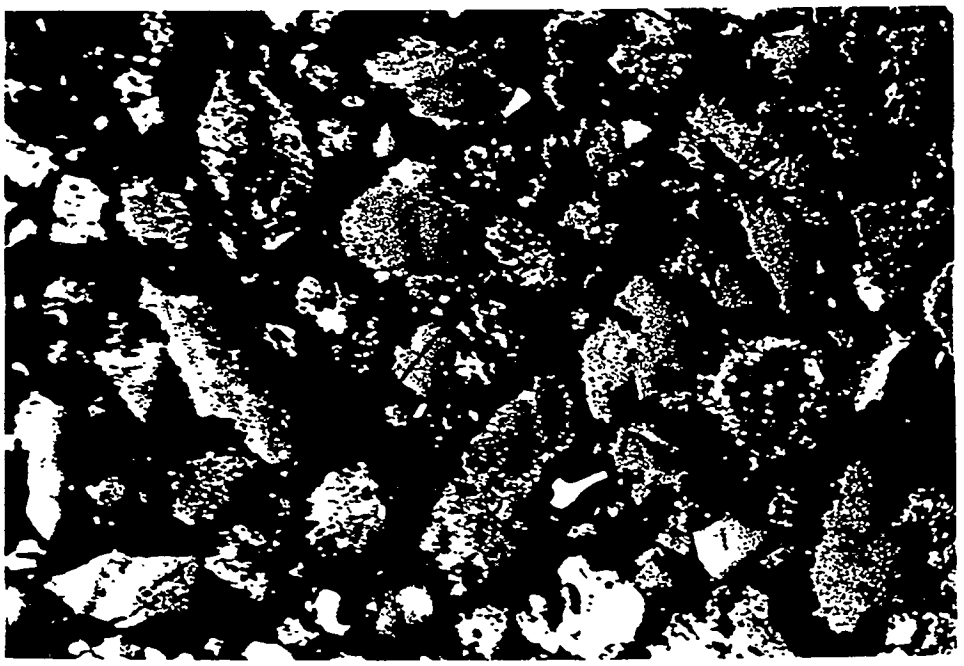
Using NaCl as the water-gas shift promoter caused the huminite (Black Thunder) to soften and melt, and agglomerate into large masses. However, the extent of this reaction varies within the product; some of the huminite macerals had melted extensively, forming areas with a finely porous microtexture, whereas other huminite macerals had softened/melted, but were still present as distinct particles (although the edges are no longer angular, and remnant botanical features were rarely observed) within the agglomerates (Figure 9-18). These features are similar to those observed in the water-insoluble product of the $NaHCO_3$ promoted CO pretreatment. The liptinite and inertinite macerals are relatively unaffected by pretreatment. Thermal treatment with H_2O and NaCl only produced negligible change in the coal, except for a significant increase in the huminite mean reflectance (0.67%) as shown in Table 9-24; similar results were reported for thermal treatment with H_2O and NaOH.

Reaction with sodium formate (HCOONa) generated a product that is very similar in appearance, and mean reflectivity, to that produced using NaCl. However, when formic acid (HCOOH) was used, the huminite macerals softened only slightly and did not agglomerate; the coal particle outlines retain a small degree of angularity, with some rounding present (Figure 9-18). The mean reflectance is only slightly higher than that of the HCOONa reaction product. Utilizing NH_4OH as a catalyst produced a material morphologically similar to that from the HCOOH reaction. Most of the huminite has softened during the reaction, but lacks any significant agglomeration. In fact, botanical structures and bedding features are commonly observed in the huminite. This pretreatment caused an increase in the huminite mean reflectance to 0.56%.

Figure 9-18



Reflected white light photomicrograph of water-insoluble product from CO pretreatment in the presence of NaCl. Width of field is 210 µm.



Reflected white light photomicrograph of product from reaction using formic acid (CHOOH) as a catalyst. Width of field = 210 µm. Dark areas are epoxy resin.

The product from coals heated at 340 °C in the absence of CO were essentially the same as those obtained at 300 °C. The higher temperature did not cause any additional change in the morphological structure of the coal. At 340 °C, much of the fine structure (eg. layering, remnants of cell structures) disappeared and there was evidence of some softening, although the general angular shapes of the particles were distinct. The reflectance of the treated material, as before, increased as the hydrogen in the WI product decreased. The products produced in the absence of CO always had less hydrogen so the higher reflectance values that were observed were expected. Since solubilities of these materials produced in the absence of CO were always quite low, qualitatively, optical microscopy provided a measure of the extent of the morphological changes that had occurred.

The pentane-insoluble products that were generated at 340 °C in H_2/tetralin were also similar to the products formed by hydrothermal treatment. The particles still retained their angular outlines in cross-section with numerous cracks extending through the particles (Figure 9-19). A generally tattered appearance not found in CO-treated coal was evident. The liptinite macerals were very difficult to identify in white light and are no longer fluorescent under blue light irradiation. However, several spores were observed intact in the sample suggesting some alteration but did not melt or dissolve. The inertinite macerals remained essentially unchanged.

When coal was treated with CO at 800 psig in the absence of any added water, only minor changes in morphology occurred. The particles appeared to have slightly softened and contained numerous cracks but did not melt and agglomerate to any significant extent. Principally, the angular shapes diminished with the addition of CO. Adding water to the coal during the CO treatment resulted in greater transformation. At 320 °C, the huminite had melted and agglomerated to form larger, porous masses. Bitumens filled some of the pores and some base-soluble, low reflecting particles were observed. Despite the increased reaction of the huminite, liptinites and inertinites remained essentially unchanged from the raw coal. Although the particles had softened, they did not melt and agglomerate to the extent observed when base was added during the CO treatment. The particles partially disintegrated (Figure 9-20) indicating the reaction had progressed further than when CO was absent. When the reaction temperature

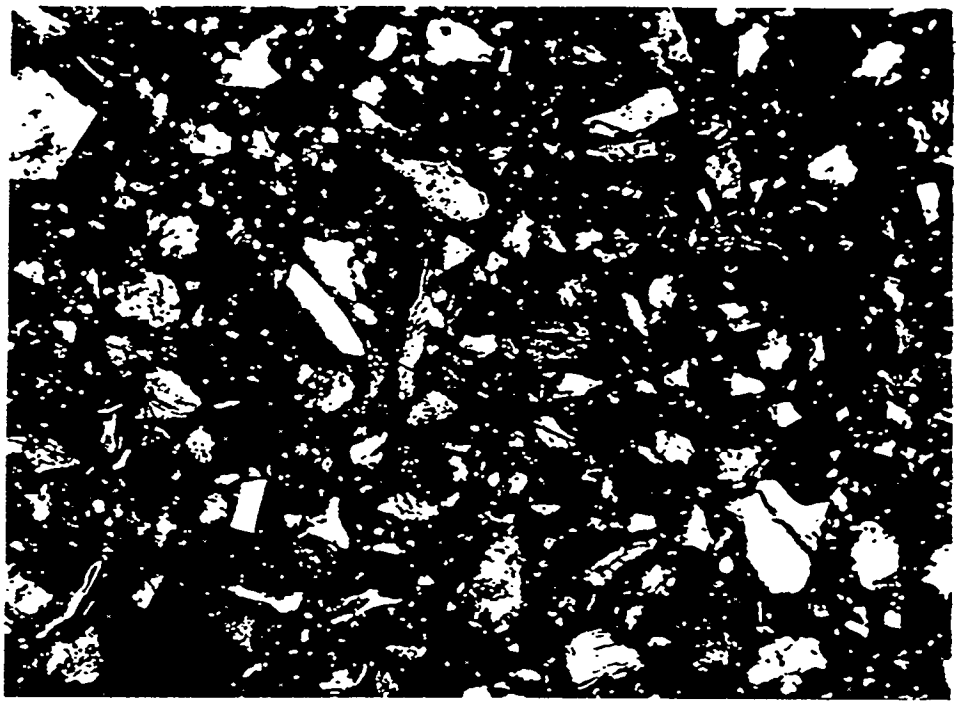


Figure 9-19. Pentane-insoluble product from treating BT coal in tetralin/H_2 at 340 °C

was increased to 340 °C, it appeared that a significant portion of the coal huminite particles had disintegrated, melted and agglomerated to form a large mass. Incorporated within this "sheet" of material are large discrete rounded pebbles with a smooth, non-porous microtexture; these are softened, but not completely melted coal particles (Figure 9-21).

The biggest change in optical properties occurs with the addition of NaOH to the CO/water system. This occurred at all temperatures. The degree of melting and agglomeration of the huminite increases with higher temperature. The 300 °C product was generally porous but contains some areas in which the agglomerates were non-porous with a smooth microtexture (Figure 9-22). The coal particles had partially melted but had undergone less extensive reaction than the porous regions. Inertinite macerals were unaffected by this treatment and the liptinites remained optically distinct

The material produced at 320 °C was more porous with fewer non-porous, smooth regions (Figure 9-23). The pores in this material tend to be smaller than those in the 300 °C product and appear to be filled with low reflecting, brightly fluorescent bitumen. Liptinites are easily distinguishable and the inertinite macerals are unchanged from the raw coal. The 340 °C material appeared to contain fewer bitumens than the 320 °C material and had more of the large pores, possibly formed from a more extensive release of volatiles within the viscous melt (Figure 9-24). The liptinites had partially reacted as evidenced by a pronounced decrease in fluorescence in blue light and loss of contrast in white light when compared to the huminite matrix. Inertinites remained unchanged. Also present in this material were dark brown, low reflecting particles with a homogeneous microtexture. Many of these dissolved when the pellet was immersed in an aqueous KOH solution, and may have been high molecular weight humic acids.

The water insoluble material produced in the 300 mL autoclave at 340 °C in the presence of NaOH had a similar appearance to that produced in the microautoclave. The huminite was extensively melted and agglomerated and was highly porous with a small number of bitumen bodies. This product resembled an ashy resid (Figure 9-25). Bituminous coal contaminant that

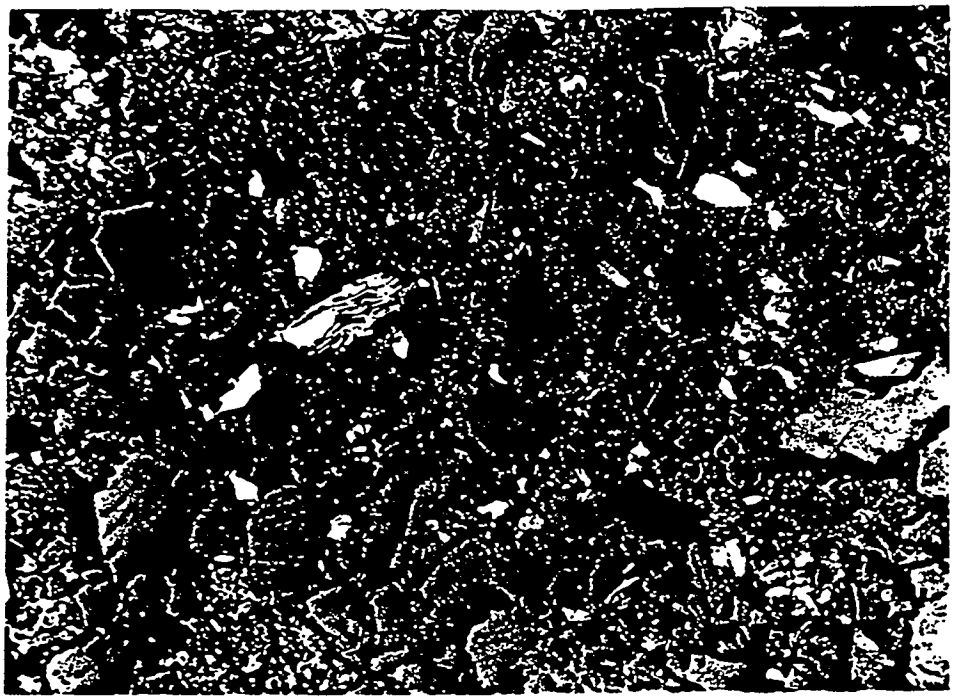


Figure 9-20. Water-insoluble product from reaction of BT coal with CO at 320 °C.

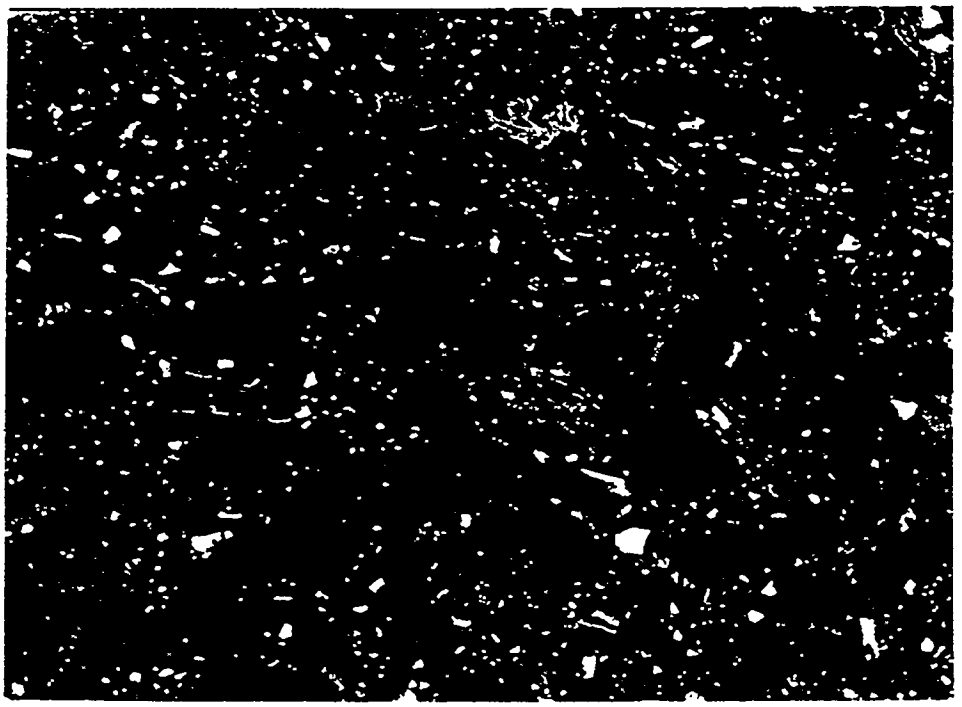


Figure 9-21. Water-insoluble product from reaction of BT coal with CO at 340 °C.

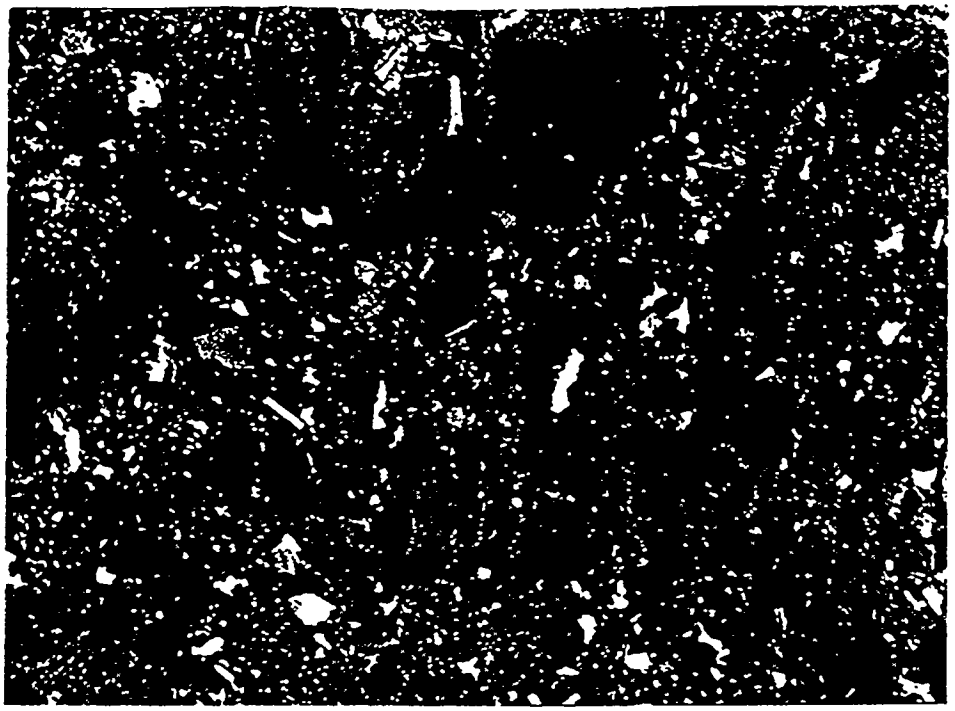


Figure 9-22. Water-insoluble product from reaction of BT coal with CO in the presence of NaOH at 300 °C.

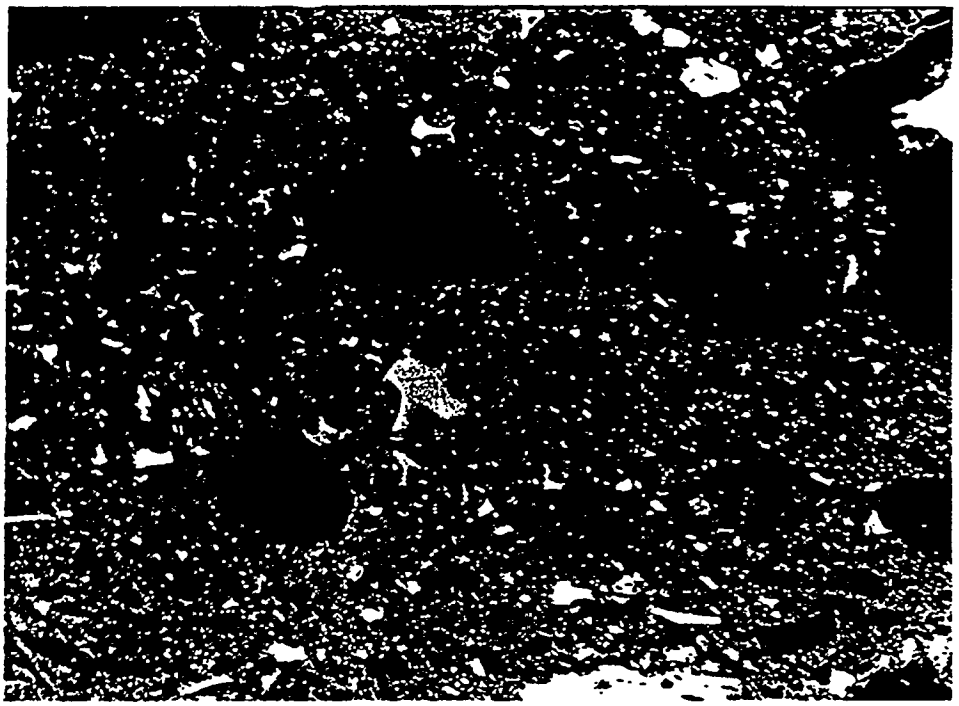


Figure 9-23. Water-insoluble product from reaction of BT coal with CO in the presence of NaOH at 320 °C.

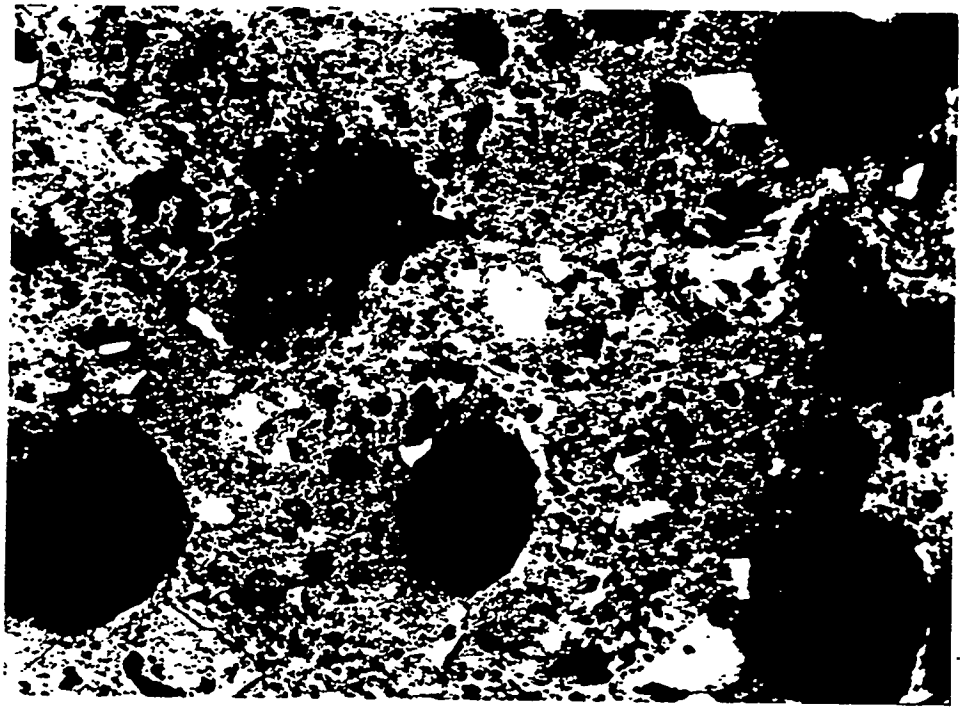


Figure 9-24. Water-insoluble product from reaction of BT coal with CO in the presence of NaOH at 340 °C.

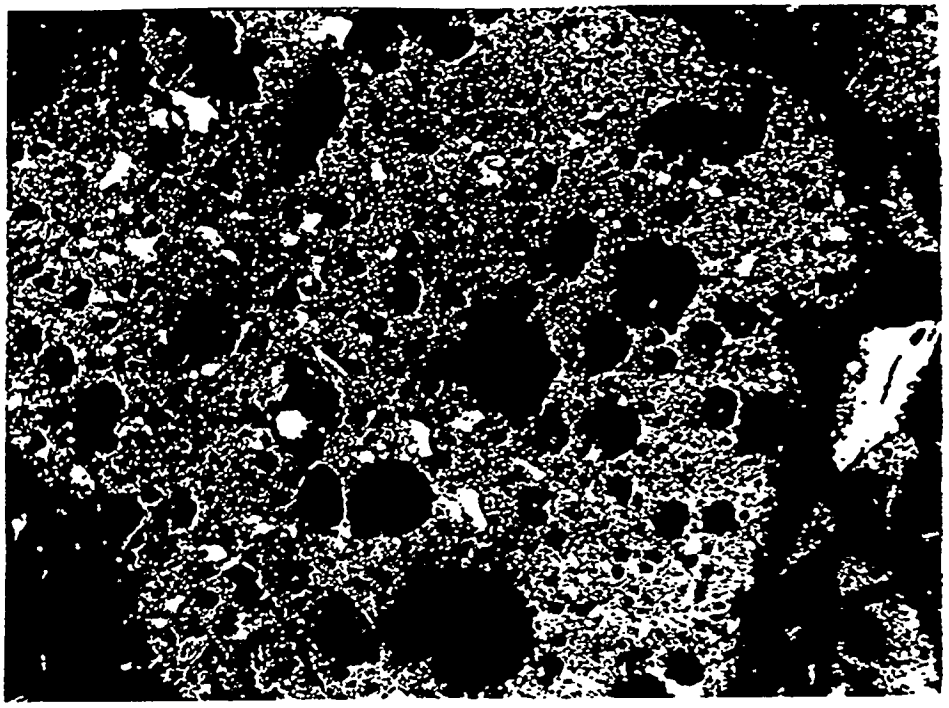


Figure 9-25. Water-insoluble product from treatment of BT coal in 300 mL autoclave in CO/NaOH/water at 340 °C.

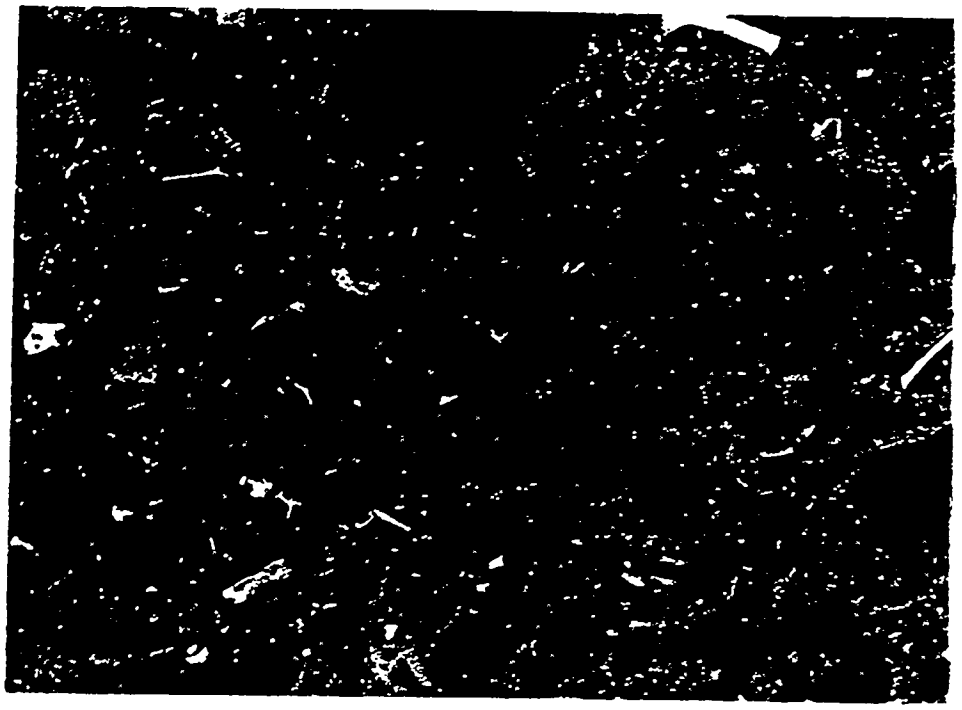


Figure 9-26. Water-insoluble product from treatment of BT coal in 300 mL autoclave in CO and water at 340 °C.

was occasionally observed in all of the samples described thus far apparently had undergone significant melting or dissolution because it could no longer be differentiated from the BT melted huminite. As is the case with the microautoclave experiments, the inertinites remained intact and the liptinites were still identifiable but less so than in the raw coal.

For the 300 mL run made in the absence of NaOH, the extent of melting and agglomeration was less and the agglomerates exhibited a lower degree of porosity than when base was used in the experiment (Figure 9-26). This trend is consistent with that observed in the microautoclave runs.

Pyrolysis of CO-Pretreated Coals. TGA/MS analysis of the various water insoluble products were performed to determine the thermal characteristics of the materials and the composition of the lower molecular weight materials in the volatile fraction. These results are shown in Table 9-25. For the treated Black Thunder coal the magnitude of the volatile fraction was greater than for the raw coal. These numbers, based upon the dry coal, represent the volatility of the total mass including the ash content. To relate the numbers for the CO-pretreated coal back to the raw coal these values would be multiplied by a factor of about 1.2, which is equal to 1/[yield water insoluble product x (1-wt fraction ash)]. The temperature of inflection in the weight loss curve, which corresponds to the temperature of maximum weight loss, was lower for the CO-pretreated Black Thunder coal than for the blank. This was, however, not true for the Clovis Point coal where the numbers were close together.

The mass spectra of the materials that were emitted during the devolatilization were followed during the TGA scans. Water, hydrogen, CO, CO_2, and methane were the most prominent peaks. The maxima for methane appeared typically around 505-515 °C for the CO-pretreated Black Thunder coal versus 521 °C for the untreated coal. For Clovis Point coal methane appeared at 540 °C for both treated and untreated coals. Carbon dioxide peaked around 450 °C for both of these coals and the CO-treated coals. This is much lower than the temperature of decomposition of Na_2CO_3 which appeared at about 800 °C. Therefore, the loss of CO_2 and the corresponding loss in CO, was attributed to the organic function of the coal and not to the

decomposition of any significant amount of Na_2CO_3 or $NaHCO_3$ present in the water insoluble product. The magnitude of the loss of $CO+CO_2$ could not be determined.

Table 9-25. Volatility of CO-Pretreated Coals[a]

Coal	Base		°C	CO psig	Volatility		Run No.
	Conc, M	cc			wt%	Max °C	
Black Thunder							
Blank	-	-	-	-	42.7	440	-
2 g[b]	0.33M NaOH	6	250	800	47.0	442	J119
100 g	0.38M NaOH	200	310	800	49.1	431	Run 1&2
2 g	0.33M $NaHCO_3$	6	300	800	44.1	432	J183
Clovis Point							
Blank	-	-	-	-	45.5	438	-
2 g	0.33M NaOH	6	300	200	44.0	445	J120
2 g	0.33M NaOH	6	300	800	43	439	J83/84
2 g	0.14 wt% Fe[c]	6	300	800	46.5	443	J137

a. TGA program: 25 to 120°C at 10°C/min, hold 15 min, 120 to 900°C at 10°C/min, hold 1 min. Volatility=100 x $(wt_{25\ min} - wt_{103\ min})/wt_{25\ min}$ which corresponds to a cutoff at 930°C.
b. Dry basis
c. Added iron by IW method.

Surface Analysis of CO-Pretreated Coals

XPS analysis of the NaOH and Na_2CO_3 treated samples were compared with raw coal. Data are shown in Table 9-26. The XPS band positions of the pretreated coal samples are shown in Table 9-27. Surface oxygen for the pretreated coal samples is diminished compared to oxygen in the bulk samples. The surface concentrations of aluminum and silicon also decreased relative to the starting coal. Sodium, however, which was contained in the reaction system, increased in both of the products relative to starting coal. The presence of sodium suggests that additional analyses will be necessary to determine the actual amount of sodium being incorporated into the product.

Table 9-26. XPS Analysis of CO-Pretreated Coal[a]			
	Black Thunder Coal	NaOH	Na_2CO_3
Elemental Composition, at %			
Carbon	78.5	84.6	83.1
Oxygen	17.0	13.7	14.1
Nitrogen	1.2	0.9	1.0
Iron	0.1	-	-
Calcium	0.2	0.3	0.2
Aluminum	1.0	0.6	0.4
Silicon	1.9	1.0	0.9
Sulfur	0.1	0.3	0.1
Sodium	-	0.2	0.2
a. Pretreatment at 310 °C, 1 hour, 800 psig CO.			

Table 9-27. XPS Band Positions of CO-Pretreated Coals			
	Sample Description		Comment
	NaOH (eV)	Na_2CO_3 (eV)	
C_{1s}	286.8	286.7	Δ = 286.7-284.6 = 2.1 ev
O_{1s}	532.1	532.3	
N_{1s}	398.8	399.9	
Ca_{2p}	347.0 350.7	347.1 350.3	$CaCO_3$
Al_{2p}	73.4	73.4	
Si_{2p}	102.3	102.4	
S_{2p}	163.3 167.8	163.4 167.9	
Na_{1s}	1071.5[a] 1072.4	1071.8	
a. Predominant peak.			

Liquefaction of Pretreated Coal

Liquefaction in Tetralin. Liquefaction experiments were performed on pretreated coal both in tetralin as well as Wilsonville Run 262E V-131B. The experiments in tetralin were run in duplicate by placing 2 g of raw or pretreated coal and 2 g tetralin into the microautoclave. Iron oxide or Shell 324 catalyst was added at a level of 1 wt % iron or 0.1 wt% molybdenum on dry coal, respectively, along with dimethyldisulfide to provide a sulfur to added metal(s) atomic ratio of 2. Hydrogen (800 psig) was added, the reactor sealed and then heated to 400 °C in the manner described above. Solid and liquid products were removed from the reactor and extracted with tetrahydrofuran (THF) in a Soxhlet thimble for 18 hours and dried overnight at 80 °C/16 kPa. The THF insolubles contained insoluble organic matter (IOM) plus ash. The soluble fraction was concentrated by removing excess THF in a rotary evaporator. A 50:1 excess volume of pentane was added and the mixture placed in an ultrasonic bath for 3 min. The pentane insoluble preasphaltenes and asphaltenes (PA+A) were filtered and dried. The soluble fraction was recovered after evaporating the pentane. The product is then separated into pentane solubles, PA+A and IOM plus ash. The molydenum, nickel and iron in the catalysts are presumed to convert to MoS_2, NiS, and pyrrhotite ($Fe_{0.9}S$), respectively, and report to the ash fraction. The product distribution was calculated assuming complete recovery of the ash plus catalyst. Oils are calculated by difference, and as a result, water produced during liquefaction, as well as any experimental error, is included in these yield data. Coal conversion equals 100 minus the yield of IOM.

The THF conversions obtained by liquefaction of CO-pretreated coal (Run V) in hydrogen and tetralin, and in the absence of a catalyst were 61 wt .% at 15 min and 83 wt % at 60 min. The corresponding values for the raw coal were lower: 49 wt.% at 15 min and 75 wt.% at 60 min (see Table 9-28). The increase in THF conversion at 15 min reported mainly to the THF-soluble/pentane-insoluble fraction (PA+A) while in the 60 min run the improvement in conversion reported to the pentane soluble (oils) fraction. Since the oxygen content of the pretreated coal is significantly lower than the untreated coal, the actual oil yield would be higher for the pretreated material. The liquefaction of coals pretreated in steam at low CO pressure (Run II), or in the absence of CO (Run VIII), gave slightly lower conversions than for raw coal.

The sharp drop in oil yield upon pretreatment in the absence of CO indicates the role of CO in modifying the coal. Even for the low pressure CO-pretreated coal, the oil yield was higher than obtained with the steam-nitrogen pretreated coal. The $CO+CO_2$ yields for all the pretreated coals were significantly reduced in both 15 and 60 min runs which agrees with the reduced oxygen content and the reduced concentration of carboxylate groups in the water-insoluble product. The combined consumption of gaseous hydrogen and hydrogen from the tetralin solvent was nearly constant over the period from 15 to 60 min for Run V even though THF conversion increased significantly. The total hydrogen consumption for the coal pretreated at the high CO pressure was significantly lower than for raw coal or pretreated coals from Runs II and VIII. Even with the additional hydrogen added during pretreatment, the overall hydrogen consumption in the two step liquefaction is less than for raw coal itself.

Table 9-28. Liquefaction of Raw and CO Pretreated Clovis Point (CP) Wyodak Coal in Tetralin 400 °C, 800 psig H_2

Reactant	CP	V[a]	CP	V[a]	II[a]	VIII[a]
Time, min	15	15	60	60	60	60
THF Conv, wt% maf coal	49	61	75	83	71	70
Products, wt% maf coal						
PA+A	34	47	43	42	44	52
Oils[b]	10	12	26	39	24	15
$CO+CO_2$	5	2	5	2	2	2
HC Gases	0.2	0.2	0.3	0.6	0.5	0.5
H_2 Gas Consumed[c]	11	19	17	18	29	30
Total Hydrogen Consumed[d]	20	24	32	26	42	42

a. Water-insoluble product.
b. Includes water
c. H_2 Gas Consumed (mg/g maf coal) = $[H_{2\,in} - H_{2\,out}]$/coal; excludes H_2 consumed by tetralin.
d. Includes both gaseous hydrogen and hydrogen from tetralin

Catalyzed liquefaction in the presence of both NiMo/alumina (Shell 324) and nanometer size iron oxide (Nanocat®) provided even sharper differentiation of the pretreated coal versus the untreated

coal as shown in Table 9-29. Compared to the catalyzed conversion of the raw Wyodak coal, the NiMo catalyst had little effect on overall conversion but increased the oil yield by 10 wt %. The iron oxide catalyst increased THF conversion by 5 wt % and the oil yield by 7 wt %. The pretreated coal runs show lower gas production and lower hydrogen consumption than the untreated coal. Compared to the conversion of Wyodak coal in the absence of catalyst (Table 9−29), both THF conversion and oil yield showed significant increases.

Table 9-29. Catalyzed Liquefaction of CO-Pretreated Coal

Reactant	XII[a]		Black Thunder Wyodak Coal		
Catalyst	Shell 324	Nanocat	None	Shell 324	Nanocat
Added Fe, wt% dry coal	-	1.0	-	-	1.0
Added Mo, wt% dry coal	0.1	-	-	0.1	-
THF Conv, wt% maf coal	84	86	75	83	81
Product Distribution, wt% maf coal					
PA+A	43	52	44	49	50
Oils[b]	39	32	26	29	25
Gases	2	2	5	5	6
Hydrogen Consumption, mg/g maf coal[c]	31	29	34	34	34

a. Water-insoluble product from pretreated coal prepared in l-liter autoclave with 0.19M Na_2CO_3 (3.7 wt% maf coal), 5.62 MPa CO.
b. Includes water
c. Includes hydrogen from tetralin solvent.

Low temperature CO pretreatment at temperatures around 300 °C produces a material through hydrogenation and modification of the coal structure, especially at higher CO pressures, that has significantly enhanced reactivity in liquefaction. Liquefaction of the product gave increased THF conversion and higher yields of oils than the starting coal. It is suggested that retrogressive reactions competing for hydrogen during liquefaction apparently have been suppressed leading to the more effective utilization of hydrogen.

Liquefaction in Wilsonville Process Solvents. The liquefaction performance of pretreated coals was measured at temperatures from 415-440 °C using various solvents from the Wilsonville pilot plant. Reactions were run at 415 °C for an hour in Run 262E V-131B composite in the presence of 0.1 wt % Mo in the form of Shell 324. No Fe was added in these experiments. The results presented in Table 9-30 are based on solvent separation. Because the THF IOM in the starting ashy solvent reacts during liquefaction, coal conversions are greater than 100% for both NaOH/CO-pretreated material and the starting coal. A considerable improvement of ca. 9 wt % was observed for the pretreated coal. Although the amount of water produced from both starting material is unknown, because of the lower oxygen content in the pretreated material, the water yield would be less for the pretreated material than the starting coal. Note also that the gas yield for the pretreated coal is marginally lower than for the starting coal.

Table 9-30. Liquefaction of CO-pretreated coal with Shell 324[a]

% wt. maf coal	BT coal	Pretreated coal[b]	Pretreated coal[b]
Gases	5.3	3.4	3.6
Oils	65.1	73.3	74.7
PA+A	31.2	26.1	22.9
IOM	-1.6	-2.8	-1.2
Conversion	101.6	102.8	101.2

a. Run Conditions: 3.0 g Black Thunder coal (~22% moisture) or 2.6 g pretreated coal (~5% moisture); 5.4 g Wilsonville recycle oil from Run 262; 1% wt Mo as Shell 324; 1000 psig H2; 415 °C; 1 h.
b. Duplicate runs.

A series of runs were made in the presence of Run 262E V-1074 1050 °F⁻ distillate at 440 °C for 22 min. In these runs either 3.0 g of Black Thunder coal (as received) or 2.6 g of pretreated material were charged together with 2.2 g of solvent into a 50 mL horizontal reactor. The reactor was sealed, leak tested and pressurized with 1000 psig of hydrogen. After reaction the products were analyzed by the solvent separation scheme. The experiments were carried out at least twice and results are shown in Table 9-31. These results show that the CO-pretreated material is significantly more reactive than the untreated coal. The average coal conversion for

the pretreated coal is 76% compared to 65% for the untreated coal. The improvement in conversion for the CO-pretreated material is reflected in the PA+A yield. The hydrogen consumption data from the gas phase is similar for both CO-pretreated and untreated coal experiments. Hence, the results are consistent with a poor hydrogenating solvent in the Run 262E V-1074.

Table 9-31. Reactions of BT Coal and CO-Pretreated Product with Run 262E Distillate[a] (wt % maf coal)

	BT Coal[b]	Pretreated[c]	Pretreated[c]
Gases	7.0	4.4	4.7
Oils+water	24.7	25.1	24.8
PA+A	33.1	46.7	46.8
IOM	35.1	23.8	23.7
Conversion	64.9	76.2	76.3

a. Coal reaction conditions: 3.0 g BT coal (~22% moisture) or 2.6 g CO-pretreated coal (~5% moisture); 2.2 g 262E V-1074;1000 psig H_2; 440 °C; 22 min.
b. Runs made in triplicate.
c Runs made in duplicate.

The reaction of pretreated product in ashy-resid containing recycle solvent was determined at 440 °C and 22 min for both starting Black Thunder coal run as well as the product from pretreating the coal in NaOH/CO. Results are shown in Table 9-32. In one of the run with the CO-pretreated product, the base case catalyst was added which included 1 wt% Fe_2O_3 and 100 ppm Mo as Molyvan L. In the other run no added Mo was used. However, recall from discussion elsewhere in this report that the activity of the recycle Mo is significantly greater than that observed for the freshly added Mo. Therefore, these results should be comparable. Although they differ, they are both significantly higher than that observed for the coal run indicating higher oil yields from the CO-pretreated product.

The products obtained from these reactions were subjected to micro-distillation. In this procedure the reaction products in the reactor after liquefaction were transferred (with THF) to

a micro-distillation apparatus. Excess THF was removed and the distillation was carried out to 627 °F at 1 torr to give an equivalent 1050 °F distillate cut at atmospheric pressure. The resid conversion obtained for the CO-pretreated material was 22.3 wt % compared to 19.5 wt % for the untreated BT coal. A comparable base case run in the presence of 100 ppm added Mo and Wilsonville iron oxide at 1% Fe gave a resid conversion of 23.5 wt%.

Table 9-32. The Reaction of BT Coal and CO-Pretreated Product with Run 262E V-131B in the Presence of Added Fe and Mo at 440 °C and 22 min (wt% maf coal)

Products, wt% maf coal	Coal	CO-Pretreated	CO-Pretreated No Added Mo
Gases	8.5	6	5
Oils	41.0	62	50
PA+A	52.0	32	46
IOM	-1.9	-	
Conversion	102	100	101

Reaction conditions: 3.0 g BT coal (~22% moisture), recycle oil; 1% Fe(WIO); 100 ppm Mo as MolyVan L; 1000 psig H_2; 440 °C.

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Chapter 10
Fluidized Coking

Background

Fluid coking (FC) was investigated as an alternative to the ROSE process for removing ash and unconverted carbon from the system. The incentive for fluid coking is the lower estimated cost relative to critical solvent deashing. In the coking process, coker distillate would be recovered and recycled back to the liquefaction process.

Based on a literature search the earliest comprehensive study related to the applicability of FC technology to processing of coal liquefaction residues was conducted by Exxon Research and Engineering in the late 1970s.[1] Preliminary coking results were obtained in which vacuum resid was subjected to batch pyrolysis. Exxon later developed the Continuous Stirred Coking Unit (CSCU) to simulate FC on a commercial scale. A simplified schematic of the CSCU is shown in Figure 10-1.

In the CSCU, tabular alumina (350 - 750 μm diameter) was used as seed for the coking reactions. The relatively high minimum fluidization velocity of this particle range material was not compatible with the residence time requirements of their test program, therefore the CSCU was mechanically stirred to simulate the fluidizing environment of a commercial scale fluid coker. The resid feedstock was melted and subsequently sprayed into the alumina bed of the CSCU reactor. Coking reactions occurred on the surface of the alumina particles. Fresh alumina was continuously added to the CSCU while coked particles were removed from the system.

Steam and coker product gases exited the reactor through a vapor space above the alumina bed and proceeded to the recovery section. The first stage of the recovery section consisted of an air cooled heat exchanger which was used to cool the reactor gases to approximately 500 °F to condense the higher molecular weight coker tars. In the second stage, a water cooled condenser

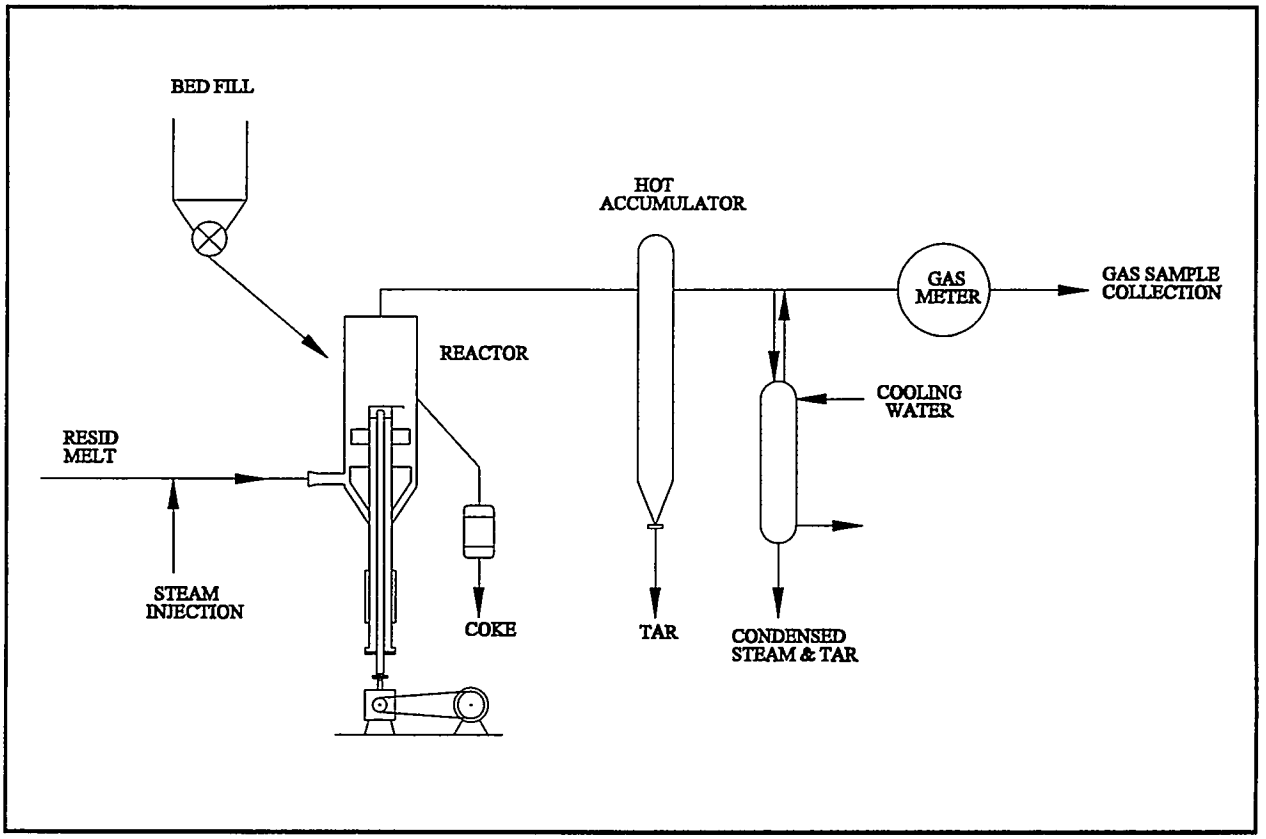


Figure 10-1. Schematic of the Continuous Stirred Coking Unit (CSCU)
(Adapted from Exxon Research and Engineering,1978)

was used to condense the steam and the lighter oils. The quantity of non-condensible product gases was measured by a wet test flow meter and the composition determined by gas chromatography. With this reactor configuration, they assessed the effect of the major operational variables such as coking temperature (1000 - 1200 °F) and steam-to-resid ratio (0.15 to 0.30). In general, coke yield decreased with increasing temperature. The liquid yield was found to remain relatively constant over the range of temperatures tested. As expected, the gas yield increased with increasing temperature. The steam-to-resid ratio had no effect on the product yield distribution.

More recently, Lummus-Crest Inc. conducted CSCU tests to process vacuum bottoms resid and established the hydrogen donor properties of the resulting coker distillate liquids. In general, the coker product liquids were found to be poor hydrogen donors and had a low solvent quality index (SQI). With increasing coking temperature, the SQI of the liquids decreased. Some of the liquids produced at the higher temperature, namely those with the lowest SQI, were hydrotreated in a micro-autoclave reactor. On hydrotreating, the calculated SQI of the coker liquids produced from an Ohio #6 feedstock increased from 51.7 to 85.9. Similarly, hydrotreating a coker liquid from an Illinois #6 coal, using a stirred autoclave, increased the SQI from 51.0 to 97.7. Although the number of data points from the hydrotreating tests were relatively few, there seemed to be promise for upgrading the coker liquids for use as an improved recycle solvent.

Program Plan

A research program was initiated to develop data from which an economic evaluation could be made for substituting fluid coking for a ROSE unit. Coking experiments were carried out at the CAER using existing equipment that was modified to conduct these experiments. Samples of product collected in these runs were then distributed to both CONSOL and Sandia National Laboratory for analysis and further treatment. Results from this program provided data from which an economic evaluation was conducted.

Experimental Apparatus

An existing 3 inch fluidized retort that was available at the CAER was modified to evaluate the coking of V-1082 ashy resid from the Wilsonville pilot plant. The objective was to determine the level of conversion that could be attained and to produce larger quantities of coker overhead for subsequent analysis and testing. In the CAER reactor, external agitation of the alumina bed was not needed, as was the case in the Exxon CSCU, since the velocity of the steam through the reactor was adequate for fluidization.

The reactor scheme for this unit is shown in Figure 10-2. The V-1082 ashy-resid feedstock was prepared by first cooling with liquid nitrogen to prevented the material from melting and then grinding to a mean particle size of less than 120 μm. This finely ground material was mixed with an alumina seed material of similar particle size. The optimal resid-to-alumina ratio was determined during the initial shake-down period of the program. During operation the alumina/resid mixture was fed into an eductor device via a calibrated screw feeder and transported in nitrogen from the eductor to the reactor fluidized bed zone. As soon as the resid particles enter the fluid bed, they melt and subsequently coke onto the alumina particles. The height of the fluidized bed zone was controlled by varying the length of an overflow tube in the center of the reactor. Coked particles were continuously withdrawn from the bottom of this tube to maintain the reactor material balance.

A mixture of steam and nitrogen was used as the fluidizing gas. These gases were heated in the pre-heater furnace to a specified temperature upstream of the fluidized bed. Heat trace lines surrounding the reactor were utilized to maintain constant fluid bed and freeboard temperatures. A two-stage recovery section, similar to that of the Exxon CSCU, was used to trap the coker tars and light oils.

Shakedown Runs

Seven shakedown runs were completed using the 3-inch fluid bed reactor system. During these runs the mechanical systems of the modified fluid bed reactor were tested, a tar sample preparation procedure was developed, and small samples of less than 50 g were prepared for

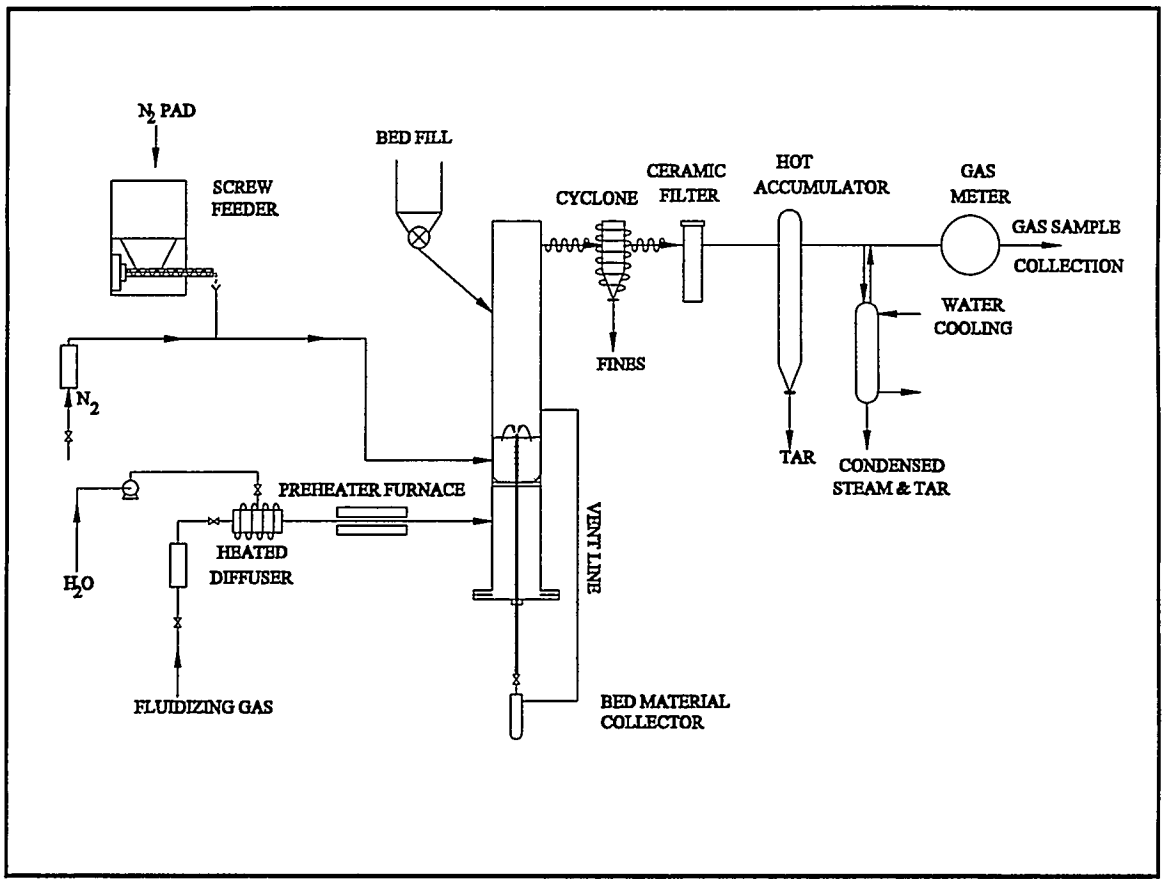


Figure 10-2. Schematic of the CAER 3-inch Fluidized Bed Coker Unit

subsequent analysis. A fabricated screw feeder system was utilized for the first shakedown tests.

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

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

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

Shakedown Runs SR-3 to SR-5 - The objective of these runs was to produce a series of scouting coker tar samples for subsequent analysis by CONSOL. A modified feed nozzle clean-out port was installed so that the feed tube could be cleared during the run. The operating conditions and approximate tar yields for the scouting samples are displayed in Table 10-1. Only the resid flow rate was varied during these tests while the steam rate was held constant (i.e. the

fluidizing velocity was a constant 0.3 m/s). The tar yield appears to be proportional to the steam/resid ratio. All of the samples were initially dissolved in methylene chloride and subsequently filtered to remove any alumina particulate matter that may have been present. CONSOL found that these samples still contained a significant amount of water.

Table 10-1. Scouting Sample Run Conditions

Sample Number	Steam/Resid Ratio(lb/lb)	Coking Temperature, °C	Tar Yield, % (tentative)
B9301	4.39	500	43
SR-3	8.52	500	44
SR-4	12.34	500	46
SR-5	13.01	500	53

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

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

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

testing in run SR-7.

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

A schematic of the modified reactor used for this run is shown in Figure 10-3. The ceramic filter used in run SR-1 was moved to the exit of the sample recovery train; this was to capture the aerosol particulate before the non-condensible gases entered the wet test meter. The resid inject nozzle remained clear throughout the entire run period of 30 minutes. However, the run was aborted due to the accumulation of tars in the ice bath and condensers in the sample recovery section of the apparatus; this created an excessive back pressure in the reactor vessel. In this run the nominal residence time of the gas in the reactor was ~0.25 sec and the average solids residence time was 15 to 20 min which is equivalent to the residence time of the unconverted resid.

Analysis of Samples

Because of the water present in these samples as received at CONSOL, the samples were then dissolved in THF, filtered and the solvent removed on a rotary evaporator. The analytical results and data analyses provided by CONSOL are shown in Table 10-2 and discussed below.[2]

The elemental analyses of the THF-solubles, which was 98% or greater for all three samples, showed little difference from the V-130 or V-1082 materials. The H/C ratio of the overheads

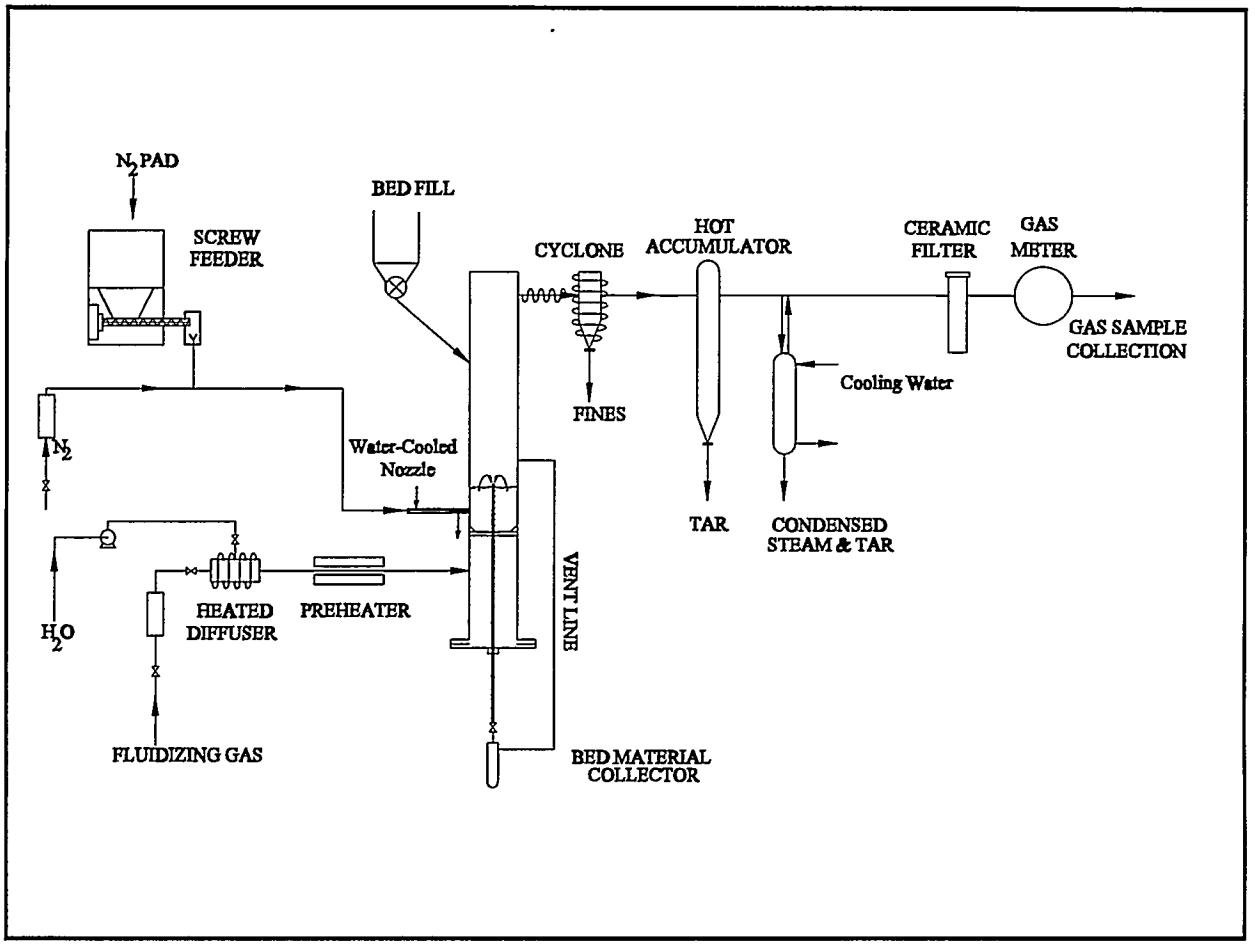


Figure 10-3. Schematic of the CAER 3-inch Fluidized Bed Coker Unit (with water cooled nozzle)

Table 10-2. Analysis of Coker Overheads and Feedstocks						
	V-1082[c]	V-130	B9301	SR-3	SR-4	SR-5
Total Moisture, wt%				22.10	6.02	4.13
Total Ash, wt % dry[a]	20.28 (16.04)			1.38	1.62	1.43
THF Insol org matter, wt % dry				0.21	0.02	0.12
THF Insol Ash, wt% dry[a]				0.43	0.04	0.29
Analysis of dry THF Solubles, wt %[b]						
Carbon	72.59	89.79		87.53	86.59	87.23
Hydrogen	5.40	7.26		6.95	6.97	6.89
Nitrogen	0.88	0.86		1.11	1.11	1.08
Oxygen (diff)	-1.08 (3.15)	1.33		3.53	5.07	3.99
Sulfur	1.93	0.03		0.05	0.04	0.03
Ash[a]	20.28 (16.04)	0.73		0.83	0.22	0.78
Phenolic -OH Anal. of dry THF Solubles						
Conc., meq/g	0.96	0.90		0.77	0.78	0.81
ϑ cm^{-1}	3296	3298		3296	3295	3295
Proton Distribution of THF Solubles, % [d]						
Cond Arom			21.4	26.6	25.9	25.4
Uncond Arom			7.8	7.4	8.4	9.8
Cyclic Alpha			15.7	18.6	18.0	16.9
Alkyl Alpha			9.8	9.4	9.7	10.2
Cyclic Beta			12.6	13.7	13.1	12.9
Alkyl Beta			22.1	15.9	16.4	16.5
Gamma			10.7	8.3	8.5	8.4
Solubility Fractionation Analysis of THF Solubles						
Oils			80.7	73.0	77.8	76.9
Asphaltenes			12.4	17.2	16.3	16.1
Preasphaltenes			6.9	9.8	5.8	7.0
Solvent Quality Index			75.5	83.3	81.4	79.5

a. Total ash and sum of soluble and insoluble ash do not agree because of analytical uncertainties.
b. Analysis of V-130 and V-1082 are analysis of whole samples, i.e., not THF solubles.
c. Values in parentheses are based on SO_3-free ash.
d. Analyzed in $CDCl_3$ solution.

is the same as that of the V-130 and slightly higher than that of the V-1082, which contains insolubles. There is possibly a several percent increase in oxygen content in the overheads. However, the phenolic −OH concentration is slightly lower in the overheads than in the feedstock.

The proton distributions indicate the products are somewhat less paraffinic, slightly less naphthenic, and slightly more aromatic than the THF solubles in the feedstock. This suggests some loss of paraffins or alkyl side chains and some aromatization. This is as would be expected for products of coking. For example, these are the same directional changes observed in the Lummus-Crest results. However, the changes are small. The absence of any significant differences from the feedstock indicates that these overheads are not products from cracking but were likely produced substantially by steam distillation accompanied by some entrainment.

Solvent quality values were obtained based upon a previously developed correlation between proton distribution and donor solvent quality. The values did not differ from those of the starting materials. The high paraffinicity of the B9301 sample overhead contributes to its relatively low calculated value.

Solubility fractionation also gave generally similar results for each of the products with no clear trend. All four samples have lower concentrations of preasphaltenes and asphaltenes and higher concentrations of oils than the THF-soluble portion of the feedstocks. Coking, therefore, appears selective for oils relative to preasphaltenes and asphaltenes.

Table 10-3 provides comparisons of the SR-3 coker run and the Lummus continuous stirred coker Run CSCU-8. This Lummus run was conducted at 544 °C, the lowest temperature that was examined. The Lummus steam/feed ratio of 0.5 was lower than in SR-3. The feedstock for Run CSCU-8 was bituminous coal, yet its characteristics were similar to the Run 262E feed material from Black Thunder coal. The overhead yields from the two runs were quite similar

Table 10-3. Comparison of Lummus and SR-3 Coker Runs				
	Lummus		SR-3	
Wilsonville Feedstock	Run 254 Vac Bottoms		Run 262E V-1082	
Temperature, °C	544		500	
Steam/Feed Ratio	0.34		8.52	
Overhead Yield, wt %	44.5[a]		44[b]	
Characteristics	Feed	Coker Overhead	Feed	Coker Overhead[c]
Ash, wt %	15.4		16.0	
Carbon, wt% maf	88.1	91.0	86.5	88.3
Hydrogen, wt% mfa	6.5	6.3	6.4	7.0
Nitrogen, wt % maf	1.0	1.0	1.0	1.1
Sulfur, wt % maf	2.6	0.1	3.8	0
Oxygen (diff)	1.8	1.6	2.3	3.6
Insol org matter, wt % maf	9.2		25.1	
Proton Distribution				
Aromatic %	29.5	42.1	28.9	34.0
Cyclic Beta%	14.6	10.3	14.5	13.7
Paraffin %[d]	25.8	21.4	26.4	24.2
Solvent Quality Index	82.6	68.8	85.4	83.3

a. wt % ash-free recovered material
b. Tentative
c. All analyses on SO_3-free basis
d. Alkyl beta plus gamma

at about 44%. Although the feedstocks were similar, the coker overheads from the two runs differed. The Lummus overhead is more aromatic, contains less hydrogen, and has a lower calculated solvent quality index.

The composition of recoverable product as well as its yield in the SR-3 run was essentially the same as produced by the ROSE unit in the base case. The absence of any significant reduction in boiling point fails to provide any additional yield of distillate. It was concluded that since the experimental results were essentially the same as the Lummus results, per analysis by CONSOL, additional experimental results would be of no further benefit for the economic analysis.

References

1. Exxon Research and Engineering, "Fluid Coking of Coal Liquefaction Residues", Interim Technical Progress under U.S. DoE Contract No. EX-76-C-01-2422, October 1978.

2. CONSOL, Inc. Quarterly Progress Report, Subcontract No. UKRF-4-25582-92-76, Jan. - Mar. 1993, p. 17-21.

Chapter 11
Reaction Model Development

Introduction

A kinetic model for coal liquefaction was developed in order to provide a more comprehensive organization of the results in order to allow for better comparison and evaluation of experimental data. From this model changes in reaction parameters can be quantified and the effect of catalysts on these parameters can be measured. Results that were obtained at 415 °C in both tetralin and full range Run 262E V-131B recycle solvent were used to assess the suitability of the proposed model.

A considerable background exists on the development of kinetic models for coal liquefaction. As early as 1951, Weller and his coworkers[1] suggested a sequential reaction model to explain liquefaction of bituminous coals. This model proposed the initial conversion of coal to asphalt which was subsequently converted to oils.

$$\text{coal} \xrightarrow{k1} \text{asphalt} \xrightarrow{k2} \text{oils}$$

These invariant "lumps" in the reaction sequence were defined by a solvent classification system. They also identified a "refractory organic material which is not liquefied, even at long reaction times." This quantity was accounted for in the rate equation by reducing the amount of moisture and ash free coal present at zero time.

Later, Curran et al.[2], working with a bituminous Pittsburgh seam coal and tetralin in the 324 to 440 °C range, developed a rate expression for the dissolution of coal. The coal was dissolved by solvent extraction in air in batch microautoclaves. Conversion was measured by extracting the products with xylenol at 220 °F. Here the authors identified three coal fractions: labile, refractory and unreactive. These were incorporated into a rate expression, as shown

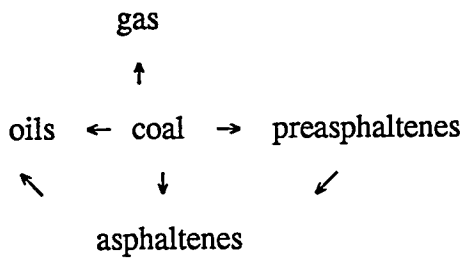
below, where γ represents the fractional part of labile coal in the overall reactive portion of the coal and k1 and k2 are the corresponding rate constants for the labile and refractory portions of the coal.

$$C_T\text{-}C = \gamma C_T e^{-k1t} + (1\text{-}\gamma)C_T e^{-k2t}$$

The unreactive fraction is implicit in the C_T term, which represents the ultimate possible conversion of the coal (in this case 91%).

In 1979, Brunson[3], using data from a 50 lb/day integrated donor solvent pilot plant operating on Illinois No. 6 coal between 370 and 480 °C, developed a kinetic model in terms of an empirical classification of four reactive coal constituents: γ, α, β, ω. The first fraction, γ, converts instantaneously and is determined by carbonizing a sample of feed coal in a distillation procedure. The α and β fractions correspond roughly to typical preasphaltene and asphaltene fractions, while the ω fraction is unreactive. This last fraction includes ash and is determined by petrographic analysis of the coal.

Cronauer and Ruberto[4], using Belle Ayr subbituminous coal at 400 to 470 °C in hydrogenated anthracene oil (and in other oils) proposed the following kinetic model with six pseudo first order, irreversible rate constants:



This model is similar to others previously reported, except that gases and a portion of the asphaltenes are assumed to be formed directly from coal. This model also includes an unconvertible weight fraction of coal, C_{un}.

Pradhan et al.[5] proposed a kinetic model to evaluate finely divided catalysts using Wyodak coal in tetralin. This model was similar to the Cronauer and Ruberto model, but did not have as many lumped product fractions. Gases were not analyzed and were calculated by difference. While allowing both series and parallel conversion pathways to oils, they also incorporated parallel catalytic pathways. Again, an unreactive maf coal fraction was included for each temperature in a particular solvent.

A more detailed review of coal liquefaction modelling is found elsewhere[6].

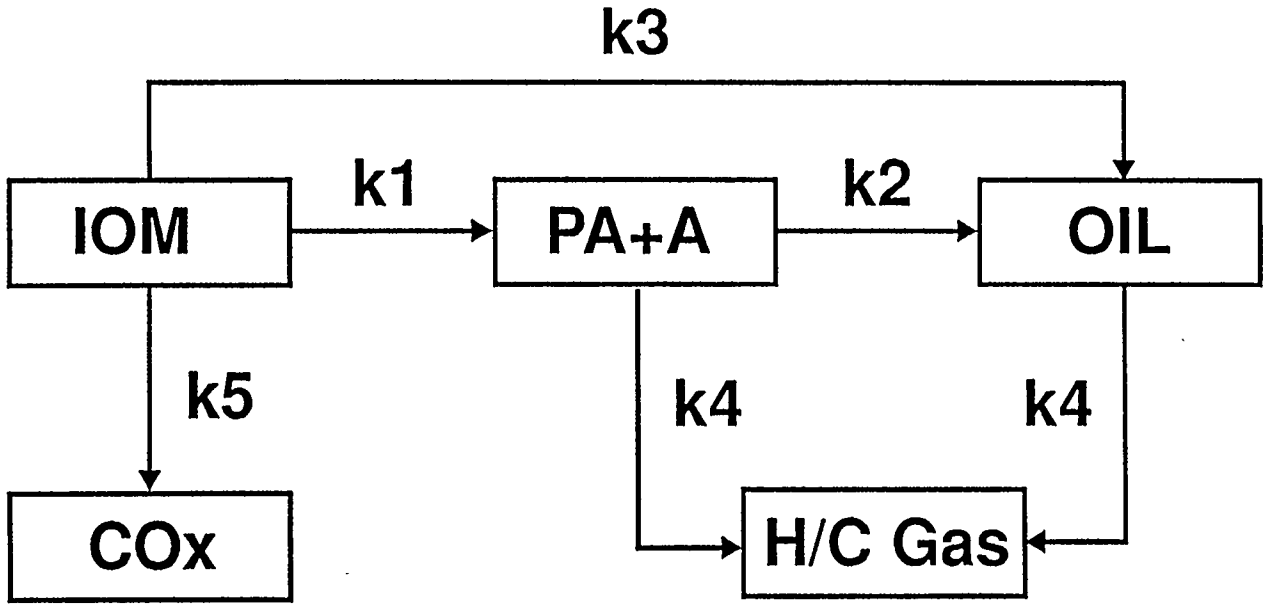
Kinetic Model - The model proposed here is similar to the one proposed by Cronauer and Ruberto with the following exceptions; the preasphaltenes and asphaltenes are treated collectively (PA+A), the carbon oxide gases (CO and CO_2) are assumed to be formed directly from the coal, and the hydrocarbon gases (CH_4 to C_2H_6) are formed from conversion of PA+A and oils together. As shown in Figure 11-1, IOM is converted to oils, PA+A and CO_x and its disappearance is proportional to rate constants k1, k3, and k5. Since PA+A is converted to other products it goes through a maximum. Its rate of formation is a function of k1 and the concentration of IOM and its disappearance is proportional to rate constants k2 and k4. Note that oils are formed from PA+A as well as directly from IOM. Hydrocarbon gases are formed from PA+A and oils and their concentration is proportional to rate constant, k4.

In the model presented here, an unreactive IOM fraction, $I\omega$, is included which is defined by the IOM remaining at maximum coal conversion in a specific solvent at a particular reaction temperature. For example, $I\omega$ is a fixed value for reactions at 415 °C in tetralin, regardless of the catalyst used, but is different for reactions in Run 262E V131B recycle solvent at 415 °C. Listed below are values of $I\omega$ for three reaction systems at 415 °C.

Reaction systems	$I\omega$
Coal in tetralin, wt% maf coal	10.1
Recycle solvent without coal, wt% total feed	7.9
Coal in recycle solvent, wt% maf coal	5.6

Figure 11-1

Coal Dissolution Kinetic Model



I_ω = unreactive coal fraction

This parameter is important since it determines the agreement of the IOM model with the data at 60 minutes reaction time, which is about 8 half-lives with respect to the disappearance of IOM.

In short, the model will appear successful if it provides:

- Agreement with experimental data at short reaction times, since we have considered both labile and the more refractory IOM fractions as one.

- Agreement with gas yield data.

- Good agreement with experimental yields in general, in view of considering each fraction, regardless of source (e.g., PA+A freshly derived from coal and that exposed to severe hydroliquefaction conditions), as having the same reactivity.

Treatment of Data - Using the kinetic model shown in Figure 11-1, a system of ordinary, first order, linear differential equations was formulated to describe the reaction rates for five reactants and products: IOM, PA+A, oils, hydrocarbon gases, and $CO+CO_2$. Each reaction step is irreversible and assumed to be first order with respect to reactant concentration. The concentration of each reactant as a function of time is provided through integration and rearrangement of these five rate equations. Each of these five equations is thus one component of the model for the overall system. An example of one of these individual product fraction equations in the model is the one for IOM, which is a function of k1, k3, and k5, but not k2 or k4. Using the outcome of liquefaction experiments conducted for a series of prescribed times (e.g., 7½, 15, 30, or 60 minutes), simultaneous solution of this set of equations yields a set of rate constants, k1...k5.

Ideally, in the absence of experimental error and with a perfect model, each experiment would provide the same value of k1...k5. However, in practice the k's vary, and each time period

yields k's that fit a particular time period best. A constrained non-linear regression analysis was used to minimize the residual sum of squares (RSS), which were the sum of residuals squared $(Y_{model}-Y_{exp})^2$ for each individual product fraction, to give the best overall fit. Total residuals were considered at a minimum when any individual element of the model began to fit poorly, for example, if a "multiple correlation coefficient squared value" began to deviate below 0.85 (the "constraint"). This was required since the minimum RSS value was found without regard to the smaller gas fractions, which do not contribute much to the overall "total sum of squares".

The "multiple correlation coefficient squared value" of the model, or R^2, was calculated as one minus the ratio of the "sum of the residuals squared" to the "total sum of squares". This value indicates the deviation about the mean which can be accounted for by the kinetic model. Initial concentrations of each reactant/product are included in this calculation, since the fit of the model to the initial conditions is an important aspect of the overall model correlation.

Results

Liquefaction in Tetralin - Table 11-1 shows the results of coal liquefaction experiments at 415 °C using Black Thunder coal in tetralin without any added catalyst or sulfur. Experiments were conducted at 7½, 15, 30 and 60 minutes. Figure 11-2a shows the results of a regression analysis of the data for both IOM and PA+A concentrations as a function of time. The PA+A model provides good agreement with the experimental data. However, the IOM model does not provide a good fit to the short run-time data. Further, Iω is somewhat low for thermal runs without catalyst, which is apparent in the 60 minute conversion data. However, the overall R^2 value for the model is 0.941, indicating good agreement for all fractions. Predicted and experimental values for oils are shown in Figure 11-2b, while the corresponding data for $CO+CO_2$ and HC gases are given in Figure 11-2c.

Liquefaction results on a 0.77 wt % iron incipient-wetness impregnated as-received coal, that were run under the same conditions as the thermal case in Table 11-1, are shown in Table 11-2. The liquefaction results with this impregnated coal were improved over the coal itself, as was

Table 11-1. Thermal Liquefaction of Black Thunder Coal in Tetralin[a] Products of Reaction				
Reaction temp, °C	415	415	415	415
Reaction time, min	7.5	15	30	60
Catalyst added	none	none	none	none
Products, wt% maf Coal				
HC Gases	0.3	0.4	0.7	1.0
$CO+CO_2$	3.9	4.2	4.4	4.9
Oils	21.7	20.7	28.0	43.4
PA+A	28.2	41.0	43.6	35.8
IOM	45.9	33.7	23.3	14.9
THF Conv	54.1	66.3	76.7	85.1
mg H_2/g maf Coal	31.3	30.0	28.0	36.2
Run number	3-76-1	2-154-2	2-154-1	2-160-2
a. 3 g Black Thunder coal, 5.4 g tetralin, 6.89 MPa H_2 cold.				

discussed previously.[7] A model was developed using a Iω value taken from the 60 minute IOM value. The overall fit of the model is much improved over the first case discussed above having an overall R^2 of 0.994. The fit of the data to the model are shown in Figure 11-3. In Figure 11-3a the fit of the IOM is quite good at 60 minutes with the 30 minute data showing some departure. Oil yields are excellent with PA+A deviating at 30 minutes. The data for gases shown in Figure 11-3b are in good agreement with the experimental data.

Comparing the rate constants for the thermal and the IW-impregnated Fe coal showed a 46% increase for the value for k1 for the IW-impregnated Fe coal (see Table 11-3), while much smaller changes were observed in the other rate constants, which may be an artifact of the curve fitting procedure.

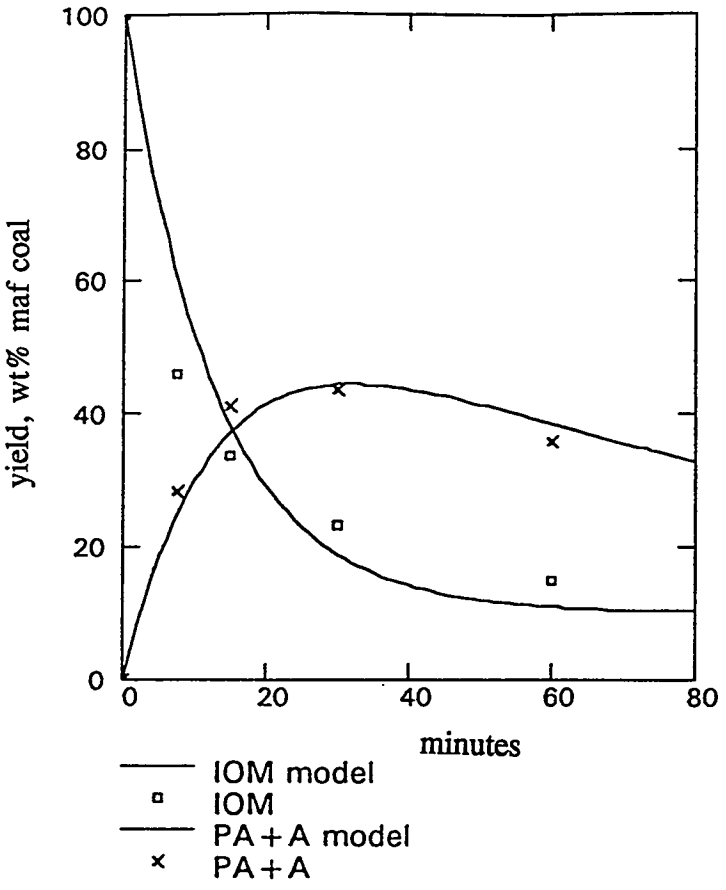
Figure 11-2a

IOM and PA+A yields from liquefaction of Black Thunder Coal in tetralin at 415°C

Rate constants, 1/min

k1 · 1000 = 50.278
k2 · 1000 = 8.3
k3 · 1000 = 22.826
k4 · 1000 = 0.336
k5 · 1000 = 4.477

RSquared = 0.941



IOM and PA+A yields (wt% maf coal) from thermal liquefaction of Black Thunder Coal in tetralin at 415 C, versus time.

Figure 11-2b

Oil yield from liquefaction of Black Thunder Coal in tetralin at 415°C

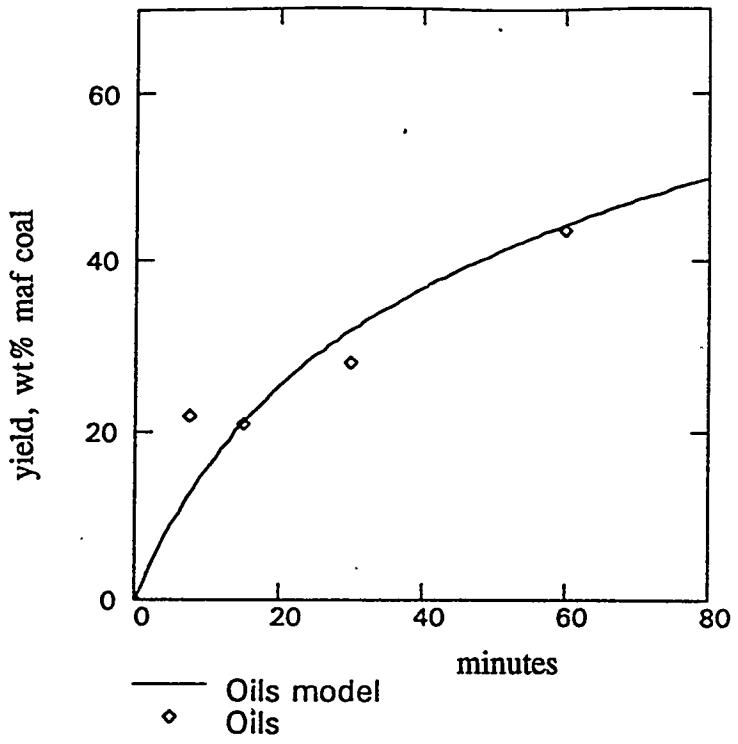


Figure 11-2c

Gas yield from liquefaction of Black Thunder Coal in tetralin at 415°C

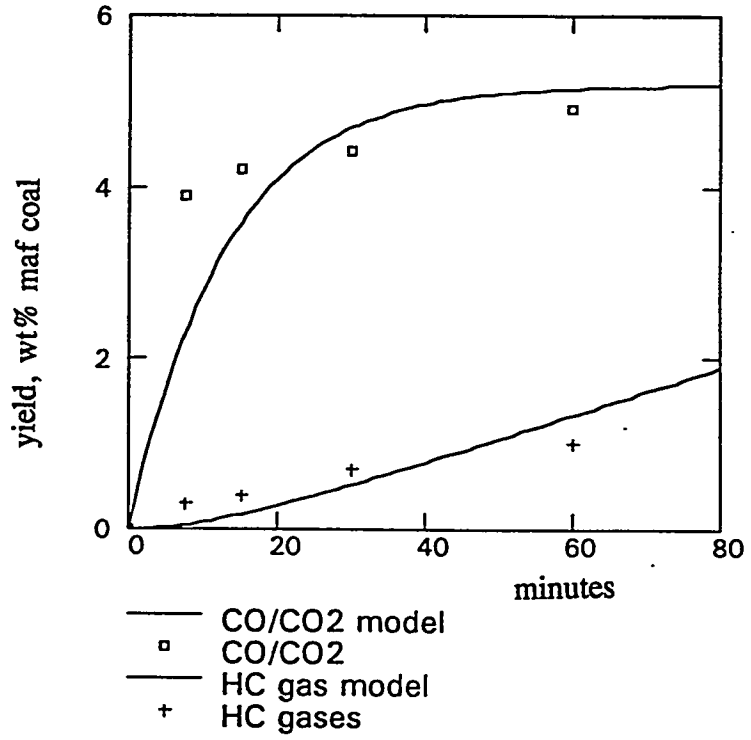


Table 11-2. Fe Catalyzed Liquefaction of Black Thunder Coal at 415°C in Tetralin[a] Products of Reaction			
Reaction time, min	15	30	60
Added Fe, wt% dry Coal[b]	0.77	0.77	0.77
Added S, wt% dry Coal	1.62	1.63	1.64
S/Added Fe, m/m	3.69	3.69	3.71
Products, wt% maf Coal			
HC Gases	0.8	1.1	1.3
$CO+CO_2$	3.3	3.4	3.4
Oils	18.6	28.5	38.9
PA+A	49.4	48.6	46.1
IOM	27.9	18.4	10.3
THF Conv	72.1	81.6	89.7
mg H_2/g maf Coal	37.3	39.6	44.6
Run number	2-226-1	2-227-1	2-226-2
a. 3 g Black Thunder coal, 5.4 g tetralin, 6.89 MPa H_2 cold. b. 0.77 wt% Fe in FeOOH, prepared by incipient wetness/ precipitation.			

Table 11-3. Summary of Rate Constants[a] k x 1000, min^{-1}		
	Thermal/ tetralin	0.77% IW Fe/ tetralin
k1	50.3	73.2
k2	8.30	6.98
k3	22.8	23.7
k4	0.34	0.43
k5	4.48	4.49
$I\omega$	10.1	10.1
a. k's were calculated from regression analysis.		

Reactivity of Wilsonville Recycle Oil - The model has been applied to liquefaction of coal in Wilsonville V-131B recycle solvent taken from Run 262 when running with Black Thunder coal. Both iron oxide and Molyvan L were added at Wilsonville during the run. First, the reactivity of the Run 262E V-131B under liquefaction conditions in the absence of coal and any added catalysts was determined. Data for reactions conducted for 3¾, 7½, 15, 30, and 60 minutes are shown in Table 11-4.

A model was developed for reaction of the Run 262E V-131B in the absence of coal. Figure 11-4 shows the experimental data as it compares with the model. Since the initial conversion of the IOM reaches 23% within 3¾ minutes and increases further to only 33% after 60 minutes, this model fails to provide a good fit to the IOM plot shown in Figure 11-4a. Likewise, the model fails to accurately describe the behavior of the PA+A fraction. In fact, the actual data passes through a minimum rather than a maximum as predicted by the model. Oppositely, the oils model predicts a steady increase, as seen in Figure 11-4b, rather than the observed rapid increase followed by the subsequent decrease after 10 to 15 minutes, presumably via retrogressive reactions. There is, however, good agreement between predicted values and actual concentrations of the gas fractions as shown in Figure 11-4c. Note here that CO and CO_2 approach their final concentration (0.07% maf recycle solvent) at the shortest reaction time. However, the uniform though small hydrogen consumption over this entire range of reaction times indicates that hydrogen consumption occurs at the shortest times and then fails to increase any further. Overall, the model provides a very poor fit to the observed concentrations of the various fractions, which means that it fails to describe the reactions that are occurring here.

The very rapid IOM conversion at these short reaction times suggests that these changes are not related to conversion of coal macerals, but appear to be related to a rapid solubilization of a significant portion of the IOM fraction of the Run 262E V-131B. This transformation does not appear to be related to hydroliquefaction. In order to determine whether this phenomena is a mere resolubilization of predissolved coal macerals, tests were run at lower temperatures for 15 min in N_2 and H_2 and compared with results at 415°C (see Table 11-5).

Figure 11-3a

IOM, PA+A and oil yields from liquefaction of IW-impregnated Fe on Black Thunder Coal in tetralin at 415°C

Rate constants, 1/min

k1 · 1000 = 73.234
k2 · 1000 = 6.979
k3 · 1000 = 23.694
k4 · 1000 = 0.432
k5 · 1000 = 4.491

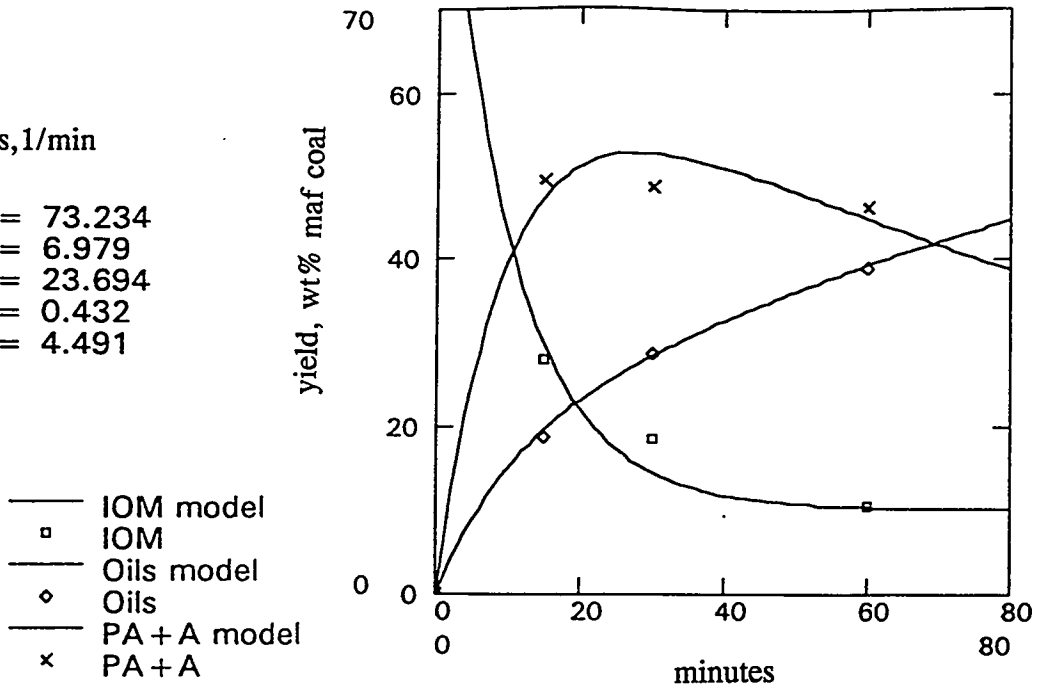


Figure 11-3b

Gas yields from liquefaction of IW-impregnated Fe on Black Thunder Coal in tetralin at 415°C

RSquared = 0.994

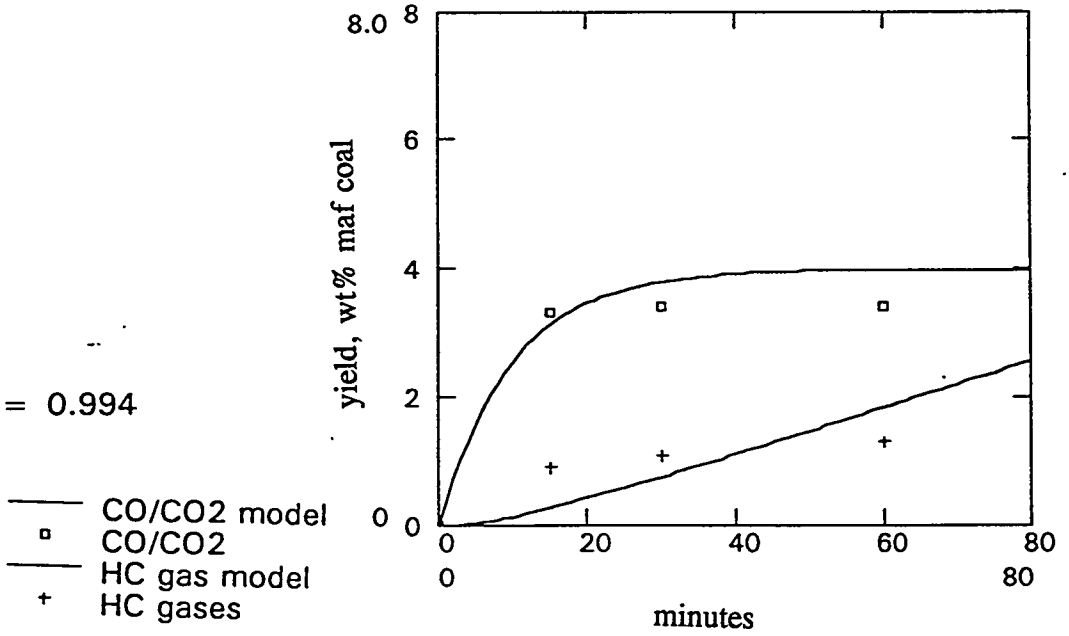
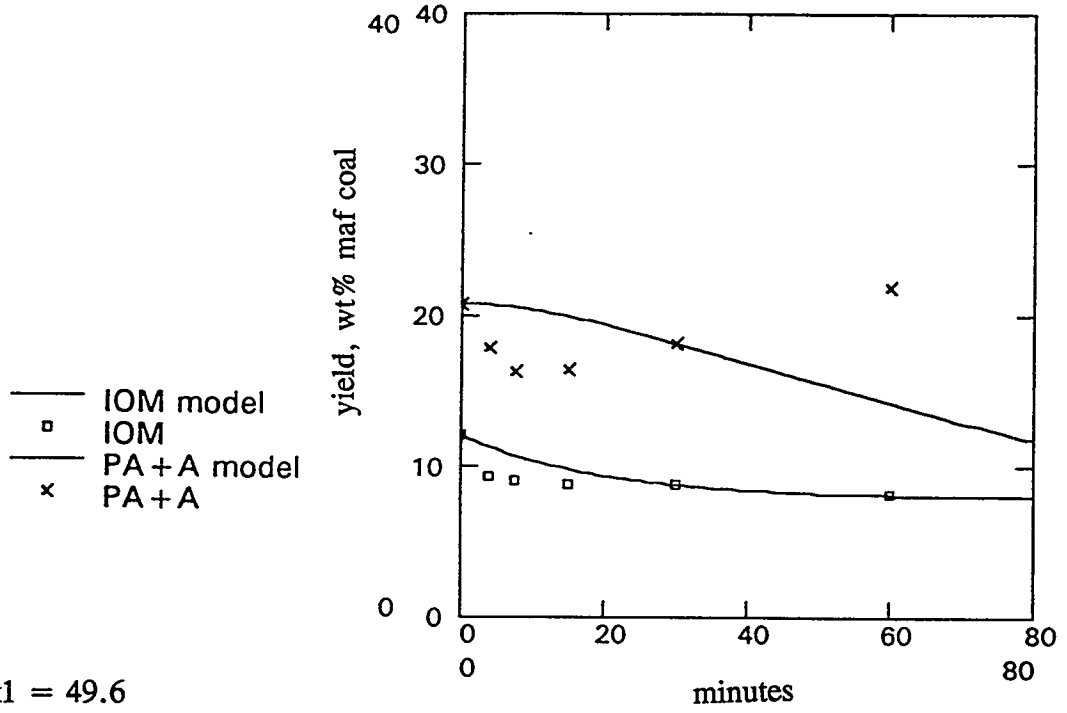


Table 11-4. Thermal Liquefaction of Recycle Solvent at 415°C[a]						
Reaction time, min	-	3¾	7½	15	30	60
	Reactants	Products	Products	Products	Products	Products
wt% maf Run 262E V-131B						
HC Gases	0.0	0.03	0.04	0.09	0.15	0.31
$CO+CO_2$	0.0	0.07	0.06	0.07	0.10	0.07
Oils	67.2	72.7	74.5	74.7	72.8	69.7
PA+A	20.8	17.9	16.4	16.4	18.2	21.8
IOM	12.1	9.3	9.0	8.7	8.8	8.1
THF Conv	87.9	90.7	91.0	91.3	91.2	91.9
mg H_2/g maf Run 262E V-131B	-	10.2	9.0	12.3	11.7	12.8
% IOM Conversion	-	23.3	25.2	28.1	27.4	32.7
Run number		3-188-2	3-188-1	3-188-3	2-155-2	2-140-1
a. No coal, 5.4 g Run 262E V-131B, 6.89 MPa H_2 cold.						

Table 11-5. Thermal Liquefaction of Recycle Solvent at 15 minutes[a]				
Gas	-	H2	N2	H2
Temperature, °C		300	300	415
	Reactants	Products	Products	Products
wt% Recycle Solvent, maf				
Gases	0.0	0.02	0.04	0.15
Oils	67.2	71.0	68.3	74.7
PA+A	20.8	20.0	22.0	16.4
IOM	12.1	9.0	9.7	8.8
Run number		3-189-1	3-200-1	3-188-3
a. No coal, 5.4 g Run 262E V-131B, 6.89 MPa gas cold.				

Figure 11-4a

IOM and PA+A yields from heating Run 262E V-131B at 415°C



k1 = 49.6

k2 = 9.656

k3 = 0.192

k4 = 0.054

k5 = 1.556

Figure 11-4b

Oil yield from heating Run 262E V-131B at 415°C

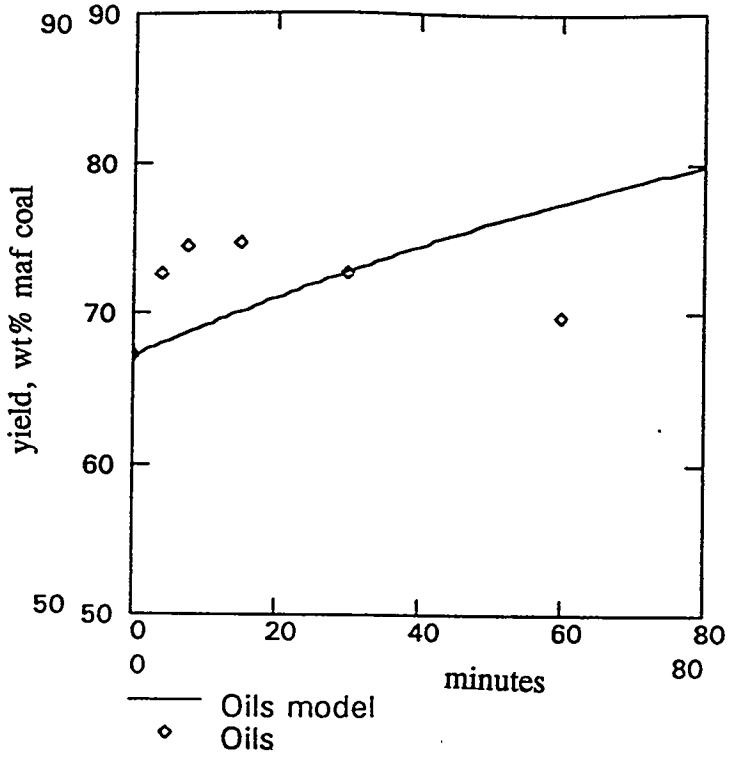
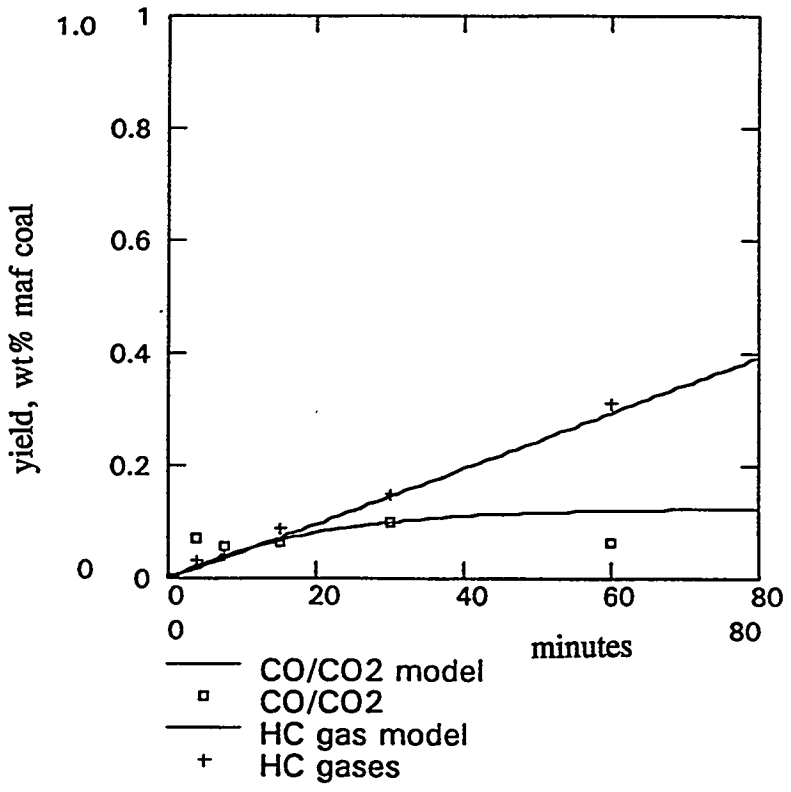


Figure 11-4c

Gases yield from heating Run 262E V-131B at 415°C



IOM decreased in nitrogen at 300 °C, almost to the same extent as in hydrogen at 415 °C. In hydrogen at 300 °C the remaining IOM was the same as observed at the higher temperature. The only difference in these two runs was a higher oil yield at the higher temperature. There was also a slightly higher oil yield in hydrogen versus nitrogen at the lower temperature.

Coal Conversion in Recycle Solvent - Results from coal liquefaction in the absence of any added catalysts in Wilsonville Recycle Oil from Run 262 are presented in Table 11-6. As mentioned previously, the concentrations of iron and molybdenum in the ashy resid were quite high. The concentration of iron was 4.4 wt% maf coal and the concentration of molybdenum was 404 mg/kg maf coal. The best fit using the model with an Iω value of 7.9 was determined and is compared with the experimental data (see Figure 11-5). It is apparent that the mixture of coal and Run 262E V-131B provides good agreement with the experimental data for IOM, PA+A and oils as shown in Figure 11-5a. R^2 was calculated to be 0.977. The model provides a good fit for the gas fractions as shown in Figure 11-5b.

Data on liquefaction of Black Thunder coal with added catalyst are summarized in Table 11-7. In these runs 1.0 wt% Fe contained in superfine iron oxide (SFIO) on as-received coal in Run 262E V-131B to which was added 2.6 mol S/mol Fe as DMDS. At 60 minutes, total conversion is 1.3% higher and oils yield is 5.4% higher on an maf coal basis than in the case without added SFIO and sulfur. These experimental data provide an excellent fit to the model as shown in Figure 11-6 giving an R^2 value of 0.991.

Adjustment of Solubility Fractions

Since a portion of the IOM is immediately soluble in the process solvent at reaction temperature, the IOM and PA+A concentrations in the starting material were adjusted to reflect this change. IOM concentration in the starting solvent was adjusted downward to a level based upon the final IOM concentration observed in nitrogen after 15 minutes at 300°C. PA+A was adjusted upward by an equal amount. Rate constants for the thermal liquefaction of Black Thunder coal in Run 262E V-131B were determined based upon this revised feed composition. From these values,

Table 11-6. Thermal Liquefaction of Black Thunder Coal in Run 262E V-131B[a]

	Reactants	Products	Net Coal Yield[b]	Reactants	Products	Net Coal Yield[b]	Reactants	Products	Net Coal Yield[b]
Reaction Time, min	-	15	15	-	30	30	-	60	60
Wt% maf mixture/ (Coal)									
HC Gases	0.0	0.2	(0.5)	0	0.3	(1.1)	0	0.61	(1.9)
$CO+CO_2$	0.0	1.4	(4.5)	0	1.5	(5.0)	0	1.5	(5.0)
Oils	46.3	52.9	(21.3)	46.5	57.7	(36.4)	46.6	62.3	(51.3)
PA+A	14.3	32.2	(57.6)	14.4	31.7	(56.2)	14.4	29.2	(48.4)
IOM	39.4	13.3	(16.1)	39.2	8.7	(1.3)	39.0	6.4	(-6.6)
Total	100.0	100.0	(100.0)	100.0	100.0	(100.0)	100.0	100.0	(100.0)
THF Conv	60.6	86.7	(83.9)	60.8	91.3	(98.7)	61.0	93.6	(106.6)
Run number	2-148-2	2-148-2	2-148-2	2-167-2	2-167-2	2-167-2	2139-1 2167-1 2337-1	2139-1 2167-1 2337-1	2139-1 2167-1 2337-1

a. 415°C, 3 g Black Thunder coal, 5.4 g Run 262E V-131B, 6.89 MPa H_2 cold. No catalyst or sulfur added.
b. [Fraction, wt%] = 100 x [Wt. Fraction in Product - Wt. Fraction in feed]/[Wt. Coal, maf]

Figure 11-5a

IOM, PA+A and oil yields from liquefaction of Black Thunder coal in Run 262E V-131B at 415°C

Rate constants, 1/min

k1 · 1000 = 55.835
k2 · 1000 = 4.023
k3 · 1000 = 22.751
k4 · 1000 = 0.124
k5 · 1000 = 4.225

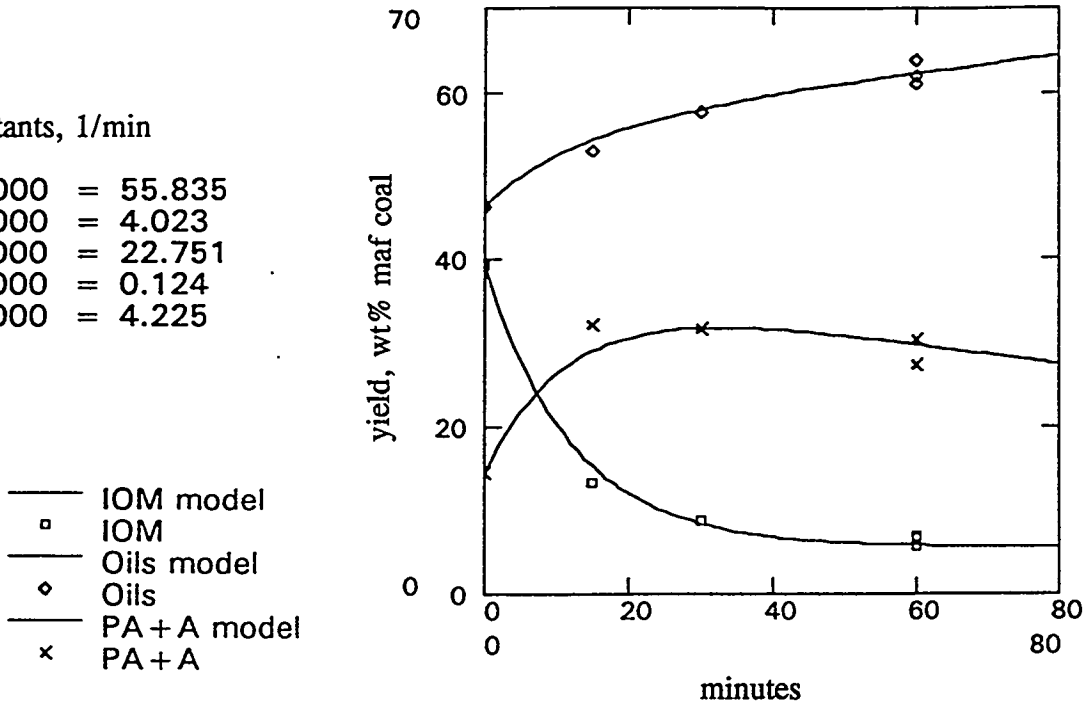


Figure 11-5b

Gases yields from liquefaction of Black Thunder coal in Run 262E V-131B at 415°C

RSquared = 0.977

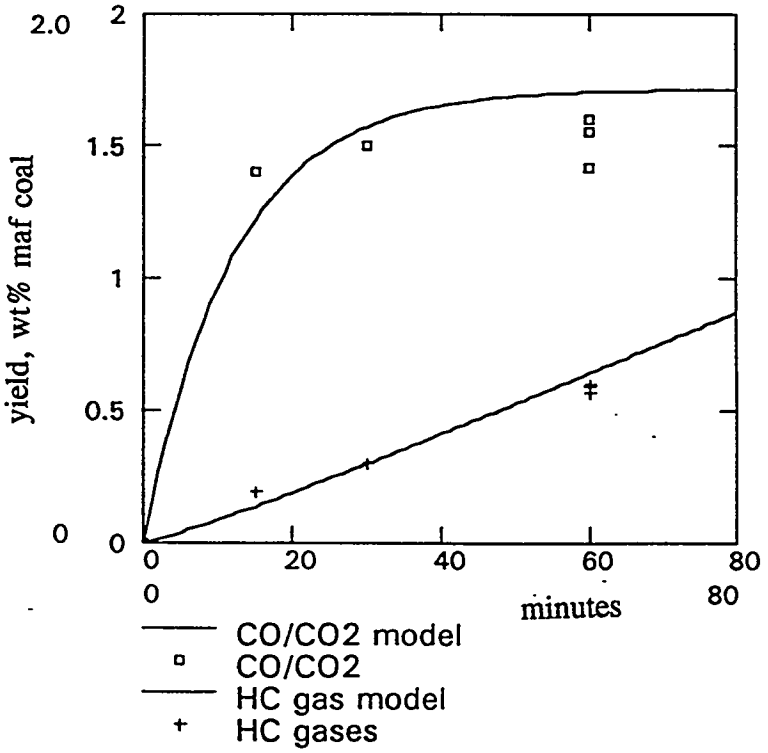


Table 11-7. Liquefaction of Black Thunder Coal with SFIO in Run 262E V-131B[a]

	Reactants	Products	Net Coal Yield[b]	Reactants	Products	Net Coal Yield[b]	Reactants	Products	Net Coal Yield[b]
Reaction Time, min		15			30			60	
Catalyst Added		SFIO			SFIO			SFIO	
Added Fe, wt% Coal		1.0			1.0			1.0	
Added S, wt% Coal		1.5			1.5			1.6	
S/Added Fe m/m		2.6			2.6			2.7	
Wt% maf mixture/(Coal)									
HC Gases	0.0	0.4	(1.2)	0.0	0.5	(1.7)	0.0	0.4	(1.2)
$CO+CO_2$	0.0	1.3	(4.1)	0.0	1.5	(4.9)	0.0	1.6	(5.0)
Oils	46.2	55.5	(29.7)	46.2	60.3	(45.1)	46.4	63.9	(56.7)
PA+A	14.3	31.3	(54.4)	14.3	30.7	(52.6)	14.3	28.3	(45.0)
IOM	39.5	11.6	(10.6)	39.5	7.0	(-4.3)	39.3	5.8	(-7.9)
Total	100.0	100.0	(100.0)	100.0	100.0	(100.0)	100.0	100.0	(100.0)
THF Conv	60.5	88.4	(89.4)	60.5	93.0	(104.3)	60.7	94.2	(107.9)
Run number	3-74-2	3-74-2	3-74-2	3-74-1	3-74-1	3-74-1	2-272-1	2-272-1	2-272-1

a. 415°C, 3 g Black Thunder coal, 5.4 g Run 262E V-131B, 6.89 MPa H_2 cold.
b. [Fraction, wt%] = 100 x [Wt. Fraction in Product - Wt. Fraction in feed]/[Wt. Coal, maf]

corresponding values providing a best fit were calculated. The experimentally observed values are shown in Figure 11-7 along with the k values providing the best fit.

The revised k values versus the unadjusted case are shown in Table 11-8. The biggest changes are in the values of k2 and k3 which increase and decrease by 20%, respectively. By increasing the initial concentration of PA+A the corresponding rate of disappearance of PA+A, k2, decreases. An explanation for the decrease in k3 is less straightforward but may be intertwined with the apparent shift of oils formation through the PA+A fraction. The 5% increase in k1 reflects the lower initial IOM conversion. The fit of the IOM data in the adjusted case in Figure 11-7a appears to be little changed from the earlier case in Figure 11−5a. There does, however, appear to be a slightly better fit of the PA+A and oils in the adjusted case in Figure 11-7a versus the non-adjusted case in Figure 11-5a.

Table 11-8. IOM Adjusted Rate Constants[a]
k x 1000, min^{-1}

	Thermal/ Run 262E V-131B	
	IOM Non-Adjusted	IOM Adjusted
k1	55.8	58.6
k2	4.02	4.8
k3	22.8	18.2
k4	0.12	0.12
k5	4.2	4.3
Iω	5.6	5.6

a. k's were calculated from regression analysis.

Overview

Each of the rate constants is summarized in Table 11-9. In going from tetralin to Run 262E V-131B, the values for k1 increases from 50 x 10^{-3} min^{-1} to 56 x 10^{-3} min^{-1}, which may be, in

Figure 11-6a

IOM, PA+A and oil yields from liquefaction of Black Thunder coal in Run 262E V-131B at 415°C with 1.3 wt% Fe in SFIO

Rate constants, 1/min

k1 · 1000 = 66.181
k2 · 1000 = 5.755
k3 · 1000 = 24.071
k4 · 1000 = 0.09
k5 · 1000 = 5.282

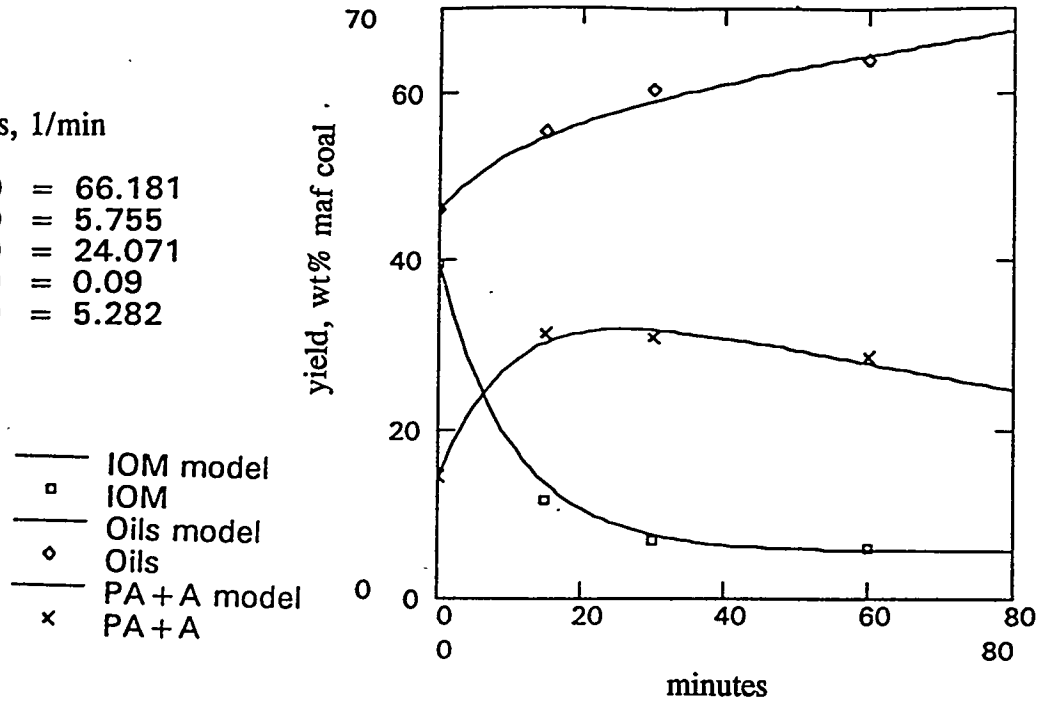


Figure 11-6b

Gases yields from liquefaction of Black Thunder coal in Run 262E V-131B at 415°C with 1.3 wt% Fe in SFIO

RSquared = 0.991

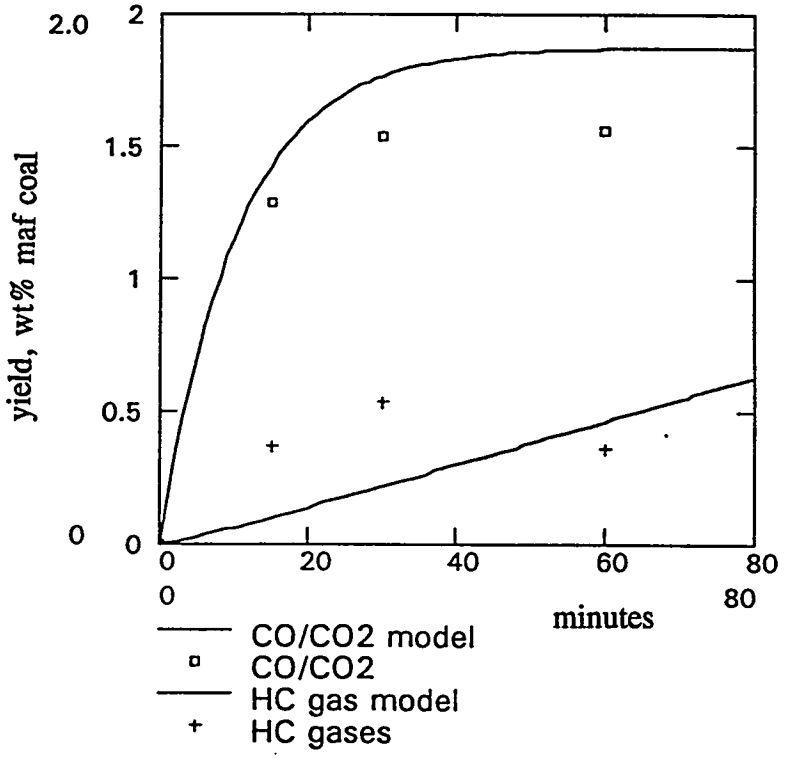


Table 11-9. Summary of Rate Constants[a] k x 1000, min^{-1}				
	Thermal/ tetralin	.77% IW Fe/ tetralin	Thermal/ Run 262E V-131B	1.3% Fe in SFIO/ Run 262E V-131B
k1	50.3	73.2	55.8	66.2
k2	8.30	6.98	4.02	5.76
k3	22.8	23.7	22.8	24.1
k4	0.34	0.43	0.12	0.09
k5	4.48	4.49	4.23	5.28
Iω	10.1	10.1	5.6	5.6
a. k's were calculated from regression analysis.				

part, a response of the model to account for the rapid solubilization of the portion of the Run 262E V-131B IOM that was found to dissolve, even at temperatures as low as 300 °C. With added SFIO, k1 further increases to 66 x 10^{-3} min^{-1}, which reflects a catalytic effect on the conversion of the coal macerals, since the IOM is not particularly affected by the SFIO.

Also, k2 is 43% higher in Run 262E recycle solvent for the SFIO catalyzed reaction. Interestingly, k3 (for direct conversion of IOM to oils) is not only about the same for coal liquefaction in Run 262E recycle solvent, but is also about the same value for all reaction systems. It also appears to be an important pathway for the production of oils. The rate constant for hydrocarbon gas production, k4, decreased significantly moving from the tetralin to the Run 262E solvent system. This was primarily the result of the diluting effect of the PA+A and oils added in the plant solvent which did not produce as much gas as did the freshly formed PA+A and oils formed from the coal in the tetralin reaction system. Finally, the rate constant for CO and CO_2 production remained about the same for all reaction systems.

In both tetralin and plant solvent, k1 increased upon addition of iron. In tetralin, the k3 value

for the IW-impregnated Fe case increased by 45% over the base thermal case while in plant solvent the addition of particulate SFIO resulted in an 18% increase over the base thermal case. This is strong evidence for the catalytic effect of iron on the dissolution step, whereas the influence on the k2 value is not consistent in both of these systems.

Figure 11-7a

IOM, PA+A and oil yields from liquefaction of Black Thunder coal in Run 262E Solvent at 415°C Modified for Run 262E V-131B IOM partial solubility

Rate constants, 1/min

k1 · 1000 = 58.585
k2 · 1000 = 4.797
k3 · 1000 = 18.168
k4 · 1000 = 0.125
k5 · 1000 = 4.277

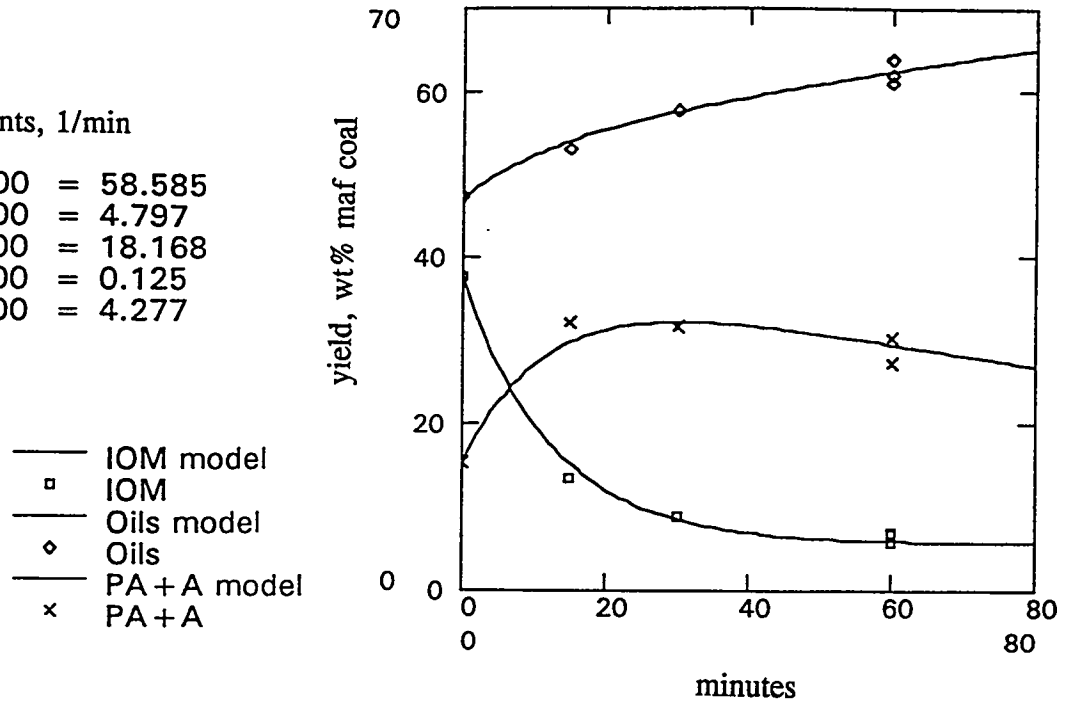
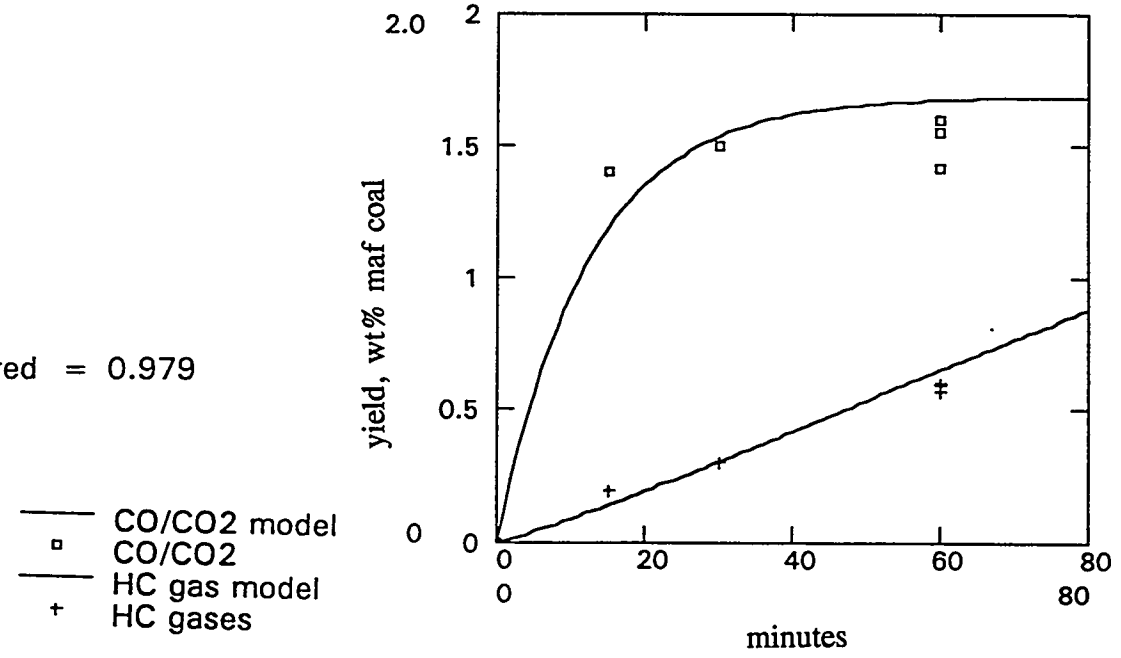


Figure 11-7b

Gases yields from liquefaction of Black Thunder coal in Run 262E V-131B at 415°C Modified for Run 262E V-131B IOM partial solubility

RSquared = 0.979



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SECTION TWO

CONSOL Inc.

FINAL REPORT
FOR THE PERIOD NOVEMBER 26, 1991, THROUGH FEBRUARY 28, 1995
SUBCONTRACT No. UKRF-4-25582-92-76

EXECUTIVE SUMMARY - CONSOL

MAJOR ACCOMPLISHMENTS

CONSOL acquired, documented, prepared, analyzed, stored and distributed the Wilsonville two-stage liquefaction samples that were used by all the participants in this program. The principal samples were from Wilsonville Run 262E and included:

- Black Thunder coal
- V-1074 heavy distillate
- V-130 deashed resid
- V-1082 ashy resid
- iron oxide and Molyvan-L catalysts

Three dewaxing methods (ketone, liquid extraction, and thermal) were tested to remove the wax component from the distillate portion of recycle solvent from two-stage coal liquefaction. Dewaxing was shown to improve the hydrogen donor solvent quality of the recycle distillate alone, or in combination with hydrogenation of the dewaxed distillate.

Ketone dewaxing of the Wilsonville Run 262E V-1074 heavy distillate was tested with acetone, MEK, toluene and various mixtures of these at temperatures from -35 °C to 0 °C. The degree of dewaxing was found to be a function of solvent composition and temperature. Significant findings are:

- Solvent quality improves rapidly with dewaxing up to ~20 wt % wax removal and then levels off.

- Black Thunder coal conversion increases from ~87 wt % to 90 wt % when dewaxed distillate is substituted for the untreated distillate in the Wilsonville Run 262E solvent in 5-min microautoclave tests at 824 °F, 1.5 S/C, 1500 psig (cold) H_2.

- Hydrogenating the dewaxed distillate further improves coal conversion to ~91 wt %.

- Clean wax byproduct, similar to commercial petroleum based waxes, is produced by de-oiling the slack wax that is removed from coal-derived distillate.

- The slack wax properties indicate that it should be an excellent feedstock to produce high yields of light products in an FCC.

N-methylpyrrolidinone (NMP) and furfural were used at ambient temperatures to extract the aromatics from the heavy distillate fraction of the recycle solvent. Significant findings are:

- The slack wax yield is greater, but the wax is of lower quality than that from ketone dewaxing (>40 wt % vs ~20 wt %).
- The extracted material is more aromatic than the ketone dewaxed distillate (~30% aromatic hydrogen vs ~20%).
- The residual extraction solvent is difficult to remove completely from the aromatic fraction.
- The solvent quality of the aromatic fraction is the same as that of the feed distillate.
- Hydrogenation of the aromatic fraction is expected to improve solvent quality.

Thermal dewaxing was tested by heating the heavy distillate to over 900 °F for five minutes to selectively crack the aliphatic compounds. Significant findings are:

- Dewaxed oil yield is ~75 wt % at 925 °F, and lower.
- Gas yield is <5 wt % at 925 °F, and lower.
- The dewaxed material is more aromatic than most ketone dewaxed distillates (~25% aromatic protons in 925 °F dewaxed distillate).
- Hydrogenating the dewaxed (925 °F) distillate produces an improved liquefaction solvent (Black Thunder coal conversion increases by 2 wt % when this hydrogenated thermally dewaxed distillate is substituted for untreated distillate in recycle solvent).

Oil agglomeration using the heavy recycled distillate as the agglomerating oil was successful in reducing the ash content of the feed coal to liquefaction. Significant findings are:

- Coals of rank from lignite through bituminous are reduced in MF ash content through agglomeration by 15 to 75 % relative to the feed coal, as shown below:
  - ▸ Black Thunder subbituminous coal at low pH: 3.7% MF product ash; 46% rejection.
  - ▸ Black Thunder coal at natural pH: 4.6% MF product ash; 31% ash rejection.
  - ▸ Clean Burning Star 2 coal: 7.6 wt % MF product ash; 38% ash rejection.
  - ▸ Kemmerer subbituminous coal: 1.9 wt % MF product ash; 50% rejection.
  - ▸ Martin Lake lignite: 9.9 wt % MF product ash; 28% rejection.
  - ▸ Beulah-Zap lignite at low pH: 2.5 wt % MF product ash; 75% rejection.
  - ▸ McKinley subbituminous coal: 4.6 wt % MF product ash; 64% rejection.

- An empirical model was created to relate agglomeration physical deashing performance of coal of various ranks with silica content.

Oil agglomeration was found to be a suitable recovery method for pretreated coal. This was demonstrated by recovering coal at temperatures of 50 to 175°C from: 1) coal which had been pretreated by CAER at temperatures greater than 300 °C with CO in basic slurry (agglomerated from slurry and from dry coal); 2) wet coal which had been impregnated with Fe by CAER by ion exchange; 3) wet coal which had been impregnated with Fe and Mo by CAER by incipient wetness; and by 4) successfully agglomerating various coals using several oils over a range of pH, temperature, and slurry concentration.

Oil agglomeration was shown to be effective for recovery of catalyst impregnated coals as demonstrated by complete retention of Fe and Mo in incipient-wetness-treated Black Thunder coal agglomerates, and retention of 71% of the Fe in ion-exchanged coal.

Other significant findings of the oil agglomeration research include:

- Nearly quantitative recovery of the coal and oil as the agglomerates was demonstrated.

- The reactivity of Black Thunder coal was demonstrated to be unchanged by agglomeration, within measurement limits.

- Agglomeration water requirements were estimated, and the agglomeration coal slurry concentration was increased to decrease the water requirement and associated costs; this modification was also found to improve deashing.

- The benefits of integrating agglomeration into liquefaction were identified. Development needs to refine costs and benefits and to resolve uncertainties of process integration were defined. Key development topics include:

  ▸ Water availability and use (sour water use, recycle and integration possibilities).

  ▸ Drying (how much needed, where in process).

  ▸ Continuous liquefaction testing, which is needed to quantify/validate expected benefits.

- The potential for physical cleaning of several coals (Black Thunder, Burning Star 2, and Martin Lake) was assessed by float/sink tests, and by column flotation (Black Thunder only).

Significant accomplishments in solids separation were:

- The composition and yield of light ROSE-SR deashed resid was simulated using cyclohexane extraction of Wilsonville deashed resid.

  ▸ This material should be amenable to hydrogenation to improve solvent quality.

- ▸ Most of the resid components which are detrimental to the hydrogenation catalyst are removed in this operation.

- ▸ Possible flowrates were estimated.

- Segregation of the feed coal into a lower ash cleaned coal product that can be fed to liquefaction and a higher ash reject that can be gasified to produce hydrogen was shown to be an potentially attractive option to improve liquefaction economics.

- Several additional solids separation concepts were tested, which offer some potential for future development. However, they are not ready for Phase II development.

SPECIFIC ACTIVITIES

Sampling and Analysis

CONSOL obtained, prepared, analyzed, stored and distributed the Wilsonville feed coal and process-derived materials that were used in this project. Descriptions and chemical analyses of key samples are summarized in this report. Complete sample descriptions and analyses can be found in References 1-12.

Dewaxing and Solvent Improvement

Solvent dewaxing was examined as a means of improving coal liquefaction economics through solvent upgrading. The purpose of dewaxing is to remove paraffinic (and naphthenic) materials from the recycle distillate in the coal liquefaction process. Coal liquids, and subbituminous coal liquids in particular, contain a paraffinic wax component. Because of their relative inertness, these paraffins tend to concentrate in the recycle solvent over time. These aliphatic materials dilute the hydrogen donors in the process recycle solvent, and are poor physical solvents for the coal reaction products. Therefore, they can contribute to the retrograde reactions which are thought to impair the dissolution and upgrading of low rank coals. In addition, removal of the paraffins as a wax stream reduces the burden on the reactors to crack them to light distillate products. The reduced reactor burden may translate into higher reactor throughput. The gas production and hydrogen consumption that must accompany the paraffin cracking also are avoided.

Three dewaxing schemes were evaluated for potential use in removing the wax from the recycle solvent in a coal liquefaction plant. The features and benefits of each of these dewaxing routes are summarized below.

Ketone Dewaxing

Features

- All or part of the heavy distillate stream is dewaxed in a ketone-based solvent.

- Dewaxed distillate is recycled, as is or after hydrogenation, to the first stage liquefaction reactor.

- The extent of dewaxing is easily selectable by the choice of conditions.

- Ketone dewaxing is commercially proven technology.

- The removed wax is either purified and sold as a high-value by-product or it is converted to product distillate in an FCC unit.

Benefits

- Ketone dewaxing produces a nearly paraffin-free distillate that is an improved donor solvent that may allow.

    - ▸ Improved coal conversions at current liquefaction conditions. Experimental data suggest 3-4 wt % improvement in coal conversion is possible. An increase in single pass coal conversion from 87 to 91 wt % could result in about an 6 wt % decrease in rejected organics and a similarly improved product yield.

    - ▸ Operation at lower severity conditions (lower T, P, RT) while maintaining current levels of performance.

    - ▸ Operation at higher severity conditions by reduction of retrograde reactions (increases in coal conversions of ~4 wt % were obtained by ~50 °F higher reaction temps); could improve throughput.

- Paraffin-rich wax can be upgraded to a salable clean wax product or fed to an FCC unit for conversion to distillate product. Sale of clean by-product wax can help defray processing costs.

Liquid Extraction Dewaxing

Features

- All or part of heavy distillate stream is dewaxed by liquid extraction with N-methylpyrrolidinone (NMP), furfural or similar selective solvent prior to hydrogenation and recycle to the liquefaction plant.

- Commercially proven technology for removal of aromatics from paraffinic lube oils but not for paraffin removal from aromatic-rich distillates.

- Operation at modestly elevated temperatures (100-200 °F) and atmospheric pressure.

Benefits

- Produces highly aromatic, nearly n-paraffin-free distillate that should be easily hydrogenated.
- Operating costs estimated by LDP Associates to be lower than those of ketone dewaxing.
- With hydrogenation, coal conversion improvements should equal those obtained by ketone dewaxing plus hydrogenation (~3-4 wt % with Black Thunder coal); associated cost benefits of increased product yield through less IOM rejection or lower severity operation are expected.

Thermal Dewaxing

Features

- All or part of heavy distillate stream is heated to >900 °F for several minutes to thermally crack paraffins and naphthenes.

- The light cracked product is removed as net product and the aromatic-rich heavy distillate is recycled to the liquefaction reactor with or without prior hydrogenation.

- Very simple process flow sheet.

- Similar to British coal "satcracking"; should be easy to demonstrate in bench-scale continuous unit.

Benefits

- Waxes are removed as distillable oils and gases.
- Produces highly aromatic distillate that should be easily hydrogenated (in a separate hydrogenation reactor or in the first stage liquefaction reactor) to produce a superior donor solvent with similar benefits to other dewaxing methods.

Agglomeration and Coal Cleaning

CONSOL studied coal agglomeration as a potential means of ash rejection and catalyst incorporation with the goal of improving liquefaction economics by increasing yields and lowering catalyst requirements. Several agglomeration scenarios are presented to summarize this work. These scenarios include: agglomeration at natural pH; agglomeration of low-rank coal at natural pH, with pretreated coal recovery; agglomeration at natural pH, with catalyst impregnation; agglomeration of low-rank coal at low pH; and segregation of feed coal based on ash content for liquefaction and gasification.

There are three basic issues to be addressed in developing agglomeration as an integrated component of a coal liquefaction process. These are:

- What is the agglomeration performance at a given set of conditions?

- What is the cost of agglomeration at those conditions?

- What is the liquefaction benefit and economic value of the agglomeration?

The first question can be answered by a few definitive lab experiments. For the most part, the Phase I work falls into this category. The latter two questions deal more directly with development and scale-up of the process, and will be addressed more specifically in Phase II work. The latter issues are sensitive to the specific liquefaction plant concept, especially to how the liquefaction process is operated with the lower-ash feed, and to the degree of integration of agglomeration within the overall plant. These are where the major uncertainties lie, and are expected to be better defined as the process is scaled up and tested. The underlying problem is in choosing an environment or scenario that makes the whole process economically attractive. This requires that the three basic issues be addressed in an integrated or overlapping fashion, rather than as separate issues. The liquefaction benefits are not easily measured in the lab, thus requiring testing at the larger scale.

Agglomeration at Natural pH

Features

- Coal ranging in rank from lignite through bituminous can be reduced in MF ash content by ca. 15 to 64 relative percent.
- Natural pH or minor adjustment to pH ≈6-8.
- Oil dosage of ca. 15 to 35%, 50-65 °C, coal slurry concentration of 20-43%.
- Uses sour water (low pH may enhance ash rejection from some coals).
- Dissolved salts bled to Texaco gasifier.
- All organics, most iron, and pretreated catalyst retained.
- Some silica and ≈50% of sodium rejected from low-rank coals
- No coal reactivity loss.

Benefits

- Lower organic rejection results in perhaps a few percent higher MAF distillate yield.
- Lower ash content feed lowers viscosity and allows:
  - ▸ Reduced solvent/coal ratio to perhaps 1.6, or
  - ▸ Higher internal ashy recycle and reduced size of ROSE-SR unit.
- Reduced make-up of disposable catalyst with increased ashy recycle.
- Catalyst exposure to metal poisons may be reduced (especially Na in low-rank coals), resulting in lower catalyst replacement rate.
- Recovers coal from any aqueous pretreatment

In this scenario, coal is slurried with waste sour water from liquefaction and recycled water, and it is agglomerated with heavy distillate. The agglomerates are rinsed over screens, blown with air to remove surface moisture, and sent to liquefaction. Additional drying prior to liquefaction is optional and depends on other factors (i.e., it is not a requirement of agglomeration). A slipstream of the agglomerate rinse water with mineral matter is used to slurry ash concentrate and coal for Texaco gasification. The remaining agglomerate rinse water with mineral matter is treated to remove solids, and then recycled for slurrying coal and rinsing agglomerates. Any additional water requirement would use gasification sour water, and any excess agglomeration waste water would go to water treatment with the gasification sour water. Because liquefaction is a net producer of water, both from coal drying, and from hydrogenation, it is anticipated that there will be an adequate water supply for agglomeration. The cost of water use and treatment will be minimized by using waste streams wherever possible.

Agglomeration of Low-Rank Coal at Natural pH, with Pretreated Coal Recovery

Features and Benefits

- Any aqueous coal pretreatment will require a recovery step.
- Recovery of coal from CO-pretreatment (as dry coal and as slurry) was demonstrated in Phase I work.
- Recovery of coal after two types of catalyst impregnation steps was also demonstrated in Phase I work. This avenue is pursued further in the discussion of agglomeration at natural pH, with catalyst impregnation, below.
- Other features and benefits are as generally described in the discussion of agglomeration at natural pH.

This concept differs from that of untreated coal recovery by agglomeration at natural pH in that aqueous coal slurry from a pretreatment step is agglomerated, instead of using sour water to slurry the coal. This concept is not restricted to any particular pretreatment, but was demonstrated in Phase I with CO-pretreated coal, and with catalyst-impregnated coal. Any use of sour water in the pretreatment or agglomeration steps depends on the specific pretreatment requirements. It is possible that rinsing of agglomerates with sour water could be done. Although not limited to any particular coal rank, it is anticipated that pretreatment will be most useful when low-rank coal is the feedstock.

Agglomeration at Natural pH, with Catalyst Impregnation

Features and Benefits

- Catalyst impregnation involving aqueous coal pretreatment can be followed by agglomeration for recovery, or impregnation can be incorporated into the agglomeration step.
- Other features and benefits are as generally described for agglomeration of untreated coal and pre-treated coal at natural pH.

In this concept, the agglomeration feed could be a pretreated coal, or a pre-treated coal slurry (as in agglomeration of low-rank coal at natural pH, with pretreated coal recovery, above), or an untreated coal for treatment during part of the agglomeration process. This concept is not restricted to any particular pretreatment, but it was demonstrated in Phase I with two methods of catalyst impregnation of coal, and catalyst impregnation is a likely pretreatment step. Any use of sour water in the pretreatment or agglomeration steps depends on the specific pretreatment requirements. It is possible that rinsing of agglomerates with sour water could be done. Although not limited to any particular coal rank, it is anticipated that pretreatment will be most useful when low-rank coal is the feedstock.

Agglomeration of Low-Rank Coal at Low pH

Features

- Coal ranging in rank from lignite through subbituminous can be reduced in MF ash content by ca. 50 to 76 relative percent.

- pH of 1 or 2 using H_2SO_4.
- Oil dosage of 21 to 54%, 50°C, coal slurry concentration of 20 to 43%.
- Uses sour water (low pH may reduce acid requirement).
- Dissolved salts bled to Texaco gasifier.
- All organics and most iron retained; perhaps pretreated catalyst also retained.
- Some silica and ≈90% (projected) of Na, K, Ca, Mg rejected.
- No coal reactivity loss.

Benefits
- Lower organic rejection results in perhaps a few percent higher MAF distillate yield (estimated to be about 4% for Black Thunder coal).
- Lower ash content feed lowers viscosity and allows:
  - ▸ reduced solvent/coal ratio to perhaps 1.3, or
  - ▸ increased internal ashy recycle and reduced size of ROSE-SR unit.
- Reduced make-up of disposable catalyst with increased ashy recycle.
- Supported catalyst exposure to metal poisons, especially Na and Ca, significantly reduced, resulting in lower catalyst replacement rate by 30% (est.).
- Recovers coal from any aqueous pretreatment.

In the low pH agglomeration scheme, low-rank coal is slurried with waste sour water from liquefaction and pH-adjusted recycled water and agglomerated with heavy distillate. The agglomerates are rinsed over screens, blown with air to remove surface moisture, and sent to liquefaction. Additional drying prior to liquefaction is optional and depends on other factors (i.e., it is not a requirement of agglomeration). A slipstream of the agglomerate rinse water with mineral matter is used to slurry ash concentrate and coal for Texaco gasification. The remaining agglomerate rinse water with mineral matter is treated to remove solids and re-establish low pH, and then recycled for slurrying coal and rinsing agglomerates. Any additional water requirement would use gasification sour water, and any excess agglomeration waste water would go to water treatment with gasification sour water. Because liquefaction is a net producer of water, both from coal drying, and from hydrogenation, it is anticipated that there will be an adequate water supply for agglomeration. The cost of water use and treatment will be minimized by using waste streams wherever possible.

Segregation of Feed Coal Quality for Liquefaction and Gasification

Features
- Column flotation or other fine-coal cleaning method.
- For bituminous and subbituminous coals.

- No reject, as discussed here.

Benefits

- Reduces ash content of liquefaction feed coal from 6.3 to 3.8% MF while increasing gasifier feed coal ash to 14.7% MF for fine Black Thunder coal (not SO^3-free).
- Reactive maceral enrichment improves coal conversion by 1% MAF (est.).
- Increases product yield by 3.5% MAF (est.) by reducing deasher reject.
- reduced solids loading allows:
  - lower solvent to coal ratio, or
  - higher solids recycle, which reduces deasher size by 1/5 (est.) and make-up of dispersed catalyst.

In this scenario, the ground feed coal to the plant is fed to a fine-coal cleaning plant to produce two streams: A low-ash liquefaction feedstock and a higher ash gasifier feedstock. Since the gasifiers process all the coal ash fed to the plant anyway, either as native coal ash or as ROSE bottoms ash, this step does not burden the gasifiers with additional ash, but does substantially reduce the ash burden on the liquefaction section.

Solids Separation

Another possible improvement to current liquefaction practices that CONSOL examined was the recovery and utilization of light deashed resid during ash removal. In this scheme, the ROSE-SR unit would be operated in stages to produce a "light" de-ashed resid (LDAR) stream for hydrogenation with the distillate to improve solvent quality prior to recycle. The "heavy" de-ashed resid (HDAR) will be recycled without additional treatment and IOM/ash component will be partially recycled and partially rejected. Such operation provides a hydrogenation feed which is amenable to hydrogenation, but is not high in heteroatomic components which are detrimental to the hydrogenation catalyst, and is not high in paraffinic components which are poor hydrogenation feeds.

Solvent Improvement by Staged ROSE-SR Operation

Features

- Three-stage ROSE-SR unit operated to produce light (44-75%) and heavy (25-56%) deashed resid.
- For all coal ranks.
- Light resid is fed with distillate to solvent hydrogenation.
- Heavy resid is recycled to slurry with ash concentrate.
- A portion of the ash concentrate is gasified.
- All V-1082 is deashed; as much light resid as possible recycled back.
- Up to 57 wt % of recycled soluble resid is sent through solvent hydrogenation.

- The light resid cut (yield and properties) is determined by choice of deashing solvent and conditions.

- Light resid has a moderate content of aromatics and paraffins and is low in phenolic -OH concentration, indicating its suitability as a hydrogenation feedstock.

Benefits

- Provides a solvent component which is amenable to hydrogenation to improve solvent quality, without most of the components which are detrimental to the hydrogenation catalyst.

- Solvent quality improvements will improve conversion and yields.

Miscellaneous Concepts in Solids Separation

CONSOL also pursued research on several solids separation concepts which are not recommended for Phase II development. Most of this work concerned alternative methods for resid deashing. These concepts include resid deashing by low-temperature agglomeration, resid deashing by high-temperature agglomeration, alternate resid deashing schemes. A related concept, that of ash concentrate upgrading and utilization, was developed as the Phase I work progressed.

Each of the topics mentioned in this summary, pertinent supporting data and recommendations for future research are discussed in the attached final report.

TASK 1.2 - LABORATORY SUPPORT (CONSOL)

SUMMARY

CONSOL obtained, prepared, analyzed, stored and distributed the Wilsonville feed coal and process-derived materials that were used in this project. Descriptions and chemical analyses of key samples are summarized in this report. Complete sample descriptions and analyses can be found in References 1-12.

DISCUSSION

CONSOL served as the repository for sample storage and as the clearinghouse for sample distribution during this study. Most of the samples obtained and distributed were from three runs that were made at the Wilsonville coal liquefaction pilot plant. Two drums of Black Thunder coal and several hundred pounds of solvent samples were obtained from Wilsonville Run 262E. These samples, which served as the base samples for much of the work in this contract, are described below. Samples were also obtained from Wilsonville Runs 258K and 255. Run 258K was made with Black Thunder coal, the same coal used in Run 262E; however, fresh Mo catalyst was not added during this run period, therefore, Mo was nearly absent from the recycle solvent. Martin Lake (Texas) Lignite was the feed coal used in Wilsonville Run 255.

Samples of Black Thunder coal (pulverized and un-ground), heavy distillate (V-1074), de-ashed resid (V-130) and ashy resid (V-1082) from Wilsonville Run 262E were received from Wilsonville. Wilsonville personnel provided the blend ratio of process solvent components for operations on September 16, 1991, the date our oil samples were obtained. The process (recycle) solvent blend used

at Wilsonville consisted of 42.7% distillate, 6.6% de-ashed resid, and 50.7% ashy resid by weight. These samples were taken at Wilsonville between material balance periods D and E of Run 262.

The heavy distillate (V-1074) sample from Wilsonville Run 262 was warmed to ~100 °C, mixed, and divided into aliquots for distribution to the University of Kentucky and Sandia. The remainder was saved for later use. Although it is a tar-like solid at room temperature, this material readily melts and, at 100 °C, has a viscosity similar to that of water.

The deashed (V-130) and ashy (V-1082) resid samples were ground in a hammer mill to approximately -1/4". Solid samples (coal, V-130 and V-1082) were prepared as follows for both shipping and storage. Ground samples were first placed in appropriately sized Zip-Loc bags, then purged with N_2 via a lance inserted into one side of the bag, partially evacuated and then sealed. The sealed Zip-Loc bag then was placed inside a triple-layer (polyethylene, aluminum and Tyvek) bag. The triple-layer bag then was purged with N_2, partially evacuated and heat sealed.

The chemical analyses of the coals and Wilsonville process streams that were used in this work are shown in Tables 1 and 2, respectively. The Black Thunder mine coal used in this work was the ground 9/16/91 (-200 mesh) sample from Wilsonville Run 262. The other coals listed in Table 1 were obtained as potential alternative feedstocks. These consisted of a lignite (Martin Lake), two other subbituminous coals (McKinley mine and Rosebud mine), an Illinois bituminous coal (Burning Star No. 2), and the dried and partially deashed Rosebud Syncoal.

The Texas-lignite-derived (Wilsonville Run 255) process stream samples shown in Table 2 were obtained from Amoco and analyzed, but they were not used in this project. The Mo-free resid that was used in the process simulation tests (PST) was derived from the recycle solvent sample (V-131B) from Wilsonville Run 258K. CONSOL received one gallon of this Mo-free V-131B recycle solvent sample from UK/CAER. Approximately 1700 g of this sample was distilled at 320 °C and 2 torr (1025 °F atmospheric pressure equivalent) to produce a Mo-free simulated V-1082 ashy resid sample. Under these conditions, 34.8 wt % of the V-131B material was collected as distillate and 64.9 wt % remained in the distillation pot as 1025 °F$^+$ resid. The overall material balance was 99.7 wt %. The chemical analyses of these distillation fractions are shown in Table 3. This is the Mo-free ashy resid that was used in the PST.

Most of the Advanced Liquefaction Concepts laboratory-scale work during Phase I of this contract was conducted with the Black Thunder coal and process stream samples from Wilsonville Run 262E. A brief description of these samples and of some of the more important samples that were derived from them are listed in Table 4. The sample numbers that are shown in this table were assigned by CONSOL and were used consistently throughout the project. The hydrogen contents, the ^{1}H-NMR proton distributions and the phenolic -OH contents of the most widely used Wilsonville Run 262E process stream liquids are given in Table 5. In some instances, more than one analysis was reported during this work for some of these materials.[1-12] The analyses listed in this table are those that we believe are the most accurate.

Iron oxide (Fe_2O_3) catalyst and Molyvan-L from Wilsonville Run 263 also were obtained by CONSOL and distributed for use in this project.

TASK 2.1.2.1 - PRETREATMENT WORK AT CONSOL - DEWAXING AND SOLVENT IMPROVEMENT

SUMMARY

Three dewaxing schemes were evaluated for potential use in removing the wax from the recycle solvent in a coal liquefaction plant. The features and benefits of each of these dewaxing routes are summarized below.

Ketone Dewaxing

Features

- All or part of the heavy distillate stream is dewaxed in a ketone-based solvent.
- Dewaxed distillate is recycled, as is or after hydrogenation, to the first stage liquefaction reactor.
- The extent of dewaxing is easily selectable by the choice of conditions.
- Ketone dewaxing is commercially proven technology.
- The removed wax is either purified and sold as a high-value by-product or it is converted to product distillate in an FCC unit.

Benefits

- Ketone dewaxing produces a nearly paraffin-free distillate that is an improved donor solvent that may allow:
  - ▸ Improved coal conversions at current liquefaction condition. Experimental data suggest 3-4 wt % improvement in coal conversion is possible. An increase in single pass coal conversion from 87 to 91 wt % could result in about an 6 wt % decrease in rejected organics and a similarly improved product yield.
  - ▸ Operation at lower severity conditions (lower T, P, RT) while maintaining current levels of performance.
  - ▸ Operation at higher severity conditions by reduction of retrograde reactions (increases in coal conversions of ~4 wt % were obtained by ~50 °F higher reaction temps); could improve throughput.
- Paraffin-rich wax can be upgraded to a salable clean wax product or fed to an FCC unit for conversion to distillate product. Sale of clean by-product wax can help defray processing costs.

Liquid Extraction Dewaxing

Features

- All or part of heavy distillate stream is dewaxed by liquid extraction with N-methylpyrrolidinone (NMP), furfural or similar selective solvent prior to hydrogenation and recycle to the liquefaction plant.

- Commercially proven technology for removal of aromatics from paraffinic lube oils but not for paraffin removal from aromatic-rich distillates.
- Operation at modestly elevated temperatures (100-200 °F) and atmospheric pressure.

Benefits

- Produces highly aromatic, nearly n-paraffin-free distillate that should be easily hydrogenated.
- Operating costs estimated by LDP to be lower than those of ketone dewaxing.
- With hydrogenation, coal conversion improvements should equal those obtained by ketone dewaxing plus hydrogenation (~3-4 wt % with Black Thunder coal); associated cost benefits of increased product yield through less IOM rejection or lower severity operation are expected.

Thermal Dewaxing

Features

- All or part of heavy distillate stream is heated to >900 °F for several minutes to thermally crack paraffins and naphthenes.
- The light cracked product is removed as net product and the aromatic-rich heavy distillate is recycled to the liquefaction reactor with or without prior hydrogenation.
- Very simple process flow sheet.
- Similar to British coal "satcracking"; should be easy to demonstrate in bench-scale continuous unit.

Benefits

- Waxes are removed as distillable oils and gases.
- Produces highly aromatic distillate that should be easily hydrogenated (in a separate hydrogenation reactor or in the first stage liquefaction reactor) to produce a superior donor solvent with similar benefits to other dewaxing methods.

DISCUSSION

A key feature of the Advanced Liquefaction Concepts that was examined in this study was solvent quality improvement. Most coals, and subbituminous coals in particular, contain a "wax" component that is produced during liquefaction and, because of the relative inertness of these paraffins, tends to build up in the recycle solvent over time. For instance, the single-pass paraffin yield from the liquefaction of Black Thunder coal was estimated to be 3.5-4 wt %,[5] yet the recycle oil can contain ~8-10% paraffins and the recycle distillate an contain ~15-20% paraffins. The purpose of dewaxing is to remove these paraffinic (and naphthenic) materials from the recycle distillate in the coal liquefaction process. These aliphatic materials dilute the hydrogen donors in the process

recycle solvent, and are poor physical solvents for the coal reaction products. Therefore, they can contribute to the retrograde reactions which are thought to impair the dissolution and upgrading of low rank coals. In addition, removal of the paraffins as a wax stream removes the burden on the reactors of cracking them to light distillate products. The reduced reactor burden may translate into higher reactor throughput. The gas production and hydrogen consumption that must accompany the paraffin cracking also is avoided.

Simplified flow sheets comparing the current two-stage liquefaction process with an integrated coal liquefaction process scheme that employs solvent dewaxing as a pretreatment step are shown in Figure 1 and Figure 2. In this integrated advanced concept liquefaction plant, the wax is removed from the distillate part of the recycle solvent. The dewaxed distillate is then recombined with the rest of the recycle solvent (either "as is" or after further upgrading by hydrogenation) and sent to the slurry mix tank, Figure 2.

Three potential methods of dewaxing the coal-derived distillate were investigated. These were ketone dewaxing, wax separation by liquid extraction, and thermal dewaxing. All three were effective in removing the wax components from the coal-derived distillate, and depending on the liquefaction plant design and intended utilization of the wax, the use of any of these methods should benefit liquefaction economics.

Ketone Dewaxing

The amount of wax that is removed by ketone (acetone) dewaxing depends on the dewaxing temperature and solvent. A range of temperatures from -35 °C to 0 °C were tested for acetone dewaxing the Wilsonville Run 262E V-1074 heavy distillate.[2,3] Lowering the temperature from 0 °C to -35 °C increased the wax removal from about 8 wt % to over 35 wt %. Acetone dewaxing, even at the highest temperature tested, removed virtually all of the n-paraffins in the distillate.[2] As the dewaxing temperature was lowered, the wax component became richer in naphthenic compounds and, below about -20 °C, aromatic components began to report to the wax fraction. The solvent quality of the dewaxed distillate from Wilsonville Run 262E, as defined by the CONSOL equilibrium solvent quality test with Old Ben (Indiana V) coal,[13] showed a steady increase with wax removal up to about 20 wt % wax removal (from an initial reactivity of ~65 wt % to ~85 wt % at 20 wt % wax removal[4]). Above this level of dewaxing, little improvement in solvent quality was observed with increased wax removal.[5]

A second measure of solvent reactivity was developed during this program to compare various dewaxing methods.[5] This method, a 5-min, 824 °F microautoclave test (Black Thunder coal, 1.5 S/C, Wilsonville Run 262E solvent blend, 1500 psig (cold) H_2 pressure), gave coal conversions that simulated those observed in the first stage liquefaction reactor at Wilsonville during Run 262 (~87 wt %). This microautoclave test was used to compare the coal conversion reactivities of treated (dewaxed, hydrogenated, etc.) solvents with each other and with that of the untreated Wilsonville solvent. In the solvent quality improvement work, only the distillate (~700 °F x 1050 °F) portion of the recycle solvent was treated. This 5-min Black Thunder coal microautoclave liquefaction test allowed general comparison of the effects of changes in solvent properties on coal conversion at simulated Wilsonville conditions. However, the reproducibility of the results from this test is not as good as that of the equilibrium solvent quality test (~2.5 wt % vs. ~1 wt %).

When this microautoclave test was used to compare solvent qualities with Black Thunder coal, the following results were observed. The coal conversion with the untreated Wilsonville V-1074 heavy distillate in the Run 262E recycle solvent was 87.0 wt %. When V-1074 that had been dewaxed in acetone at -5 °C was substituted for the distillate in the solvent, the coal conversion increased to 89.9 wt %. Hydrogenating the -5 °C acetone dewaxed V-1074 had little effect on the coal conversion (89.0 wt %). The distillate produced by acetone dewaxing the V-1074 at -35 °C was somewhat less reactive than the -5 °C acetone dewaxed distillate (88.3 wt % coal conversion vs 89.9 wt %). However, the -35 °C acetone dewaxed V-1074 was more amenable to hydrogenation than the -5 °C dewaxed distillate; coal conversion improved to 90.3 wt % when the hydrogenated -35 °C acetone dewaxed V-1074 was used in the Wilsonville Run 262E solvent blend. Hydrogenating the whole V-1074 distillate, without dewaxing, also improved the coal conversion relative to that with the untreated V-1074 in this 5-min microautoclave first-stage liquefaction simulation. Coal conversion increased by 1.5 wt % (to 88.5 wt %) when hydrogenated V-1074 distillate was used in the solvent.

The observed increases in coal conversion that are attributable to improvements in solvent quality that result from dewaxing and/or hydrogenation of the distillate portion of the recycle solvent should lead to decreased rejection of organic matter from the process. The actual decrease in organic matter rejection that will result from increased coal conversion should be somewhat greater than the observed increase in coal conversion since some soluble resid is inevitably rejected with the ash and insoluble organic matter (IOM) during ash rejection. In actual operation, the rejection ratio of ash, IOM and soluble resid is approximately 1:1:1, therefore, a 4 wt % increase in coal conversion (e.g., from 87 wt % to 91 wt %) may result in up to 6 wt % less organic matter rejection.

The improved solvent performance that results from dewaxing and/or hydrogenating the distillate portion of the recycle solvent can be utilized in ways other than taking advantage of the increased coal conversion at current conditions to reduce organic matter rejection. An improved solvent may permit maintaining current levels of coal conversion (and process performance) at less severe conditions. Reduction of first stage residence time could increase overall plant throughput. Lowering the first-stage temperature, as well as removal of paraffins from the solvent, may lead to lower gas make which would improve product yields and reduce hydrogen consumption. Improved solvent performance could alternatively allow reduction in the required hydrogen pressure in the liquefaction reactors.

Alternatively, use of these improved solvents may allow operation of the first stage liquefaction reactor at more severe conditions; further improving coal conversion and further decreasing organic matter rejection. Removal of the paraffin components from the recycle distillate should reduce the tendency toward retrogressive reactions during coal liquefaction and, therefore, permit operation at higher temperatures or longer residence times.

It also was shown in this study that the wax that is removed from coal-derived distillate can be easily cleaned to a product that is similar to commercial petroleum-derived paraffin waxes.[4,5] LDP Associates predicts that income from the sale of clean wax byproduct from a liquefaction plant that uses ketone dewaxing to upgrade the recycle solvent may completely offset the cost of the dewaxing step.[14] It was also shown that the slack wax byproduct from distillate dewaxing would be a suitable FCC feedstock from which distillable product could

be produced.[5,9] Therefore, utilization and/or disposal of the wax component that is removed from the recycle solvent is expected to be straightforward.

Liquid Extraction Dewaxing

In liquid extraction dewaxing, the aromatic components are dissolved in a suitable solvent and separated from the insoluble paraffinic components. This technology is used commercially to remove aromatic components from lube base oils. The two most commonly used solvents for this type of extraction are N-methylpyrrolidinone (NMP) and furfural. These solvents are less toxic and easier to handle than other solvents that were used historically for this purpose (liquid SO_2 and phenol). Both NMP and furfural have relatively high boiling points (202 °C and 162 °C, respectively) and specific gravities greater than 1. The high specific gravities of NMP and furfural facilitate density separations of the solvent plus aromatic phase from the relatively low specific gravity non-aromatic phase. However, the high boiling points of these solvents (particularly that of NMP) make it experimentally difficult to strip the solvent from the aromatic distillate fraction. Modestly elevated temperatures (100-200 °F) and atmospheric pressure are used commercially for such extractions.

Experiments in which Wilsonville Run 262E V-1074 was extracted at room temperature showed that the aromatic-aliphatic fraction split was about 70-30 in N-methylpyrrolidinone (NMP), and approximately 60-40 in furfural.[11] The aromatic proton contents (~20% to 25% aromatic protons) of the aromatic fractions from these extractions were higher than most of those observed in our ketone dewaxing studies. These highly aromatic extracts should be easily hydrogenated to excellent hydrogen donor solvents. However, such high aromatic contents will probably necessitate post extraction hydrogenation in order to reap the benefits of dewaxing. This differs from ketone dewaxing, with which significant improvement in coal conversion can be attained by dewaxing alone (i.e., dewaxing without subsequent hydrogenation).

With hydrogenation of the dewaxed distillate, the gains in coal conversion resulting from liquid extraction of the distillate in NMP or furfural are anticipated to be comparable to those attained by ketone dewaxing with hydrogenation (~3 to 4 wt %).[5,11] More of the distillate is removed with the paraffinic (wax) fraction when liquid extraction is used (~20 to 40 wt %) than when ketone dewaxing is used (10 to 20 wt %); however, LDP Associates predicts that the overall operating costs will be lower for a liquefaction plant in which NMP extraction is used than for one in which ketone dewaxing is used.[15]

It is expected that, with hydrogenation, the benefits discussed above for ketone dewaxing will also apply to dewaxing by liquid extraction. Improvements in coal conversion of 3 to 4 wt % should be possible with the associated cost benefits of increased product yield through less IOM rejection or lower severity operation.

Thermal Dewaxing

In thermal dewaxing, paraffinic and naphthenic components in the recycle distillate are selectively cracked to distillable product by short-time exposure to high temperatures. This dewaxing scheme is similar to the British coal 'satcracking' process. This dewaxing method has a less complicated flow sheet than either of the solvent dewaxing scenarios discussed above; only a thermal

reactor and a hydrotreater are required. It will be relatively easy to demonstrate the benefits of thermal dewaxing in a bench-scale continuous unit.

Laboratory experiments showed that heating the Wilsonville Run 262E V-1074 heavy distillate to ~900 °F, 925 °F, 950 °F and 975 °F for 5 min (including ~2.5 min heat-up) produced material which is progressively more aromatic (up to ~37% aromatic protons at 975 °F), accompanied by progressively higher gas yields (from ~1 wt % gas yield at 900 °F to nearly 20 wt % at 975 °F).[12] When the V-1074 was heated to 925 °F for 5 min., some of the distillate was cracked to gas (~3 wt %) and 700 °F$^-$ distillable liquids (~21 wt %). The remaining 700 °F$^+$ material had a very high aromatic proton content of nearly 32%. Upon hydrogenation, this thermally dewaxed (925 °F, 5-min) V-1074 gained 1.4 wt % hydrogen. Since this hydrogenation was done in a microautoclave, the total amount of hydrogen available was approximately 5 wt % of the dewaxed distillate. Therefore, it is possible that the level of hydrogenation was limited, to a degree, by the amount of available hydrogen (~30 wt % of the available hydrogen was consumed). When this hydrogenated thermally dewaxed distillate was substituted for untreated V-1074 in the 5-min microautoclave Black Thunder coal liquefaction tests described above, a 1.5 wt % increase in coal conversion was observed. Thus, simple thermal treatment of the recycle distillate followed by hydrogenation appears to produce a superior donor solvent. The benefits of this improved solvent are expected to be similar to the benefits derived from the use of solvents that incorporate distillate that is dewaxed by the solvent methods discussed above.

Based on the experimental results obtained in this study, it is recommended that ketone dewaxing and thermal dewaxing, each coupled with hydrogenation, be tested in a continuous bench-scale unit in Phase II of the Advanced Liquefaction Concepts program. It is further recommended that the ketone dewaxing be conducted at -5 °C with acetone used as the dewaxing solvent. The resulting dewaxed distillate should be hydrogenated to obtain the highest possible solvent quality prior to recombination with the rest of the recycle solvent. Thermal dewaxing tests at the bench-scale should be made at conditions of time and temperature chosen to approximate the ca. 75 wt % yield of 700 °F$^+$ distillate that was obtained in the laboratory tests at 925 °F, 5-min. It is expected that the results from these proposed dewaxing-hydrogenation runs will provide adequate operating data and scale-up information to estimate process economics, regardless of the final dewaxing method that is selected.

TASK 2.1.2.2 - PRETREATMENT WORK AT CONSOL - AGGLOMERATION

SUMMARY

This section describes various agglomeration scenarios, based on Phase I work performed under Task 2.1.2.2 - Pretreatment Work at CONSOL - Agglomeration. The format used for this discussion is to describe the features and general benefits for each scenario, give specific results and benefits for different coals under that scenario, and to give recommendations for that scenario. The scenarios include: agglomeration at natural pH; agglomeration of low-rank coal at natural pH, with pretreated coal recovery; agglomeration at natural pH, with catalyst impregnation; agglomeration of low-rank coal at low pH; and segregation of feed coal quality to liquefaction and gasification.

There are three basic issues to be addressed in developing agglomeration as an integrated component of a coal liquefaction process. These are:

- What is the agglomeration performance at a given set of conditions?
- What is the cost of agglomeration at those conditions?
- What is the liquefaction benefit and economic value of the agglomeration?

The first question can be answered by a few definitive lab experiments. For the most part, the Phase I work falls into this category. The latter two questions deal more directly with development and scale-up of the process, and will be addressed more specifically in Phase II work. The latter issues are sensitive to the specific liquefaction plant concept, especially to how the liquefaction process is operated with the lower-ash feed, and to the degree of integration of agglomeration within the overall plant. These are where the major uncertainties lie, and are expected to be better defined as the process is scaled up and tested. The underlying problem is in choosing an environment or scenario that makes the whole process economically attractive. This requires that the three basic issues be addressed in an integrated or overlapping fashion, rather than as separate issues. As an example, the limited ash rejection achieved by agglomerating Black Thunder coal at natural pH provided an impetus for exploration of low-pH agglomeration of this coal. Although low-pH agglomeration is more difficult and costly, it has a significantly greater potential benefit for the liquefaction process. The liquefaction benefits are not easily measured in the lab, thus requiring testing at the larger scale.

Agglomeration at Natural pH

Features

- Coal ranging in rank from lignite through bituminous can be reduced in MF ash content by ca. 15 to 64 relative percent.
- Natural pH or minor adjustment to pH ≈6-8.
- Oil dosage of ca. 15 to 35%, 50-65 °C, coal slurry concentration of 20-43%.
- Uses sour water (low pH may enhance ash rejection from some coals).
- Dissolved salts bled to Texaco gasifier.
- All organics, most iron, and pretreated catalyst retained.
- Some silica and ≈50% of sodium rejected from low-rank coals
- No coal reactivity loss.

Benefits

- Lower organic rejection results in perhaps a few percent higher MAF distillate yield.
- Lower ash content feed lowers viscosity and allows:

  - ▸ reduced solvent/coal ratio to perhaps 1.6, or
  - ▸ higher internal ashy recycle and reduced size of ROSE-SR unit.

- Reduced make-up of disposable catalyst with increased ashy recycle.

- Catalyst exposure to metal poisons may be reduced (especially Na in low-rank coals), resulting in lower catalyst replacement rate.

- Recovers coal from any aqueous pretreatment

In this scenario, coal is slurried with waste sour water from liquefaction and recycled water and it is agglomerated with heavy distillate. The agglomerates are rinsed over screens, blown with air to remove surface moisture, and sent to liquefaction. Additional drying prior to liquefaction is optional and depends on other factors (i.e., it is not a requirement of agglomeration). A slipstream of the agglomerate rinse water with mineral matter is used to slurry ash concentrate and coal for Texaco gasification. The remaining agglomerate rinse water with mineral matter is treated to remove solids, and then recycled for slurrying coal and rinsing agglomerates. Any additional water requirement would use gasification sour water, and any excess agglomeration waste water would go to water treatment with the gasification sour water. Because liquefaction is a net producer of water, both from coal drying, and from hydrogenation, it is anticipated that there will be an adequate water supply for agglomeration. The cost of water use and treatment will be minimized by using waste streams wherever possible.

Agglomeration of Low-Rank Coal at Natural pH, with Pretreated Coal Recovery

Features and Benefits

- Any aqueous coal pretreatment will require a recovery step.

- Recovery of coal from CO-pretreatment (as dry coal and as slurry) was demonstrated in Phase I work.

- Recovery of coal after two types of catalyst impregnation steps was also demonstrated in Phase I work. This avenue is pursued further in the discussion of agglomeration at natural pH, with catalyst impregnation, below.

- Other features and benefits are as generally described in the discussion of agglomeration at natural pH.

This concept differs from that of untreated coal recovery by agglomeration at natural pH in that aqueous coal slurry from a pretreatment step is agglomerated, instead of using sour water to slurry the coal. This concept is not restricted to any particular pretreatment, but was demonstrated in Phase I with CO-pretreated coal, and with catalyst-impregnated coal. Any use of sour water in the pretreatment or agglomeration steps depends on the specific pretreatment requirements. It is possible that rinsing of agglomerates with sour water could be done. Although not limited to any particular coal rank, it is anticipated that pretreatment will be most useful when low-rank coal is the feedstock.

Agglomeration at Natural pH, with Catalyst Impregnation

Features and Benefits

- Catalyst impregnation involving aqueous coal pretreatment can be followed by agglomeration for recovery, or impregnation can be incorporated into the agglomeration step.

- Other features and benefits are as generally described for agglomeration of untreated coal and pre-treated coal at natural pH.

In this concept, the agglomeration feed could be a pretreated coal, or a pretreated coal slurry (as in agglomeration of low-rank coal at natural pH, with pretreated coal recovery, above), or an untreated coal for treatment during part of the agglomeration process. This concept is not restricted to any particular pretreatment, but it was demonstrated in Phase I with two methods of catalyst impregnation of coal, and catalyst impregnation is a likely pretreatment step. Any use of sour water in the pretreatment or agglomeration steps depends on the specific pretreatment requirements. It is possible that rinsing of agglomerates with sour water could be done. Although not limited to any particular coal rank, it is anticipated that pretreatment will be most useful when low-rank coal is the feedstock.

Agglomeration of Low-Rank Coal at Low pH

Features

- Coal ranging in rank from lignite through subbituminous can be reduced in MF ash content by ca. 50 to 76 relative percent.

- pH of 1 or 2 using H_2SO_4.

- Oil dosage of 21 to 54%, 50°C, coal slurry concentration of 20 to 43%.

- Uses sour water (low pH may reduce acid requirement).

- Dissolved salts bled to Texaco gasifier.

- All organics and most iron retained; perhaps pretreated catalyst also retained.

- Some silica and ≈90% (projected) of Na, K, Ca, Mg rejected.

- No coal reactivity loss.

Benefits

- Lower organic rejection results in perhaps a few percent higher MAF distillate yield.

- Lower ash content feed lowers viscosity and allows:
  - reduced solvent/coal ratio to perhaps 1.3, or
  - increased internal ashy recycle and reduced size of ROSE-SR unit.

- Reduced make-up of disposable catalyst with increased ashy recycle.
- Supported catalyst exposure to metal poisons, especially Na and Ca, significantly reduced, resulting in lower catalyst replacement rate by 30% (est.).
- Recovers coal from any aqueous pretreatment.

In the low pH agglomeration scheme, low-rank coal is slurried with waste sour water from liquefaction and pH-adjusted recycled water and agglomerated with heavy distillate. The agglomerates are rinsed over screens, blown with air to remove surface moisture, and sent to liquefaction. Additional drying prior to liquefaction is optional and depends on other factors (i.e., it is not a requirement of agglomeration). A slipstream of the agglomerate rinse water with mineral matter is used to slurry ash concentrate and coal for Texaco gasification. The remaining agglomerate rinse water with mineral matter is treated to remove solids and re-establish low pH, and then recycled for slurrying coal and rinsing agglomerates. Any additional water requirement would use gasification sour water, and any excess agglomeration waste water would go to water treatment with gasification sour water. Because liquefaction is a net producer of water, both from coal drying, and from hydrogenation, it is anticipated that there will be an adequate water supply for agglomeration. The cost of water use and treatment will be minimized by using waste streams wherever possible.

Segregation of Feed Coal Quality to Liquefaction and Gasification

Features

- Column flotation or other fine-coal cleaning method.
- For bituminous and subbituminous coals.
- No reject, as discussed here.

Benefits

- Reduces ash content of liquefaction feed coal from 6.3 to 3.8 % MF while increasing gasifier feed coal ash to 14.7 % MF for fine Black Thunder coal (not SO^3-free).
- Reactive maceral enrichment improves coal conversion by 1% MAF (est.).
- Increases product yield by 3.5% MAF (est.) by reducing deasher reject.
- Reduced solids loading allows:
  - lower solvent to coal ratio, or
  - higher solids recycle, which reduces deasher size by 1/5 (est.) and make-up of dispersed catalyst.

DISCUSSION

Figure 3 is a simplified flow sheet for agglomeration in an integrated plant that includes both coal liquefaction and gasification. Coal is slurried with waste

sour water from liquefaction and recycled water and it is agglomerated with heavy distillate. The agglomerates are rinsed over screens, blown with air to remove surface moisture, and sent to liquefaction. Additional drying prior to liquefaction is optional and depends on other factors (i.e., it is not a requirement of agglomeration). A slipstream of the agglomerate rinse water with mineral matter is used to slurry ash concentrate and coal for Texaco gasification. The remaining agglomerate rinse water with mineral matter is treated to remove solids, and then recycled for slurrying coal and rinsing agglomerates. Any additional water requirement would use gasification sour water, and any excess agglomeration waste water would go to water treatment with the gasification sour water. Because liquefaction is a net producer of water, both from coal drying, and from hydrogenation, it is anticipated that there will be an adequate water supply for agglomeration. The cost of water use and treatment will be minimized by using waste streams wherever possible.

Agglomeration at Natural pH

Basis and Assumptions

The Revised Base Case (RBC) baseline economic assessment prepared by LDP Associates,[16] provides the basic flow rates for conversion estimates with low-rank coal. These flow rates can be adjusted for feed coal ash concentration.

Agglomeration performance is assumed to be the same, regardless of whether the oil is untreated, dewaxed, or hydrotreated. Earlier CONSOL work[17,18] demonstrated that a variety of oils will be successful, though the physical deashing performance may vary. At the present stage of development, it appears to be neither very practical nor useful to determine the performance dependence on specific oil characteristics.

All waste sour water from liquefaction would be used for agglomeration, and net (non-recycled) waste water from agglomeration goes to slurry the ash concentrate and the coal (as an option) for Texaco gasification (water to gasification = sour water in). Any additional water requirement would be supplied by gasification sour water, and any excess agglomeration waste water would go to water treatment with gasification sour water. Because liquefaction is a net producer of water, both from coal drying, and from hydrogenation, it is anticipated that there will be an adequate water supply within the plant for agglomeration (provided that water quality is suitable). We increased the coal slurry concentration in our latest agglomeration tests specifically to reduce the agglomeration water requirement for cost savings.[11] As to the amount of water required, and expected to be available in a liquefaction facility, some rough estimates can be found. In considering phenolics recovery from liquefaction sour water (no specific feed or liquefaction process), Zhou[19] estimated the sour water flow rate to be equal to that of the MAF feed coal. In the RBC,[16] the water yield is 12.45% of the MF Black Thunder coal fed. This is from hydrogenation; no strict accounting of water from drying, or of sour water, or of the requirement for gasification, was given. In LDP Associates' evaluation of the Bechtel Low-Rank Coal Case,[20] the water in is 5.58% of the feed Black Thunder coal (at 2% moisture); the sour water out is 21.10% of the coal in (net of 15.52% of the coal in). (Bechtel reports water yield as 15.80 wt % of MAF coal.) Thus, under suitable conditions of recycle water quality and flow rate, there should be a sufficient supply.

In order to estimate water requirements for agglomeration, for subbituminous and bituminous coals we will use 0.65:1 as a general estimate for the ratio of available liquefaction sour water:as-received coal, based on Zhou's rule-of-thumb estimate (discussed above).[19] A conceptual commercial liquefaction plant design has so many factors that affect water use, that a reliable value for relative sour water flow rate could only be determined for a fairly specific plant design and feed. We will assume that the coal slurry water requirement is 1.33:1 water:as-received coal, as expected at a coal slurry concentration of 43%. We will also assume that the agglomeration rinse water requirement is ≈3 times this coal slurry water requirement (making the rinse requirement 4:1 water:as-received coal). Thus, the overall water requirement for agglomeration is about 5.33:1 water:as-received coal. For this overall water requirement, and the assumed availability of 0.65:1 sour water:as-received coal for agglomeration water feed (i.e., the make-up water), the recycle water: sour water (make-up) ratio is (5.33-0.65):0.65, or 7.2:1. At the extreme low coal slurry concentration of 20%, the slurry and rinse would each be 4:1 water:as-received coal, with an overall agglomeration water requirement of about 8:1 water:as-received coal. Under these conditions, the recycle water: sour water (make-up) ratio would increase to (8.00-0.65):0.65, or 11.3:1. For both extremes in slurry concentration, the recycle water requirement is significant, and the full consequences of recycle are difficult to predict. This area is one of the principal technical uncertainties in implementation of agglomeration as a liquefaction pretreatment, at the present level of development. It is an important area for developmental work in Phase II.

Reject water is assumed to require only thickener plus flocculent or hydrocycloning prior to recycle for coal slurrying and for rinse water (i.e., it is assumed that water quality after solids removal is suitable for recycle and reuse). The basis for this assumption is that this is conventional practice in coal preparation plants. It is also presumed that staging or a countercurrent flow arrangement can accommodate the necessary rinse water quality if required.

It is assumed that low-grade waste heat can be used to supply much of the heat required for agglomeration at ~50°C.

It is assumed that agglomerated coal can be dried by mechanical means (such as shaking and blowing air) to the moisture content of the feed coal (i.e., no heat required to remove surface moisture).

Iron and any added catalyst (such as by incipient wetness, or IW) is assumed to be preferentially retained in agglomerates.[8,9] Such an application of agglomeration to catalyst-impregnated coal is described in more detail later.

It is assumed that, in low rank coals, some silica is preferentially lost to reject,[8] and ≈50% of sodium is lost to the reject and reject water.[18] In Phase I, we created an empirical model to relate agglomeration performance of coal of various ranks with silica content.[8] Various ion exchange studies have indicated that the amount of sodium and other elements rejected through dissolution depends on the coal, natural pH, etc.[21-25]

Coal liquefaction reactivity is assumed to be unchanged by agglomeration. In the case of Illinois 6 coal, CONSOL found increased reactivity.[17] In the PST results in Phase I of this contract, the reactivity of Black Thunder coal was unchanged by agglomeration, within measurement limits.[9] Not a great deal of reported

research has addressed the liquefaction reactivity of agglomerated coal. Outside of batch liquefaction tests, the coal reactivity may be confounded with other liquefaction conditions. To some extent, agglomeration of low-rank coal at natural pH will leach out soluble cations, such as Na^+. Researchers have obtained mixed results when investigating the liquefaction reactivity of ion-exchanged low-rank coal.

Advantages

The major liquefaction system benefits are derived from the use of a feedstock which is lower in ash content. Lower organic rejection results in perhaps a few percent higher MAF distillate yield. The lower ash content feed results in reduced slurry viscosities which allows the solvent/coal ratio to be reduced to perhaps from 2.3 to 1.6, or allows internal ashy recycle to be increased, with a reduced size of the ROSE-SR unit. Increased ashy recycle rates may allow reduced make-up rates for disposable catalyst. In bench unit run CC-6, HRI obtained 1.5% higher MAF coal conversion and 6% higher distillate yield when feeding Illinois 6 coal which had been agglomerated with heptane and asphalt. A 4% shift in yield toward distillate and away from resid was also noted in comparing agglomerated coal performance with that of coal cleaned by other techniques.[26] Agglomeration decreased the coal ash content from 15.2 to 4.6% ash (MF?), and the coal, as fed, contained 1.93% asphalt. HRI used solids-free recycle, and recycle/coal ratios of 1.8 and 1.3. The degree that the improved conversions reflect the lower catalyst age used for agglomerate liquefaction, and the conversion of asphalt is not known.[27-31] The run was successful, and it seems to indicate that it is reasonable to expect improvements of a few percent in coal conversion and distillate yield. Because of differences in conditions, such as recycle/coal ratio, and ashy vs. solids-free recycle, it does not provide any straightforward estimate of expected performance in this program. Holm and Knudson[22] saw little benefit to the use of increased ash or organic recycle when testing liquefaction of low-rank coals with CO/H_2. However, they surmised that native catalyst in the materials they were using may have deteriorated during storage, or that enhanced catalytic effects from increased mineral recycle may have required a better donor solvent to be manifested. They were not using any extraneous catalyst, such as we have explored in this program with Black Thunder coal.

Agglomeration is useful for coal recovery if any aqueous pretreatment is used. This was demonstrated in Phase I with successful agglomeration of CO-pretreated coal,[5] CO-pretreated coal slurry,[7] and catalyst-impregnated coal[8,9] (these are discussed in more detail in later scenarios).

Another advantage is that incipient wetness (IW) dispersed catalyst was quantitatively retained when tested with subbituminous coal.[8,9] Also, there is nearly quantitative recovery of the organics with the agglomerates. This was consistently demonstrated in Phase I work, and it was addressed more specifically in the PST.[9]

This process uses the liquefaction recycle distillate for agglomeration - most agglomeration concepts tested to date have used use an external oil.

Integration opportunities exist anywhere in the whole plant that water is generated or used; and anywhere that low-grade heat is available.

Sour water use may improve ash reduction, especially in low-rank coals, because of its reduced pH. Catalyst exposure to metal poisons from these coals may, therefore, be reduced, potentially extending catalyst activity and life. Ash reduction enhanced by low pH and ion-exchange is discussed in more detail in the discussion of low pH agglomeration. Use of sour water also may allow retention of sulfur on the agglomerates, consequently decreasing the sulfiding agent requirement for liquefaction of low-rank coals.

Requirements/Disadvantages

Heat is required for agglomeration at 50 to 65 °C. Capital equipment also is required, but it is generally this equipment is unpressurized and relatively inexpensive. An adequate water supply of suitable quality is required and additional drying may be warranted, depending on overall process requirements. The water requirement is uncertain - make-up and additional treatment may be required.

Research Needs

The water chemistry, including recycle and integration, is ill-defined and would benefit from recycle tests, at the lab scale and larger. The drying needs and options should be assessed in light of system integration (i.e., what degree of drying is desired prior to slurry mix/liquefaction?).

Continuous-unit testing of agglomerated coal is necessary to test integration and demonstrate liquefaction system benefits (including catalyst benefits).

Specific Results and Benefits with Bituminous Coal

Clean Burning Star 2 coal was reduced in MF ash content from 11.6 to 7.6 wt % (including SO_3) in agglomeration run A34.[6] Other conditions and performance were: coal slurry concentration of 20%; natural pH, oil dosage of 33%; 65 °C; and 38.0% total ash rejection/32.7% physical ash rejection. A number of tests gave similar results at various conditions, such as 50 °C, pH adjusted to 8 with NaOH, or oil dosage as low as 15%. Thus, it appears that this level of performance is achievable at a variety of conditions. Though never tested, it is projected that similar performance could be achieved at 43% slurry concentration.

It is estimated that lower organic rejection results in perhaps 3-4% MAF higher distillate yield. Alternatively, the solvent/coal ratio could be reduced to perhaps 1.6. The Bechtel Baseline Case with Illinois 6 coal[32] could be used to provide a flow basis for more detailed evaluation.

In previous work,[17] it was found that Fe and Ti are preferentially retained in agglomerates; Ca, Si, and Al are selectively rejected; other elements such as Mg and K showed some preference for agglomerate retention; Na was retained in agglomerates, evidently in retained water which had been pH-adjusted with NaOH.

Specific Results and Benefits with Subbituminous Black Thunder Coal

Black Thunder mine coal was reduced in MF ash content from 6.6 to 4.6 wt % in agglomeration runs A56 and B42 (not ash SO_3-corrected).[11] Other conditions and performance were: coal slurry concentration of 43%; natural pH, oil dosage of 30%; 50 °C; and 31% total ash rejection/14% physical ash rejection. In run B37

of the Process Simulation Test (PST),[9] the product ash content obtained was 4.9 wt % (SO_3-free) at a coal slurry concentration of 20%; the total ash rejection was 18%, and the physical ash rejection was 11%.

It is assumed that lower organic rejection results in perhaps 2% MAF higher distillate yield (estimated from RBC flow adjustments for lower-ash feed). Alternatively, solvent/coal ratio could be reduced to perhaps 1.6.

The flow basis for additional evaluation should be LDP Associates' Revised Base Case, RBC (ash SO_3-free Wilsonville period 263J),[16] or a suitable revision of it. An appropriate revision may be one which uses Texaco gasifiers for the entire facility[33] (the RBC uses Shell gasification for coal, and Texaco gasification for ash concentrate).

Low pH from sour water use is expected to enhance ash rejection through increased ash dissolution (refer to the section on low pH agglomeration). Use of sour water may result in retention of sulfur on the agglomerates, thereby decreasing the sulfiding agent requirement.

Phase I work has demonstrated retention of all Fe and Mo in IW-treated Black Thunder coal agglomerates[8,9], and retention of 71% of the Fe in ion-exchanged coal[8] (these pretreatments for catalyst dispersion are discussed more in the section on agglomeration with catalyst impregnation).

Though not clearly demonstrated for Black Thunder coal in the absence of other factors, it is assumed that most of the iron is retained in the agglomerates, some silica is preferentially lost to reject, and ≈50% of the sodium is lost to reject and reject water. This is based on results with impregnated Black Thunder samples (IW and ion-exchanged), and on previous results with Clovis Point and Martin Lake coals at natural pH.[18] Sodium is consistently the most soluble ash element in low-rank coals, but Na_2O constitutes only about 0.5 wt % of the Black Thunder coal ash.[9] The K_2O concentration is also low (≈0.5 wt %) in Black Thunder ash, but CaO and MgO are present in much higher concentrations of 21 and 4 wt %, respectively.

To the extent that the concentrations of sodium and other metals are decreased during agglomeration, catalyst exposure to metal poisons is reduced, potentially extending catalyst life. This issue is discussed further in the discussion of low pH agglomeration.

Specific Results and Benefits with Other Low-rank Coals

McKinley Mine subbituminous coal was decreased in MF ash content from 11.7 to 4.6 wt % in agglomeration runs A51 (not ash SO_3-corrected).[6,7] Other conditions and performance were: coal slurry concentration of 20%; pH adjusted to 8 with NaOH; oil dosage of 24%; 54 °C; and 64% total ash rejection/57% physical ash rejection. Similar results were also obtained at the natural pH, and at a temperature of 50 to 65 °C (runs A46 and A52).[7]

Kemmerer Mine subbituminous coal was decreased in MF ash content from 3.7 to 1.9 wt % in agglomeration run A51 (not ash SO_3-corrected).[6-8] Other conditions and performance were: coal slurry concentration of 20%; pH adjusted to 8 with NaOH; oil dosage of 51%; 27 °C with No. 2 diesel oil; and 50% total ash rejection/30% physical ash rejection. Similar results were found in run A40: at

conditions of natural pH, 26% oil dosage, and 23 °C, the product ash content was 2.1% MF, there was 44% total ash rejection, and 30% physical ash rejection.[7] This was an old sample of Kemmerer mine coal.

Spring Creek Mine subbituminous coal was decreased in MF ash content from 5.3 to 4.7 wt % in agglomeration run A23 (not ash SO_3-corrected).[5] Other conditions and performance were: coal slurry concentration of 20%; natural pH; oil dosage of 22%; 50 °C; and 12% total ash rejection/4 % physical ash rejection. This was an old sample, and only one run was performed.

Martin Lake Mine lignite was decreased in MF ash content from 13.2 to 9.9 wt % in agglomeration run A41 (not ash SO_3-corrected).[7] Other conditions and performance were: coal slurry concentration of 20%; natural pH; oil dosage of 33%; 54 °C; and 28% total ash rejection/27% physical ash rejection. Nearly identical results were obtained in run A43, in which the pH was adjusted to 8 with NaOH.[7]

Recommendations

- Specific trials are recommended for Phase II testing of agglomeration as a coal cleaning method for bituminous and subbituminous coals (probably Illinois 6 coal and Black Thunder mine coal). Development areas include water issues (sour water use, recycle and integration possibilities), drying issues, and continuous liquefaction testing to quantify and validate the anticipated benefits of agglomeration.

- Though not proposed for Phase II development, it is recommended that suitable additional candidates for agglomeration and liquefaction be identified and screened. The agglomeration and liquefaction performance of individual coals is highly variable, but a menu or range of options is highly desirable. Price and availability of feedstocks change, and liquefaction technology should not be locked in to one feedstock. Notable feedstocks explored here are Kemmerer and of McKinley Mine coals and the Beulah-Zap lignite. Kemmerer coal, which is low-ash to begin with, is cleanable at natural pH to 1.9 wt % MF ash. McKinley coal is quite cleanable to an ash content of 4.6 % MF, and has been tested by HRI in the coal-oil co-processing program. Neither of these coals was tested at low pH. Beulah-Zap lignite (discussed below) was cleanable to 2.5 wt % MF ash at low pH.

Agglomeration of Low-Rank Coal at Natural pH, with Pretreated Coal Recovery

This concept differs from that of agglomeration of untreated coal in that aqueous coal slurry from a pretreatment step is agglomerated, instead of using sour water to slurry the coal. This concept is not restricted to any particular pretreatment, but was demonstrated in Phase I with CO-pretreated coal, and with catalyst-impregnated coal. Any use of sour water in the pretreatment or agglomeration steps depends on the specific pretreatment requirements. It is possible that rinsing of agglomerates with sour water could be done. Although not limited to any particular coal rank, it is anticipated that pretreatment will be most useful when low-rank coal is the feedstock.

Black Thunder Coal Results

CO-pretreated Black Thunder coal (dry coal) was agglomerated in runs B24 and B25H,[5,7] at an oil dosage of ≈15%, natural pH, temperatures of 50 °C and 175 °C (to simulate liquefaction slurry mix tank temperature for integration purposes). The best results were at 175 °C: MF product ash content of 5.3%, 16% total ash rejection, and no physical ash rejection. In runs B31, B32H, and B33, CO-pretreated Black Thunder coal slurry was agglomerated.[7] As before, the best results were achieved in a run at 175 °C, run B32H: the MF product ash was 4.2%, 11% of the ash was rejected, of which 4% was recovered. When put on an SO_3-free ash basis, and referenced to the untreated feed, the product ash content was 4.0% MF, and 29% of the ash was rejected (3% recovered).

Black Thunder coal impregnated with catalyst by incipient-wetness and ion-exchange methods was also successfully agglomerated in Phase I. Agglomeration of all of these pretreated coals at conditions ranging from 50 to 175 °C, and agglomeration of various coals using several oils at a range of pH, temperature, and slurry concentration demonstrate that agglomeration is a robust method for recovery of fine coal from aqueous slurries. All of these tests with pretreated coal used Black Thunder coal - no other pretreated coal was tested under these conditions.

Recommendations

Agglomeration was demonstrated to be a robust method for recovery of pretreated coal. It is recommended for use if CO-pretreatment, or catalyst impregnation is pursued for further development. Developmental and integration uncertainties seem to be much greater for this scenario than for any of the others, because so much depends on the specific pretreatment scheme.

Agglomeration at Natural pH, with Catalyst Impregnation

In this concept, the agglomeration feed could be a pretreated coal, or a pretreated coal slurry (as in natural pH agglomeration of pre-treated coal, above), or an untreated coal for treatment during part of the agglomeration process. This concept is not restricted to any particular pretreatment, but it was demonstrated in Phase I with two methods of catalyst impregnation of coal, and catalyst impregnation is a likely pretreatment step. Any use of sour water in the pretreatment or agglomeration steps depends on the specific pretreatment requirements. It is possible that rinsing of agglomerates with sour water could be done. Although not limited to any particular coal rank, it is anticipated that pretreatment will be most useful when low-rank coal is the feedstock.

Black Thunder Coal Results

Catalyst impregnated Black Thunder coal (as both wet and dry coal) was agglomerated in several runs. In run B35,[8] Black Thunder coal which had been ion-exchanged to impregnate it with Fe was agglomerated at natural pH, 50 °C, and an oil dose of 40 wt %. The coal was reduced in ash content from 8.28 wt % MF to 6.20 wt % MF (SO_3-free ash basis), total ash rejection was 27%, and physical ash rejection was 16 %. Because of the catalyst addition, the final ash content is higher than that of the untreated feed coal, 5.54 wt % MF, SO_3-free ash basis. Retentions of various elements in the ion-exchange pretreated run B35 product agglomerates were: <1% for Na, 23% for K, 71% for Fe, 75% for Ca + Mg, 77% for

Si, and 95% for Al (only Fe was presented in the report[8]). The loss of some of the Fe during agglomeration may have resulted from the low natural pH of 3, at which Fe may have been ion-exchanged back out of the coal matrix.

In run B34,[8] Black Thunder coal which had been impregnated with Fe by incipient wetness (IW) was agglomerated at natural pH, 50 °C, and an oil dose of 38 wt %. The coal was reduced in ash content from 6.35 wt % MF to 5.62 wt % MF (SO_3-free ash basis), total ash rejection was 12%, and physical ash rejection was 7%.[8] In this case, the final ash content is about the same as that of the untreated feed coal, 5.54 wt % MF, SO_3-free ash basis. Retentions of various elements in the IW-pretreated run B34 product agglomerates were: 81% for Na, 47% for K, 100% for Fe, 95% for Ca + Mg, 72% for Si, and 89% for Al (only Fe was presented in the report[8]).

In the PST,[9] four agglomeration runs (B39, B40, B41, and A53) were made using Black Thunder coal which had been IW-impregnated with Fe and Mo. Conditions were natural pH (4.1 to 4.4, lower than the pH of 7.2 in run B34), 50 °C, and 36 to 40% oil dose. Results were that ash content was reduced from about 6.8 (6.68 to 6.85) wt % MF ash to about 5.3 wt % MF (5.05 to 5.51) (SO_3-free ash basis), total ash rejection was about 24% (20 to 28%), and physical ash rejection was about 4% (1 to 6%). The final ash contents from these runs were slightly lower than that of the untreated feed coal, 5.54 wt % MF, SO_3-free ash basis. In the PST runs, the total ash rejection was higher than in run B34. The acidic Fe catalyst precursor used in the PST feeds (but not in run B34) evidently aided in ash dissolution by lowering the natural slurry pH to about 4.

The calculated retentions of various elements in the IW-pretreated PST product agglomerates were: 97 to 122% for Fe, 97 to 104% for Mo, 37 to 47% for Ca + Mg, 72 to 97% for Si, and 90 to 108% for Al.[9] Not presented in the report with the others were the retentions of Na and K, which are 19 to 33% for Na, and 76 to 101% for K. In the PST IW coal runs, some ash was dissolved, yet all of the desirable catalytic elements Fe and Mo were retained. Based on the results of elemental analyses, and other observations throughout the program, it appears that Na, Ca and Mg are rejected by dissolution, Si is rejected by physical means, and Al is not rejected to a great degree. These results indicate good potential for integration of pretreatment by IW with agglomeration.

Black Thunder coal impregnated by catalyst by incipient-wetness and ion-exchange methods was successfully agglomerated in Phase I. As discussed above, agglomeration of a variety of pretreated and untreated coals at a variety of conditions demonstrates that agglomeration is a robust method for recovery of pretreated fine coal.

This concept was only tested with Black Thunder Mine coal. It is expected to be suitable for any rank of coal. Catalyst impregnation seems to be best suited to low-rank coal, but IW could be used with bituminous coal if it were advantageous (ion exchange is probably not best suited to bituminous coal).

Recommendations

Agglomeration was demonstrated to be a robust method for recovery of catalyst-impregnated Black Thunder coal (especially IW-treated). It is recommended for further development and testing if catalyst impregnation remains a viable option for further development in Phase II. Developmental needs lie primarily in the

area of closely integrating the two concepts. It is expected that ion exchange would be integrated differently than would incipient wetness. For example, IW treatment might precede slurrying for agglomeration, but ion exchange pretreatment might take place during agglomeration slurry conditioning, before addition of oil. Lab tests of various integration options would precede any testing at a larger scale.

Agglomeration of Low Rank Coal at Low pH

Basis and Assumptions

The Revised Base Case (RBC) baseline economic assessment prepared by LDP Associates,[16] provides the basic flow rates for conversion estimates with low-rank coal. These flow rates can be adjusted for feed coal ash concentration.

It is assumed that iron and any added catalyst (such as by IW) is preferentially retained in agglomerates;[8,9] some silica is preferentially lost to reject; an estimated ≈90% of sodium, potassium, calcium, and magnesium is lost to the reject and reject water. The application of agglomeration to catalyst-impregnated coal is described in more detail later. Ion exchange of low-rank coal has been investigated extensively, for example at the University of North Dakota.[22,23,25] The amount of sodium and other elements rejected through dissolution depends on the coal, pH, etc., as various ion exchange studies have indicated.[21-25]

Coal liquefaction reactivity is assumed to be unchanged by low-pH agglomeration. Reactivity of ion exchanged coal has been investigated by a number of researchers, with mixed results. For example, Joseph and Forrai[21] found that removal of Na, K, and Ca by ion exchange benefitted the liquefaction conversion of Wyodak subbituminous and lignite coals. Holm and Knudson[22] observed that addition of cations by ion exchange had minimal effect on the liquefaction reactivity of several subbituminous and lignite coals, and concluded that there was little promise of enhanced reactivity by this method. In their work, removal of metals by ion exchange typically reduced the reactivity of the coal.

A 30% improvement in supported catalyst life is estimated to result from significant reduction in the catalyst poisons Na, K, Ca, and Mg. There is no specific model of catalyst aging with metals concentration which we could apply here. Sakanishi[34] found that ion-exchange of brown coal-derived vacuum resid to replace alkali and alkaline earth metals with hydrogen improved its hydrotreatment performance. This was attributed, in part, to lower coke formation and less metals poisoning of the catalyst, due to extraction of basic coke precursors, and extraction of the metallic elements.

The adjustment of pH with sulfuric acid may aid water treatment by precipitation of gypsum prior to water recycle. This reduces the Ca ion concentration, which allows for Ca ions in the coal to be exchanged for hydronium ions. In Phase I agglomeration tests at pH below about 2.5 with sulfuric acid, gypsum formation was observed.[11]

We estimate that the disposable catalyst requirement can be reduced by perhaps 50%, with sufficiently increased ash recycle.

Advantages

The use of low pH greatly enhances ash rejection from low-rank coals. Ash rejections of 50 to 75% from low-rank coals have been obtained with agglomeration at low pH in the Phase I work. This improves the anticipated liquefaction benefits (higher distillate yield, with lower solvent/coal ratio or increased ash recycle with smaller ROSE unit and reduced disposable catalyst requirement) beyond those described in the natural pH agglomeration discussion. Because alkali and alkaline earth metals are preferentially removed, the exposure of supported catalyst to metal poisons is greatly reduced.

The solvent/coal ratio can be lowered to perhaps 1.3, if desired. Alternatively, internal ashy recycle can be increased, with a reduced size of the ROSE-SR unit. Increased ashy recycle rates may allow reduced make-up rates for disposable catalyst.

The use of sour water and sulfuric acid for agglomeration may allow retention of sulfur on the agglomerates, consequently decreasing the sulfiding agent requirement for liquefaction of low-rank coals. Experimentally, the sulfur content of the product of low-pH agglomeration run B38 (PST[9]) exceeded that of the feed by 1 wt % or more. This seemed to be accounted for by retention of pH 1 water on the agglomerates prior to air-drying.

Other advantages have already been described for agglomeration at natural pH.

Requirements/Disadvantages

In addition to items listed in the section on neutral pH agglomeration, acid is required. This will, in turn, affect water treatment requirements, and the choice of materials needed for corrosion resistance in agglomeration equipment vessels.

Research Needs

These are the same as those described in the section on neutral pH agglomeration, except that more stringent requirements will be placed on low-pH water chemistry issues of recycle quality and flows, and on integration.

Specific Results and Benefits with Subbituminous Black Thunder Coal

In PST agglomeration run B38 (ash SO_3-corrected),[9] the coal ash was decreased from 5.6 to 2.9 wt %; the coal slurry concentration was 20% (it is projected from runs B43 and B44[11] that a concentration of 43% can be used); pH of 1 adjusted with H_2SO_4, oil dosage of 33%; 50 °C; 50.3% total ash rejection/8% physical ash rejection (it is projected from runs B43 and B44 that the physical ash rejection might be 20% at a 43% coal slurry concentration). However, in no other Black Thunder coal run was the product ash content as low as 2.9%. The lowest ash content otherwise achieved was 3.7% in runs B43 (pH 2, H_2SO_4) and B44 (pH 1, HCl), both at 43% coal slurry concentration, and about 31% oil dosage, which gave about 46% total ash rejection, and about 20% physical ash rejection. For this reason, the product ash content of 3.7 wt % is preferred as the more conservative estimate. Lower organic rejection results in perhaps 4% MAF higher distillate yield.

Lower ash content feed lowers the slurry viscosity and allows reduced solvent/coal ratio to perhaps 1.3. Alternatively, the internal ashy recycle can be increased, with a reduction in the size of the ROSE-SR unit. Increased ashy recycle rates may allow reduced make-up rates for disposable catalyst.

Other Low-rank Coal Results

An Argonne Premium Coal Sample of Beulah-Zap (North Dakota) lignite was agglomerated at low pH (pH 1, H_2SO_4) in runs B20 through B22 (not ash SO_3-corrected).[5] The coal ash was decreased from 9.7 to about 2.5 wt % MF; the coal slurry concentration was 20% (it is projected that a concentration of 43% can be used); oil dosage of 21 to 54%; 50 °C; 71 to 77% total ash rejection/4 to 12% physical ash rejection.

Recommendations

This concept is specifically recommended for further development and scale-up in Phase II. The same recommendations as were described for neutral pH agglomeration apply, except that more stringent requirements will be placed on low-pH water chemistry issues of recycle water quality and flows, and on integration. Additional candidate coals for low-pH agglomeration should be identified. The Beulah-Zap lignite appears to be a good candidate from a cleanability standpoint.

Segregation of Feed Coal Quality to Liquefaction and Gasification

In this scenario, the ground feed coal to the plant is fed to a fine-coal cleaning plant to produce two streams: a low-ash liquefaction feedstock and a higher ash gasifier feedstock. Since the gasifiers process all the coal ash fed to the plant anyway, either as native coal ash or as ROSE bottoms ash, this step does not burden the gasifiers with additional ash, but does substantially reduce the ash burden on the liquefaction section. The segregation efficiencies used here were obtained from cleanability curves generated on pc-grind coals and may be difficult to accomplish in practice. The segregation efficiency would probably be poorer if coarser coals were used. The cleaning process is undefined here; however, oil agglomeration probably would not be a suitable method because it tends to provide full recovery of organics in one stream, rather than segregation into two streams as required in this scenario. The primary costs are the capital and operating costs of the cleaning plant (and any costs associated with dewatering the cleaned product). Examples are shown for Black Thunder coal, Martin Lake lignite, and Burning Star 2 coal.

Assumptions

Coal feed rates for the whole plant and for the liquefaction and gasification sections were obtained as follows: M. Peluso's Base Case Study was used for Black Thunder coal and for Martin Lake lignite; as a first approximation, the MAF lignite feedrates were assumed to be the same as for Black Thunder coal; Bechtel's Improved Baseline Design was used for Burning Star 2 coal. For this exercise, it was assumed that the segregation of coal quality would not affect the MAF coal feed rates to the whole plant or to the liquefaction or gasification sections. Separation efficiency was assumed to follow the gravity-based cleanability curves generated by CONSOL on samples of the fine coals.[6] Separation efficiencies were read from CONSOL's cleanability curves (which consist of straight-line segments connecting the data points). It may be

difficult to meet the performance of the cleanability curves in practice. For example, in a short exploratory study, Slomka et al.[5] found that the PC grind Black Thunder coal (an aliquot of the baseline coal used in this project) showed poor cleanability in column floatation. Upon further grinding of the coal, column floatation reduced the MF ash content of the coal from 6.5 wt % to 4.7 wt % at 72% coal recovery. The authors indicated that the column floatation performance of this coal could be further improved.

Results

The results are shown in Table 6. The liquefaction feedstocks can be reduced in ash contents by segregation as follows (values shown for plant feed, liquefaction feed, gasifier feed, wt % MF ash): Black Thunder coal, 6.3, 3.8, 14.7; Martin Lake lignite, 13.2, 7.5, 29.6; Burning Star 2 coal, 11.5, 4.5, 25.3. These represent liquefaction feedstock ash content reductions of 40%, 43%, and 61%, respectively.

The process and economic benefits of a liquefaction feedstock with reduced ash content are detailed in the above discussions of oil agglomeration. Similar benefits would apply to this scenario, although the greater reduction in ash content in this scenario would quantitatively increase the benefits. One additional benefit may be inferred from this scenario: it is likely that the segregation process would also somewhat segregate the coal macerals such that the more "reactive" macerals (liptinites and vitrinites) would concentrate in the low-ash stream and the "inert" macerals (e.g., fusinite) would concentrate in the high-ash stream. The inerts would not be a detriment to the gasifier, since it is a high-temperature gasifier, but the higher concentration of reactives probably would improve the liquefaction reactivity of the coal.

TASK 2.4.2 - SOLIDS SEPARATION (CONSOL)

SUMMARY

This section describes various solids separation scenarios, based on Phase I work performed under Task 2.4.2 - Solids Separation (CONSOL). The format used for this discussion is to describe the features and general benefits for each scenario, give specific results and benefits for different coals under that scenario, and to make recommendations for that scenario.

Solvent Improvement by Staged Rose-Sr Operation

Features

- Three-stage ROSE-SR unit operated to produce light (44-75%) and heavy (25-56%) deashed resid.
- For all coal ranks.
- Light resid is fed with distillate to solvent hydrogenation.
- Heavy resid is recycled to slurry with ash concentrate.
- A portion of the ash concentrate is gasified.

- All V-1082 is deashed; as much light resid as possible recycled back.
- Up to 57 wt % of recycled soluble resid is sent through solvent hydrogenation.
- The light resid cut (yield and properties) is determined by choice of deashing solvent and conditions.
- Light resid has a moderate content of aromatics and paraffins and is low in phenolic -OH concentration, indicating its suitability as a hydrogenation feedstock.

Benefits

- Provides a solvent component which is amenable to hydrogenation to improve solvent quality, without most of the components which are detrimental to the hydrogenation catalyst.
- Solvent quality improvements will improve conversion and yields.

DISCUSSION

The ROSE-SR unit will be operated in stages to produce a "light" de-ashed resid (LDAR) stream for hydrogenation with distillate to improve solvent quality prior to recycle. The "heavy" de-ashed resid (HDAR) will be recycled without additional treatment and IOM/ash component will be partially recycled and partially rejected. Proposed flow sheets for this operation are shown in Figures 4-6. Such operation provides a hydrogenation feed which is amenable to hydrogenation, but is not high in heteroatomic components which are detrimental to the hydrogenation catalyst, and is not high in paraffinic components which are poor hydrogenation feeds.

Basis and Assumptions

Solvent hydrogenation (with or without dewaxing) prior to recycle is a possible component of the process (per LDP Associates' evaluation). The flow basis is the Revised Base Case, RBC[16] (ash SO_3-free Wilsonville period 263J); no recycle distillate solvent flow adjustment was made for solvent hydrogenation. All V-1082 (ashy resid) is deashed; as much light resid as possible recycled back. The light resid is combined with distillate, hydrogenated, and recycled back to the first stage liquefaction reactor.

The lab extraction results[35] represent those expected in operation of the ROSE-SR process. A 75/25 split of LDAR to hydrogenation/HDAR to recycle from deashed resid is assumed. The wt % DAS and distillate in each (LDAR and HDAR) fraction is the same as in the original deashed resid (DAR).

The dewaxed oil used for property comparisons is the -5 °C acetone-dewaxed oil obtained in 80.2% yield in the PST test.

57.4 wt % of the recycled soluble resid (as LDAR) is sent through solvent hydrogenation.

The aromatic proton distribution is assumed to be 15.0% in V-1074 distillate, 21.1% in dewaxed distillate, 29.4% in DAR, ca. 26% in LDAR, and ca. 38% in HDAR, indicating that the LDAR is a good candidate for hydrogenation to improve solvent quality.[35] The phenolic -OH concentration is 0.44 meq/g in distillate, 0.50 meq/g in dewaxed distillate, 0.90 meq/g in DAR, ca. 0.56 meq/g in LDAR, and ca. 1.49 meq/g in HDAR, indicating relatively low heteroatom concentration in the LDAR.[35]

The paraffinic proton distribution (alkyl beta + gamma) is assumed to be 48.5% in distillate, 35.7% in dewaxed distillate, 30.8% in DAR, ca. 34% in LDAR, and ca. 20% in HDAR, indicating that the LDAR is equivalent to dewaxed distillate in proton paraffinicity.[35]

Advantages

Staged ROSE operation provides an aromatic solvent component which is amenable to hydrogenation to improve solvent quality, but protects the hydrogenation catalyst from the refractory HDAR. With hydrogenation, solvent quality improvements may surpass those obtained by dewaxing plus hydrogenation (not demonstrated).

Improved donor solvent may allow:

1. Improved coal conversions at current conditions. Experimental data suggest 3-4 wt % improvement in coal conversion is possible with dewaxing/hydrogenation. An increase in single pass coal conversion from 87 to 91 wt % could result in about a 6% decrease in rejected organics and a similarly improved product yield.

2. Operation at lower severity conditions (lower T, P, RT) while maintaining performance.

3. Operation at higher severity by reduction of retrograde reactions (increases in coal conversions of ~4 wt % were obtained at ~50 °F higher reaction temperatures using dewaxed/hydrogenated distillate); it could improve throughput.

Requirements/Disadvantages

A three-stage ROSE-SR unit is required (HRI currently using two-stage unit). This requires a 2-stage recycle oil settler as in the unit at Wilsonville, which was 3 stages total.

Recycle of heavy resid and most of ash concentrate also is required. The ROSE-SR unit will need to be 4.37 times the size of the unit in the RBC. The make-up DAS also will be 4.37 times the RBC value.

Research Needs

Testing of authentic ROSE-SR light resid is required. Integrated testing should be used to determine yields and demonstrate benefits.

Recommendations

It is recommended that the potential for solvent improvement be tested in the laboratory. To the degree that the extra deashing cost is outweighed by the solvent quality benefits (relative to, say, thermal dewaxing with hydrotreatment), then further development is indicated. This concept is more easily tested in batch or semi-continuous mode at the bench scale, unless an appropriate scale ROSE unit is available. Testing of various dewaxing concepts (which accomplish the same qualitative solvent quality goals) will indicate whether or not this is a fruitful approach to pursue.

Miscellaneous Concepts in Solids Separation

Several solids separation concepts which are not recommended for Phase II development are described in this section. There are various reasons why these concepts are not recommended for Phase II: some are less promising, some are less-developed, and others have not been explored in any detail. The purpose of this discussion is to highlight the Phase I results, and make recommendations regarding their potential future development, even though they are not ready for development now. This work was performed primarily under Task 2.4.2 - Solids Separation (CONSOL). For each concept, summary, discussion, and recommendations sections are provided. Most of this work covers alternative methods for resid deashing. A related concept, that of ash concentrate upgrading and utilization, was developed as the Phase I work progressed, and also is described.

Concept for Resid Deashing by Low-Temperature Agglomeration

Summary

In this approach to deashing liquefaction bottoms (resid) by agglomeration, the resid is used as the hydrophobic solid (instead of or along with coal), and it is agglomerated at near-ambient temperature with a compatible oil. The ashy resid (solid at room temperature) was ground and used as the agglomeration feed. Four runs were made with ball-milled ashy resid as the feed.[4,5] There was agglomeration, but no substantial deashing in the four runs. However, this approach produced substantial ash dissolution and a small amount of physical ash rejection, when used at conditions of low pH and room temperature. Under these circumstances, it appeared that low-pH agglomeration of the feed coal, instead of the ashy resid, would accomplish more.

The particle size of finely-ground (ball-milled) ashy resid was found to be quite small (volume % D_{50} of 9 μm), though the extent of ash liberation is unknown. SEM/EDX examination of a sample of the THF-insoluble fraction of the ashy resid showed that there is a significant fraction of liberated mineral matter (quartz, calcite, pyrrhotite, 10 to 20 m) in the insolubles.

Discussion

Two approaches to deashing liquefaction bottoms (resid) by agglomeration are: 1) to use the resid as the hydrophobic solid (instead of or along with coal), and 2) to use the resid as the agglomerating oil. The first approach is described here, and the second approach is described in the following section (agglomeration runs at elevated temperature and pressure). We briefly explored the first approach to rejecting ash from the ashy resid. The method employed was to grind

the ashy resid (it is solid at room temperature) and treat it as the agglomeration feed. An oil is used which allows agglomeration at low temperature, so that no melting of the resid occurs. A similar flotation method has worked for rejecting ash from tar sands.[4]

A ball mill was used to grind V-1082 ashy resid for 2 hr to 20 hr in water (50 wt % slurry). A portion of the ground resid slurry (diluted to 20 wt % slurry concentration) was agglomerated at near-ambient temperature with agglomerating oil (No. 6 fuel oil at 50 °C or white kerosene at room temperature). Four runs were made with ball-milled ashy resid as the feed: B9R, B11R, B12R, and B14R.[4] There was agglomeration, but no substantial deashing in any of the four runs. Na_2CO_3 was used as an additive in one run because it successfully promoted ash rejection in a tar sands flotation deashing technique;[36] however, it was not successful in this case. Two agglomeration runs (B16R and B17R[5]) were made at room temperature and low pH. A run at pH 1 produced a small amount of physical deashing (5%) and a significant amount of ash dissolution (33%); the run at pH 2.5 produced ash dissolution (~20%) without physical deashing. The acid reacted with the resid during grinding to produce some H_2S, perhaps from pyrrhotite present in the resid.

Overall, it seemed to be a better strategy to agglomerate the feed coal at low pH, and so much of our Phase I work was concentrated there. Sakanishi[34] found improved hydrotreatment when a brown coal resid was acid-washed (ion-exchanged). He credited removal of basic nitrogen components (coke-formers) and removal of cations with the improved performance, although there was no way to measure these effects independently. Low-pH treatment of the coal, instead of the resid, would only affect the cation components. This method of resid treatment perhaps could be further explored to determine the effect on basic coke precursors, and therefore, on expected catalyst deactivation.

Some characterization was done to assess ash liberation and deashing potential. Particle size measurements were made on one sample of V-1082 ashy resid which had been ball-milled overnight (50 % slurry in water). The ball-milled resid was found to be quite fine, though the potential ash liberation was not determined. A sample of the THF-insoluble fraction of the ashy resid was examined by SEM/EDX to provide information on the degree of mineral-organic matter association and the mineral particle morphology. There appeared to be a substantial (unquantified) fraction of liberated mineral matter (quartz, calcite, pyrrhotite, 10 to 20 m) in the insolubles. Thus, it appeared that it should be possible to reject ash from the resid by oil agglomeration, perhaps by either the low-temperature approach described here, or by the high temperature approach (described in the next section), if the solubles and IOM can be stripped from the minerals at some conditions.

Recommendations

Perhaps this overall approach could be explored further (though not in Phase II). At low pH, there may be some beneficial effect of removing basic components from resid-containing liquefaction streams. In terms of physical deashing, surfactants or other promoters may be useful.

Concept for Resid Deashing by High-Temperature Agglomeration

Summary

In this approach to deashing liquefaction bottoms (resid) by agglomeration, the ashy resid is used as the agglomerating oil, and dilution and high temperature are used to reduce oil viscosity to the desired level. The objectives were to simultaneously reject coal ash and resid ash in a manner which would allow integration in the liquefaction process. This approach has not resulted in appreciable resid deashing.

A benchtop stirred autoclave was adapted for agglomeration at elevated pressure and temperatures and used for agglomeration tests. Viscosity-temperature measurements were made on No. 6 fuel oil, Wilsonville V-130 deashed resid, V-1082 ashy resid, and three distillate/ashy resid blends to assist in establishing conditions for agglomeration tests.

Seven agglomeration runs were made at elevated pressure (150 to 250 °C, 50 to 650 psig) with Black Thunder feed coal and a distillate/ashy resid blend as the agglomerating oil. In some cases, no agglomeration took place, in others small agglomerates were produced, but there was no significant resid deashing.[4,5] Three pressure agglomeration runs were made with Black Thunder coal and ashy resid diluted with distillate at natural pH, pH 1, and pH 13 using resid only (no coal), so that resid deashing would be easily detected. Results ranged from no phase separation to 8 wt % physical ash rejection.

Discussion

In one agglomeration run (Run B23H[5]) made at 300 °C and 1300 psig with Black Thunder coal and a 75/25 wt % distillate/ashy resid blend, physical ash rejection was 4% and total ash rejection including dissolution was about 15%. This is similar to previous results obtained with this coal without the ashy resid (unpressurized, with distillate as the agglomerating oil). Therefore no resid deashing was evident.

Three agglomeration runs were made at 300 °C and 1300 psig with a 75/25 wt % distillate/ashy resid blend (Runs B26H, B27H, and B28H[5]). The runs used no coal so that resid deashing would be easily detected. The results were: no deashing at natural pH, no phase separation at pH 13.1, and 8 wt % physical ash rejection at pH 1. The calculated total ash rejection (dissolved plus physical) presents an inconsistent picture: it was high (48.7%) in the natural pH run, and negative (-15.4%) in the pH 1 run. Perhaps the negative value arises from mass balance errors or other analytical errors. The high ash rejection of nearly 50% was obtained in a single run and was not confirmed.

Recommendations

Perhaps this concept could be explored further, although not in Phase II. Viscosity reduction and perhaps encased mineral particles appear to be major technical problems to overcome to improve ash rejection. Surfactant action or lighter diluent liquids may be beneficial here (assuming easy recovery of lighter liquids elsewhere in the process). Because of the energy requirement for heat up to >100 °C, this concept would seem to be less desirable than most of the others discussed in this report. Unless other benefits are found, such as oxygen

removal at high temperature (a goal of the CO-pretreatment), it may not offer any advantages over low-temperature agglomeration or other resid deashing alternatives.

Concept for Resid Deashing by Alternate Means

Other physical methods, such as those based on electrostatic separation, or magnetic separation may be useful avenues to pursue, but not in Phase II. Emulsion-based techniques, which may be useful, were already mentioned in the previous discussions, because much of the emulsion and agglomeration chemistry is related. Many of the deashing, separation, or recovery techniques discussed in the next section would be applicable to ashy resid, as well as to ash concentrate.

Concept for Ash Concentrate Upgrading and Utilization

Summary

The V-107 ash concentrate sample from Period J of Wilsonville Run 263 was examined in order to better evaluate process options with regard to use of this stream in the liquefaction process.[5-7] Interest in better use of this stream was generated by the realization that this material had greater heating value, was lower in oxygen concentration, and was higher in catalyst concentration than the as-received feed coal. Recovery and utilization of soluble resid, DAS solvent, IOM, and/or dispersed catalyst to improve liquefaction economics was the objective of this work. Various physical and chemical approaches were considered, and a few were briefly tested in Phase I. Because little work was done in this area, it is not being recommended for Phase II work. However, it seems to be a fruitful area for additional work.

Discussion

Some potential exists for agglomeration or another method to be used to deash the ash concentrate, as a supplement or alternative to deashing the ashy resid. Possible benefits include recovery/recycle of resid, IOM, deashing solvent, and perhaps catalyst normally sent to gasification. The V-107 ash concentrate sample (dated 1/31/92) from Period J of Wilsonville Run 263 (the baseline period for the project's economic assessment) was analyzed and reported.[5-7] Examination of this material allowed us to better evaluate process options with regard to use of this stream in the liquefaction process.

Interest in better use of this stream was generated by the realization that this material had greater heating value, was lower in oxygen concentration, and was higher in catalyst concentration than the as-received feed coal. Recovery and utilization of soluble resid, DAS solvent, IOM, and/or dispersed catalyst to improve liquefaction economics was the objective of this work. Little experimental work was conducted in this area in Phase I.

Basic strategies considered for this purpose were physical and chemical methods. Physical methods would include primarily agglomeration, and magnetic and electrostatic separation, column flotation, or froth flotation. One chemical approach is to return this material to liquefaction somewhere in the process, or add an additional liquefaction step to accommodate this material. A different chemical approach is to use solvent extraction, leaching, or other chemical

treatment to selectively remove one or more valuable components from the ashy resid.

One agglomeration test (B36) at natural pH with ash concentrate as the feed gave no ash rejection.[8] The liquefaction reactivity of this material was measured in two microautoclave tests, and it was found that about 50 % of the IOM in the ash concentrate was convertible to THF solubles. The THF solubility of the V-107 ash concentrate from Wilsonville Run 263J was determined to be 9.1 wt % (14.8 wt % MAF) by pressure filtration and 18.9 wt % (30.7 wt % MAF) by overnight Soxhlet extraction. Other work in this area that was considered, but not conducted, included float/sink tests on the ash concentrate, and Soxhlet extraction of ash concentrate and ashy resid with NMP (N-methylpyrrolidinone).

There are several possibilities in the area of ash concentrate upgrading and utilization which could be explored. Other agglomeration steps, such as additional grinding, surfactant addition, etc. might provide improved ash rejection. A few ideas follow.

- Sodium pyrophosphate treatment may be effective for the separation of organic components from ash concentrate or ashy resid, as Kotlyar et al.[37] found for oil sands.

- The acid treatment of brown coal liquefaction resid had beneficial hydrotreatment effects.[34] The effect of washing the resid with acid on subsequent liquefaction behavior could be explored.

- Many solvent systems exist which will extract a substantial amount of material from coal-NMP is one of many to be found in the literature. Such solvents are good candidates for extracting much of the organic material from ash concentrate or ashy resid.

- Simple solvent stripping could provide a means to obtain DAS and a few percent or more soluble resid from the ash concentrate. Light solvent removal from the recovered resid may not be an issue, if vapors from the slurry mix tank in a liquefaction facility are normally captured and sent to gas and liquid separation and recovery portions of the plant.

Recommendations

It is recommended that ash concentrate utilization and upgrading strategies be explored further, although not in Phase II. Recovery of only a few percent additional organic material should boost distillate yield.

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TABLE 1

PROJECT COAL ANALYSES

	Black Thunder (a)	McKinley (2)	Martin Lake Lignite (3)	Burning Star 2 (d)	Rosebud (e)	Rosebud Syncoal (f)
Moisture, wt %	21.27	13.03	25.08	10.30	22.27	2.65
Proximate, dry wt %						
Ash	6.69	12.00	13.76	14.97	10.57	8.82
Volatile Matter	48.46	40.66	46.46	37.76	38.86	39.23
Fixed Carbon	45.15	47.34	39.78	47.27	50.57	51.95
Ultimate, dry wt %						
Carbon	70.32	68.21	63.76	64.11	69.33	70.54
Hydrogen	4.68	4.85	4.84	4.39	4.29	4.33
Nitrogen	1.04	1.21	1.15	1.33	1.20	1.22
Sulfur	0.50	0.47	1.41	3.81	1.02	0.49
Chlorine	0.04	<0.01	0.02	0.08	0.02	0.02
Oxygen (diff)	16.73	13.26	16.47	11.31	13.57	14.58
HHV, dry Btu/lb	11978	12029	11067	11433	11773	11992
Sulfur Forms, dry wt %						
Pyritic	0.08	0.04	0.37	1.04	0.55	0.07
Sulfate	0.08	<0.01	0.03	0.84	0.03	0.01
Organic	0.34	0.43	1.01	1.93	0.44	0.41
Ash Elementals, wt %						
Na_2O	0.48	1.54	0.98	0.71	0.73	1.15
K_2O	0.49	1.31	0.50	1.97	0.34	0.25
CaO	21.34	3.41	16.06	4.06	17.95	15.49
MgO	4.30	1.10	3.76	0.98	3.85	4.35
Fe_2O_3	5.48	5.29	6.53	18.35	5.07	1.38
TiO_2	1.14	0.96	1.17	0.85	0.78	0.83
P_2O_5	0.96	0.04	<0.02	0.17	0.23	0.28
SiO_2	31.48	60.04	38.73	48.74	39.49	41.29
Al_2O_3	15.76	20.43	13.63	18.54	15.31	18.6
SO_3	17.26	3.64	18.89	5.44	16.21	15.55
Total	98.69	97.76	100.25	99.81	99.96	99.17

Coal Sample Sources:
a. Wilsonville Run 262, 9/91
b. P&M Coal Mining Co., 7/93
c. TUMCO, 3/93
d. HRI, 4/93
e. Western Energy Co., 10/94

TABLE 2

WILSONVILLE PROCESS STREAMS

	Run 262E (a)			Run 258K(b)	Run 255			
	V-1074 Heavy Distillate	V-130 Deashed Resid	V-1082 Ashy Resid	V-131B Recycle Solvent	V-1074 Heavy Distillate	V-131B Recycle Solvent	V-181 ROSE Feed	V-107 Ash Concentrate
Ultimate, wt %								
Carbon	88.86	89.79	72.59	82.49	85.42	71.64	60.83	48.96
Hydrogen	9.91	7.26	5.40	6.62	9.50	6.97	4.27	2.86
Nitrogen	0.44	0.86	0.88	0.80	0.68	0.81	0.81	0.93
Sulfur	<0.03	0.03	1.93	0.82	0.35	1.19	2.45	3.24
Ash	0.00	0.73	20.28	10.07	2.24	16.54	32.65	44.82
Oxygen (diff)	0.79	1.33	-1.08	-0.80	1.81	2.85	-1.01	-0.81
Molybdenum, ppm	2	53	298					
Ash Elementals, wt %								
Na_2O			0.47		1.36	1.28	1.23	1.25
K_2O			0.29		0.50	0.44	0.45	0.47
CaO			16.13		19.39	14.35	13.69	14.21
MgO			3.49		4.34	3.59	3.42	3.52
Fe_2O_3			23.19		20.45	17.39	17.16	17.66
TiO_2			0.89		1.30	1.10	1.04	1.06
P_2O_5			1.14		0.27	0.18	0.17	0.18
SiO_2			22.82		26.52	31.65	31.54	32.15
Al_2O_3			10.71		14.98	12.97	12.44	13.72
SO_3			20.92		11.10	15.93	16.91	14.10
Total			100.05		99.79	98.88	98.05	98.32

Notes: Run 262 - Black Thunder Coal with Mo catalyst in recycle solvent.
Run 258 - Black Thunder Coal with no added Mo catalyst.
Run 255 - Texas Lignite

TABLE 3

WILSONVILLE RUN 258K, Mo-FREE SOLVENT (V-131B)

	Whole Solvent	1025 °F⁻ Distillate	1025 °F⁺ Resid
Ultimate, wt %			
Carbon	82.49	90.16	76.99
Hydrogen	6.62	9.48	5.07
Nitrogen	0.80	0.44	1.04
Sulfur	0.82	<0.03	1.21
Ash	10.07	0.00	15.52
Oxygen (diff)	-0.80	-0.08	0.17

Note: Sample was distilled at 320 °C, 2-torr (1025 °F atmospheric pressure equivalent).

TABLE 4

DESCRIPTION OF SAMPLES FROM WILSONVILLE RUN 262E

Sample No.	Description
1621-22-1	Unground Black Thunder Coal, 9/16/91
1621-22-2	Ground Black Thunder Coal, 9/16/91
1621-22-3	V-130 Deashed Resid
1621-22-4	V-1082 Ashy Resid
1621-22-5	V-1074 Heavy Distillate
1621-22-5-A	-35 °C Acetone Dewaxed 1621-22-5 (Composite Sample)
1621-22-5-C	-5 °C Acetone Dewaxed 1621-22-5 (Composite Sample)
1621-22-5-I	-5 °C Acetone Dewaxed 1621-22-5 (Composite Sample) Used in PST
1621-22-5-IA	Hydrogenated (at Sandia) -5 °C Acetone Dewaxed 1621-22-5 (Composite Sample) Used in PST
1621-22-5-K	Simulated 25% Acetone Dewaxed Slipstream (-5 °C) 1621-22-5 (Composite Sample) Used in PST
1621-22-5-KA	Hydrogenated (at Sandia) 1621-22-5K (Composite Sample) Used in PST
1621-22-5-L	Furfural Dewaxed 1621-22-5 (Composite Sample)
1621-22-5-OB	Thermal (925 °F, 5-min) Dewaxed 1621-22-5 (Composite Sample)
1621-22-5-OB-1	Hydrogenated (at CONSOL) 1621-22-5-OB

TABLE 5

PROTON DISTRIBUTIONS AND PHENOLIC -OH CONCENTRATIONS IN WILSONVILLE RUN 262E MATERIALS

Sample (a)	Hydrogen, wt %	^{1}H-NMR Proton Distributions, %							Phenolic -OH	
		Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Conc. meq./g	ν, cm^{-1}
1621-22-3	7.26	21.0	7.0	18.1	8.5	14.4	21.3	8.6	0.90	3298
1621-22-4	5.40	22.6	6.3	20.2	10.0	14.5	19.1	7.3	0.96	3306
1621-22-5	9.91	11.1	3.9	13.9	7.4	15.3	34.9	13.6	0.44	3306
1621-22-5-A	8.23	17.3	6.2	20.2	10.3	17.1	17.9	11.2	0.61	3304
1621-22-5-C	8.63	16.5	5.1	18.4	9.2	17.4	21.3	12.1	0.56	3304
1621-22-5-I	8.80	13.5	7.4	16.3	9.6	16.8	21.6	14.9	0.50	3307
1621-22-5-IA	9.16	13.1	4.5	22.4	10.0	18.5	20.6	10.8	0.24	3312
1621-22-5-K	9.22	12.2	6.4	15.0	9.0	16.0	25.4	16.0	0.46	3306
1621-22-5-KA	9.78	11.5	4.4	21.0	10.2	17.8	22.9	12.1	0.21	3314
1621-22-5-L		16.6	9.1	18.1	10.6	15.1	18.4	12.2	0.60	3304
1621-22-5-OB	8.41	23.7	8.2	14.6	9.5	10.2	23.5	10.3		
1621-22-5-OB-1	9.78	8.1	5.4	16.4	9.3	18.5	28.7	13.7		

a. see Table 4 for descriptions.

TABLE 6

SEGREGATION OF FEED COAL QUALITY TO LIQUEFACTION AND GASIFICATION

	Black Thunder Coal		Martin Lake Lignite		Burning Star 2 Coal	
	Design(a)	Revised(b)	Design(c)	Revised(b)	Design(d)	Revised(b)
Coal Ash Content, %MF						
Total Process Feed	6.3	6.3	13.2	13.2	11.5	11.5
Liquefaction Feed	6.3	3.8	13.2	7.5	11.5	4.5
Gasification Feed	6.3	14.7	13.2	29.6	11.5	25.3
Coal Feedrate, T/D MF						
Total Process Feed	17004	17004	18355	18355	26044	26044
Liquefaction Feed	13438	13088	14506	13612	18641	17274
Gasification Feed	3566	3916	3849	4743	7403	8770
Coal Feedrate, T/D MAF						
Total Process Feed	15933	15933	15933	15933	23049	23049
Liquefaction Feed	12592	12592	12592	12592	16497	16497
Gasification Feed	3341	3341	3341	3341	6552	6552
Ash Feedrate, T/D						
To Process	1071	1071	2423	2423	2995	2995
To Liquefaction	847	497	1915	1021	2144	777
To Gasification	225	576	508	1404	851	2218

(a) Peluso, M., Baseline Case Study, Hybrid Mode (263J), Fig. 19, p. 71 in Quarterly Report for January through March, 1993 (June 1993).
(b) Calculated from cleanability curves in Table 7 and Figs. 2, 3, and 4 (pp. 20, 25, 26, and 27) of Section 2 of Quarterly Report for April through June, 1993 (August 1993) and from corresponding data in "Design" column.
(c) Assumes that MAF coal feedrates are the same as in note a and ash content is the same as in note (b).
(d) Bechtel Corp., "Final Report on Baseline and Improved Baseline", Vols. 2 and 8, March 1993.

NOTE: All data are on an SO_3–containing ash basis.

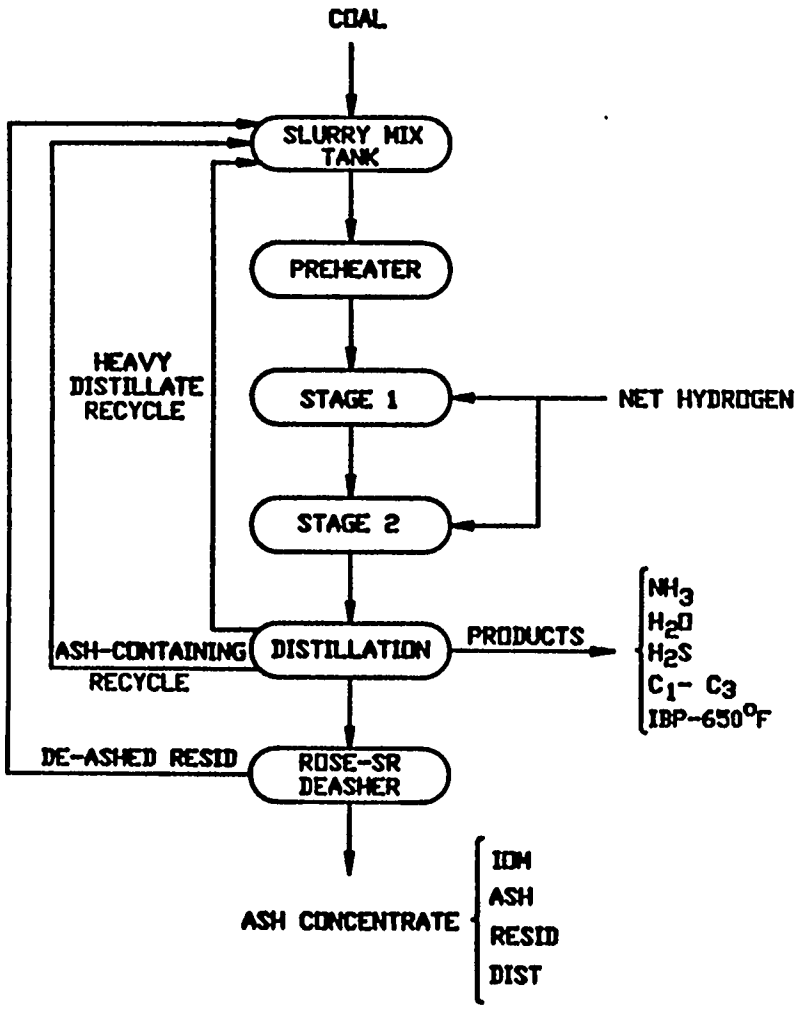


Figure 1. Schematic of Current Two-Stage Process.

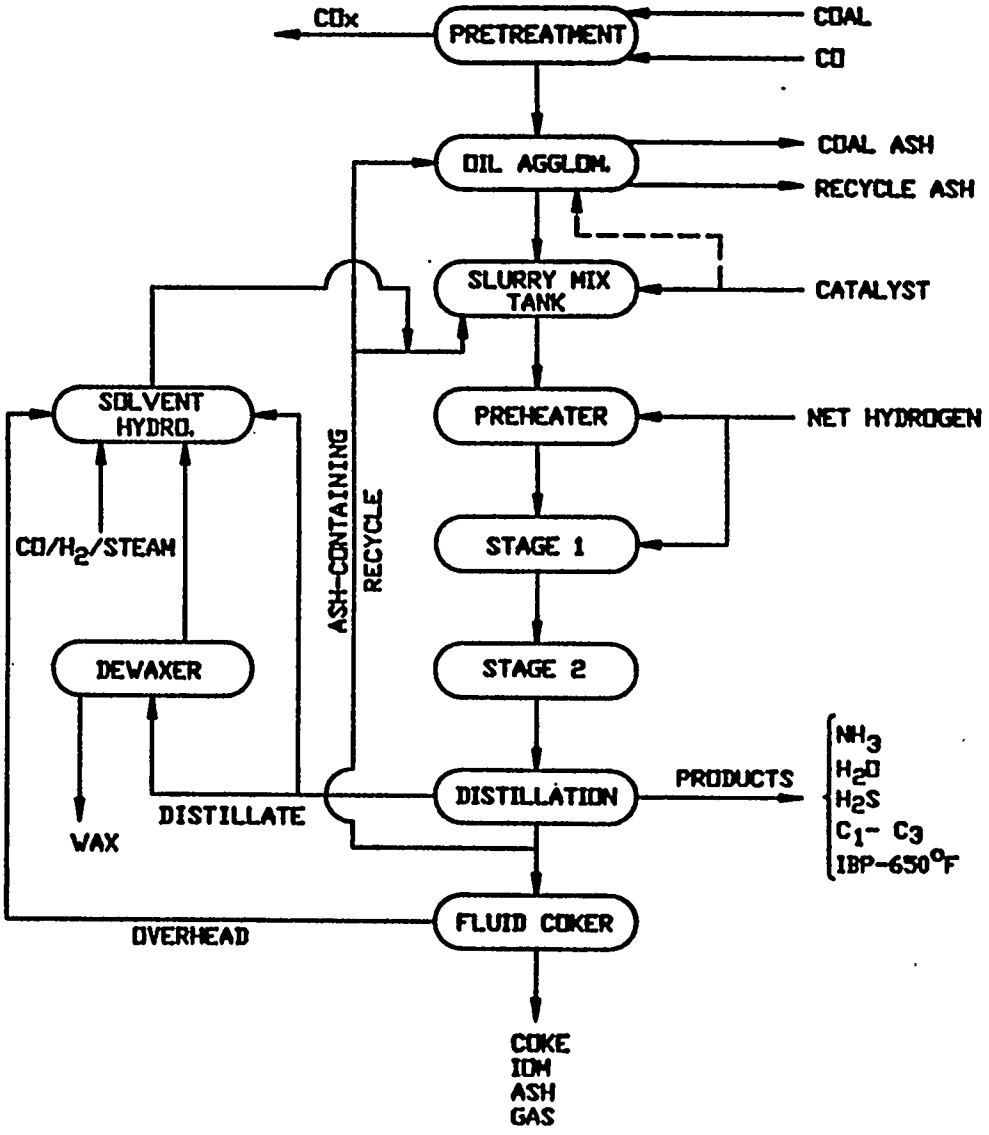
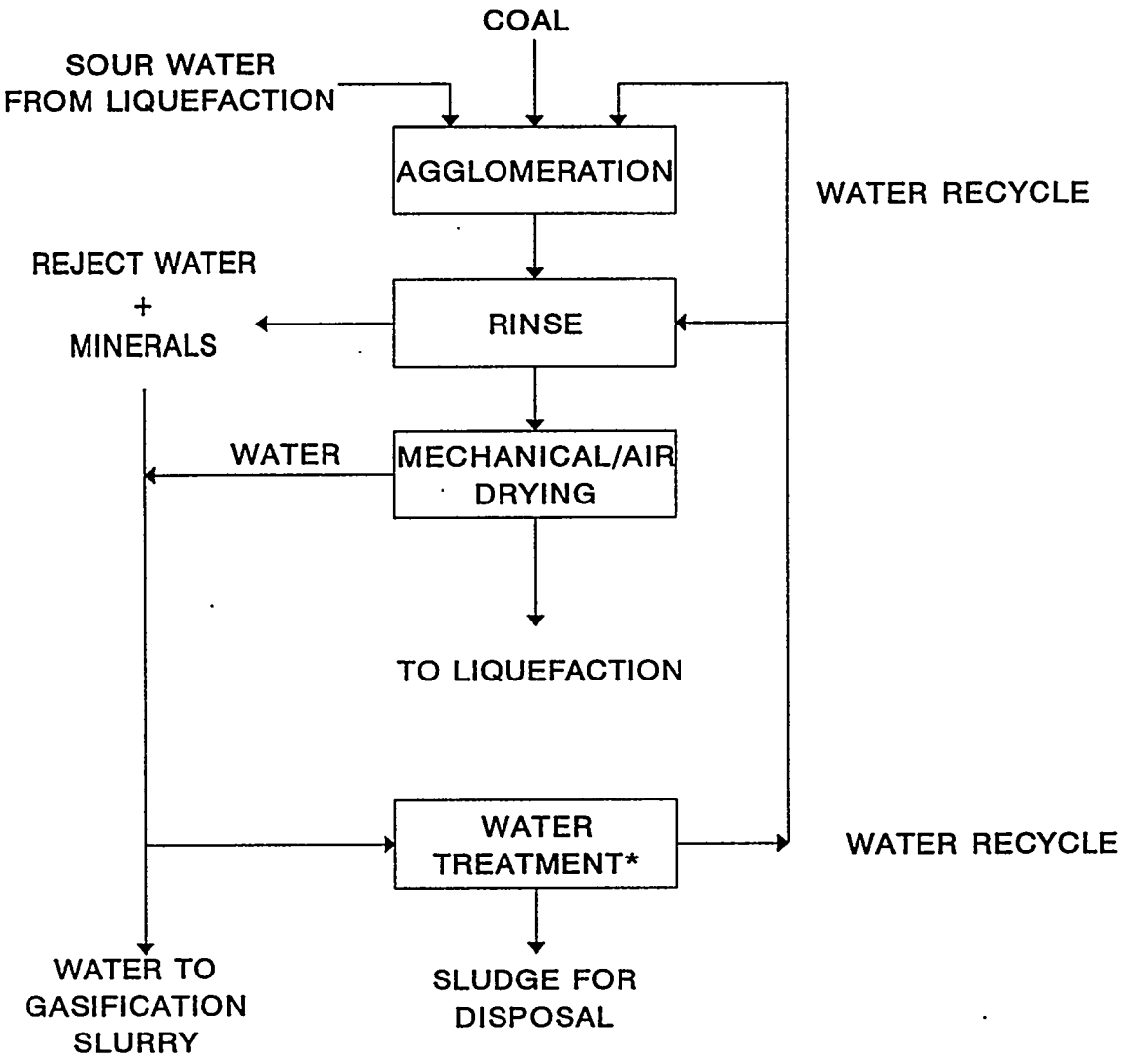


Figure 2. New Integrated Process Scheme.



*Includes acidification with H_2SO_4 in scenario A4.

Figure 3. Flow Diagram for Agglomeration.

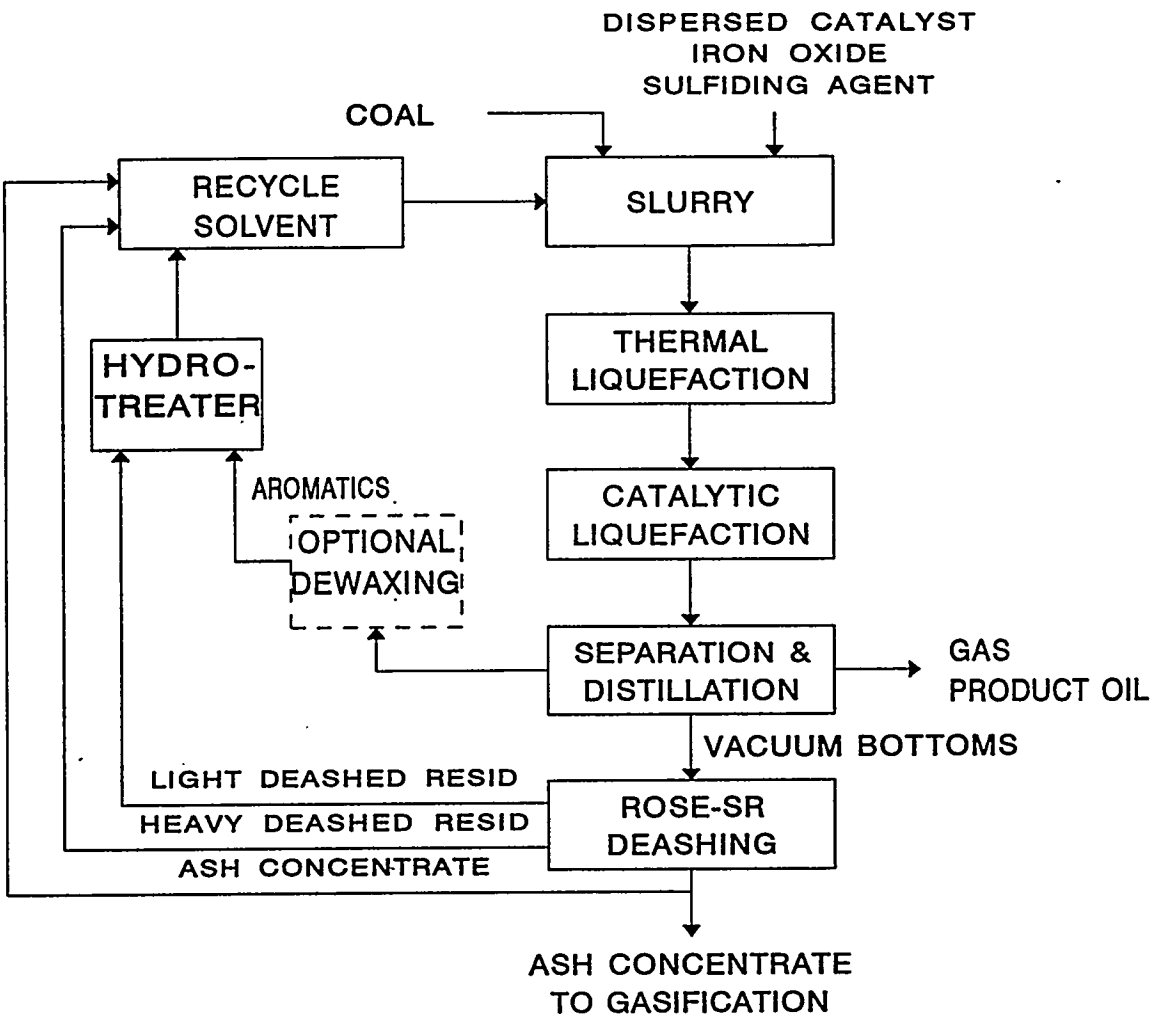


Figure 4. Staged ROSE Operation Concept.

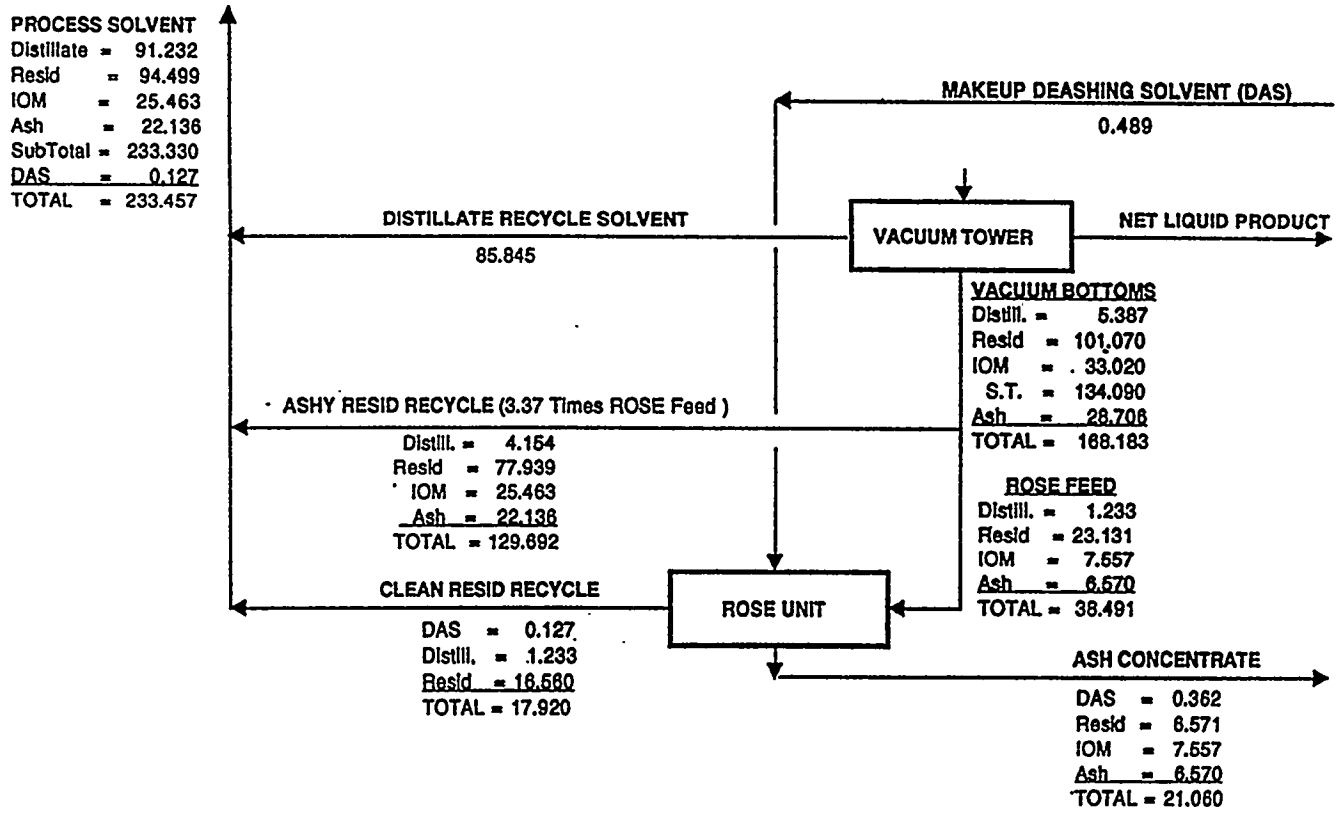
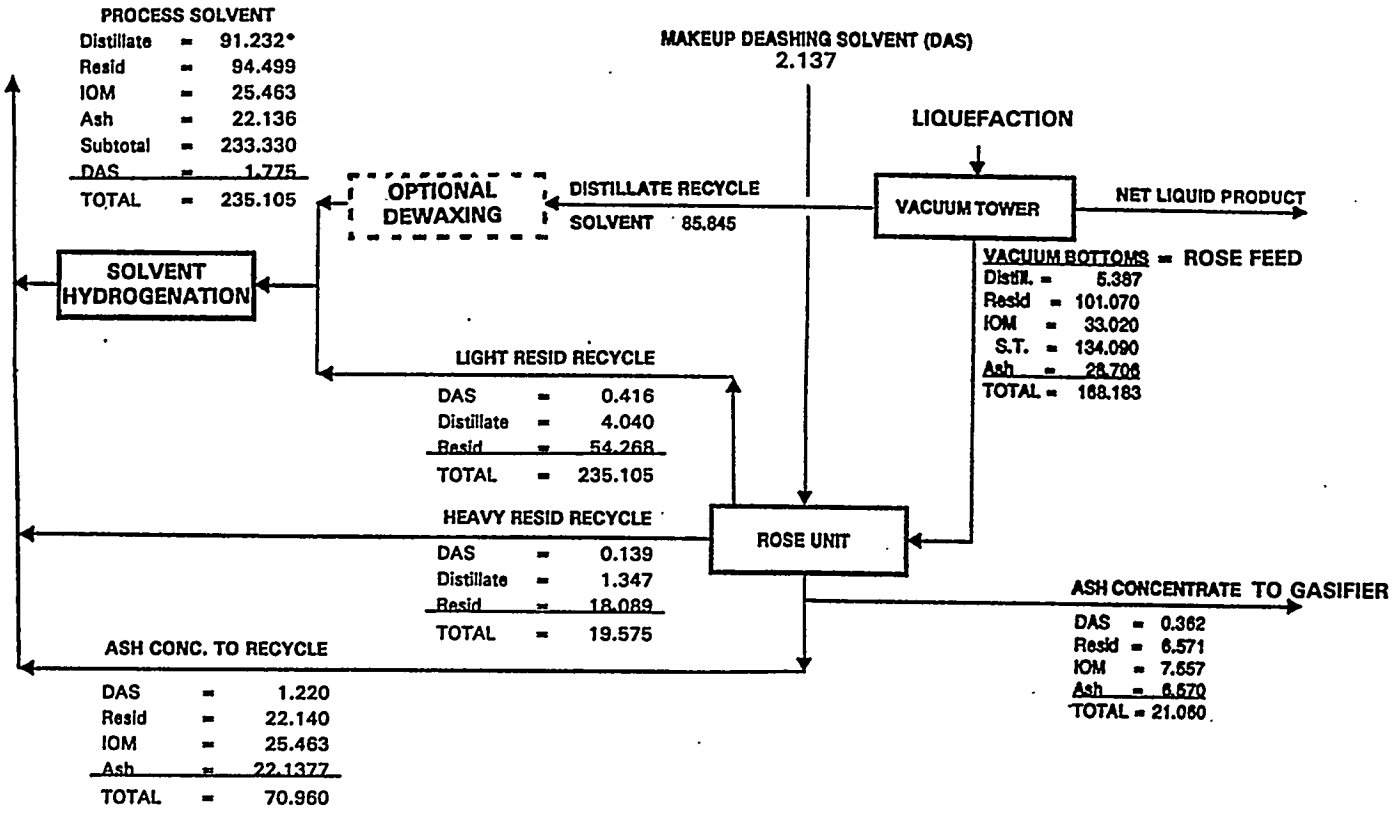


Figure 5. Simplified Resid, IOM andAsh Balance
Revised Base Case (SO_3-Free Ash Basis, WR No. 263J).
(Source: Reference 16, Figure 1A)



*Ignores any impact of dewaxing/solvent hydrogenation

Figure 6. Simplified Resid, IOM and Ash Balance
Revised Base Case (SO_3-Free Ash Basis, WR No. 263J)
Modified for Staged ROSE Operation (Adapted from Reference 16).

SECTION THREE

FINAL REPORT
ADVANCED CONCEPTS PROGRAM
TASK 3.0
TECHNICAL ASSESSMENT

BY LDP ASSOCIATES
March 1995
ADVANCED DIRECT LIQUEFACTION CONCEPTS
DOE CONTRACT DE-AC22-91PC91040

1.0 INTRODUCTION

Task 3.0 of this contract involves the technical assessment of the test results obtained in this Advanced Concepts Program. A key element of this assessment is the comparison of these new process concepts versus state-of-the-art Two Stage Liquefaction (TSL) technology. Wilsonville pilot plant operation with Black Thunder subbituminous coal was chosen as the basis for defining state-of-the art TSL technology. During Wilsonville Runs #262 & 263, the pilot plant unit was operated in the so-called hybrid mode with dispersed iron and molybdenum catalysts used in the first reaction stage and a supported nickel-moly catalyst used in the second stage ebullated bed reactor. Material balance period #263J was chosen as the basis for developing a baseline conceptual commercial plant case against which the results of this program could be compared(1).

2.0 BASE CASE ASSESSMENT - WILSONVILLE RUN# 263J

Basis

Data from Wilsonville Run#263J were reviewed and analyzed. An all-distillate product Base Case was formulated in which resid extinction was achieved in the system via a reduction in reactor space velocities as predicted by first order reaction kinetics. It was anticipated that the distillate product from liquefaction in this program could differ from the distillate product obtained at Wilsonville during Run#263J. As a result, all liquefaction distillates are assumed to be upgraded to a common basis (all-gasoline finished product) so that consistent comparisons are assured. Chevron 's work under DOE sponsorship was used as the basis for determining distillate upgrading yields and requirements (2).

The Base Case conceptual commercial plant is an all-coal facility located at a mine-mouth Wyoming location. The hydrogen needed for liquefaction is generated by water slurry gasification of ash concentrate from the ROSE unit and coal. Light hydrocarbon gases produced in liquefaction and upgrading are used to close the fuel gas balance. Any excess gas is used to generate hydrogen via the steam reforming process. It is assumed that the electricity needed to help operate the plant is purchased from a nearby utility power plant.

The capital and operating cost estimates for the Base Case were developed using the relevant portions of previous liquefaction plant studies, as well as in-house information (3,4,5).

Results

The technical and economic results for the Base Case are shown in Tables 1 to 13 and Figures 1 to 3. A simplified block flow diagram of the conceptual commercial plant is shown in Figure 2. The plant converts 17,929 T/D of Black Thunder coal (MF basis) fed to liquefaction into 68,100 barrels per day(BPSD) of gasoline product. An additional 5,204 T/D of Black Thunder must be gasified in order to meet the plants hydrogen requirements. The scheme for upgrading the distillates produced in liquefaction is shown in Figure 3.

Figure 1 presents a simplified picture of the resid, Insoluble Organic Matter (IOM) and ash flows in the liquefaction reaction and separation systems. All flows in this diagram are on the basis of 100 pounds of MF coal to liquefaction. Overall Maf coal conversion for the Base Case is 92%. The per pass conversion of resid and IOM in the first and second stage reactors is relatively low at approximately 23.5% and 18%, respectively. A high process solvent to coal ratio of 2.33 is employed since significant quantities of both IOM and ash are recirculated via the ashy recycle technique. Recycled ash is approximately 3.3 times the quantity of ash rejected from the process via the ash concentrate. This ash recirculation rate results in a 3.3 concentration effect for both the moly and iron dispersed catalysts. As a result the effective concentration of moly on coal to liquefaction is approximately 430 ppm at the Base Case fresh addition level of 100 ppm.

Reactor system parameters for the Base Case are shown in Tables 4 & 5. A once thru first stage reactor design has been assumed. Four reactor trains in parallel are required to process the 17,929 T/D of coal to liquefaction. The first stage reactor is refractory lined in order to maximize the cross sectional area per reactor. Reactor gas rates were determined based on the estimated average reactor partial pressures which existed during Wilsonville Run #263J and the recycle hydrogen gas purity. Actual reactor residence times and space velocities were also based on estimated WR#263J operation with appropriate corrections for the required resid plus IOM conversion level.

Organic rejection (i.e. resid,IOM & DAS) from the liquefaction process amounts to 14.5% on an MF coal basis.

Investment costs for the Base Case process units are shown in Table 10. Significant cost areas include the liquefaction reaction system, vacuum fractionation system, the hydrogen recovery and recycle system, the makeup hydrogen generation system and the upgrading system. No one particular system dominates investment cost.

Offsite units investment costs are shown in Table 11. Once again, investment cost is widely distributed among the various units.

The total capital requirement(instant plant basis) for the Base Case is shown in Table 12. Working capital, start-up costs and the costs of initial catalyst and chemicals adds an additional 10% to the total capital requirement of $3.842 billion.

At an assumed capital charge factor of 15%, the annualized capital costs are $26.45 per barrel of gasoline product.

Annual operating costs for the Base Case are shown in Table 13. Total operating costs are approximately $20/ Bbl. of gasoline product including a $1/Bbl. credit for ammonia, sulfur and phenol byproducts. The significance of liquefaction system additives and purchased electrical power costs and the relative insignificance of coal cost is noteworthy. Liquefaction additives costs are approximately $5.20/Bbl. of gasoline, with the iron and moly dispersed catalysts accounting for more than half of this total. Coal costs are low because of the low $5/ton-wet minemouth price for Black Thunder coal.

Assuming a capital charge factor of 15%, the Base Case required gasoline product selling price is $46.46/Bbl.

3.0 ADVANCED CONCEPTS CASE

Basis

Based on the experimental work and assessments conducted during this program, an "Advanced Concepts Case" (ACC) was formulated. Three main process variations from the Base Case are incorporated in the ACC. They are:

1. Coal impregnation with moly salt via incipient wetness,
2. Oil agglomeration of the feed coal at low pH,
3. Distillate solvent quality improvement via solvent extraction, solvent dewaxing and hydrotreating.

Used together these three techniques seek to significantly increase product yield per unit of coal feed while reducing solvent recycle rate and liquefaction system additive costs.

• Coal Impregnation With a Moly Salt via Incipient Wetness

As pointed out in the Base Case the cost of dispersed iron and moly catalysts accounts for almost $3/Bbl. of gasoline product selling price. A significant portion of this cost results from the use of an expensive moly source, the oil soluble Molyvan L. At $3.20/lb. and an 8.1 wt.% moly concentration, the cost per pound of moly is $39.50. If instead a moly salt such as Ammonium Octomolybdate (available in tonnage quantities) were used, the raw material cost per pound of moly could be reduced to $7.30. Even when processing costs for preparing the salt solution , impregnating a small portion of the feed coal to liquefaction and driving off the extra water added to the coal are added, the cost of the impregnated moly is still only about 25% of the cost of using Molyvan L. Experimental results to date indicate that the performance with moly impregnated coals is approximately equivalent to the performance with Molyvan L.

When using a moly source in this way, the cost of using moly drops below the cost of using particulate iron oxide at the 1 wt.% on MF coal dosage level of the Base Case. Using iron at a 1 wt.% level also adds to the ash in the liquefaction

system and increases the organic rejection by the process due to the assumed constant solids content of the ash concentrate. Therefore, for the purposes of this assessment an iron catalyst was not used, although test results to date have not yet proven that an iron catalyst is unnecessary.

• Oil Agglomeration at Low pH

Results to date indicate that the use of oil agglomeration at low pH can remove approximately 50% of the ash in Black thunder coal. Ash reduction at the front end of the liquefaction process reduces organic rejection at the back end of the process, thereby increasing potential product yield. It also reduces the ash recirculation rate within the process while still maintaining the same catalyst recycle enhancement factor as in the Base Case. In effect, front end ash removal purges useless inerts from the system. At low pH, potential supported catalyst poisons, such as calcium, sodium, magnesium and potassium are also removed. For this assessment it has been assumed that the second stage reactor supported catalyst replacement rate can be reduced by 30%.

Tests to date have also indicated that impregnated iron and moly are retained on the coal during agglomeration.

The oil agglomeration process is well suited for liquefaction. Distillate recycle solvent can be used as the agglomerating agent. Sour water can be used as makeup water to the system and the slurry reject of solids and dissolved salts can be utilized in the gasification slurry mixing systems. In fact, the dissolved salts may even act as a catalyst in the gasification process.

Of course, the use of oil agglomeration adds capital and operating costs to the process. While, the capital cost for low pH oil agglomeration is expected to be moderate ($60 million assumed for the ACC), a definitive process design and estimate is required to better estimate costs for the process. The cost for sulfuric acid consumed in the unit is also significant.

• Distillate Solvent Quality Improvement

For the ACC, three process steps are used to treat the waxy distillate recycle solvent used in the Base Case. These processes are Solvent Extraction, Solvent Dewaxing and Hydrotreating. In combination these processes effectively remove and recover the waxy material from the distillate solvent and enhance its donor solvent capabilities (see Figure 4). Both solvent extraction and solvent dewaxing are commercial processes used in the petroleum refining industry.

The benefit of applying these three processes are:

1. Reduction of distillate solvent recycle (coal slurry feed viscosity permitting) while improving quality
2. Recovery of a valuable byproduct wax
3. Increased potential product yield via coal conversion improvement.

It is estimated that the wax yield on MAF coal is 4 wt.%. However, this wax builds up in the distillate recycle solvent until its cracking rate equals its

production rate. Based on Wilsonville Run#263 data the wax concentration in the distillate recycle solvent is estimated to be approximately 24 wt.%. Therefore, when a substantial portion of the wax in the distillate solvent is removed, the distillate solvent recycle, now almost free of recirculating wax, could drop by almost 20% provided that the resultant feed coal slurry is still pumpable (i.e. provided it meets viscosity criteria). In the ACC the coal concentration in the feed slurry to liquefaction increases to 34.4% from 30% in the Base Case. Total solids (coal + IOM +ash) concentration in the feed slurry in the ACC is slightly less than in the Base Case (43.1% vs 44.3%). It is recommended that coal slurry feed viscosity measurements be made on projected ACC type material, in Phase II of this program, to verify that the assumed reduction in distillate solvent recycle rate is feasible.

The wax that is removed and recovered is a valuable material with a current estimated selling price (34¢/lb.) more than double that of gasoline. The ability of the wax market to absorb the significant quantity of wax produced by an ACC size plant is a key consideration.

The solvent extraction process is used upstream of the solvent dewaxing process as a means of significantly reducing the feedrate and therefore the cost of the much more expensive solvent dewaxing process. In the solvent extraction process (Figure 5), a solvent such as furfural or N-Methyl-2-Pyrrolidone is used to absorb aromatics from the feed stream. The paraffinic wax is not absorbed and passes thru the unit. For the ACC that approximately 70% of the distillate solvent feed to the extraction unit is absorbed, thereby reducing the solvent dewaxing unit feedrate by a factor of 3.

In the solvent dewaxing process (Figure 6), the paraffinic wax is separated from the feed stream by chilling, precipitation and filtration in the presence of a suitable solvent such as methyl ethyl ketone (MEK). When wax production is desired, as in the ACC, a three stage filtration system is used. In addition, a wax finishing step is also required.

Conventional fixed bed hydrotreating is used to make the final improvement in distillate solvent quality. For the ACC, a single train system operating at conditions favorable to aromatics hydrogenation (650 to 750°F & 1,800 psig) is anticipated.

In the Process Simulation Testing (PST), average MAF coal conversion improved 2.4 percentage points when the distillate recycle solvent was fully dewaxed and hydrotreated as compared to using the as-is distillate solvent. Hydrogen uptake in the small scale hydrotreating runs for the PST's was less than half of the 1 wt.% expected based on Exxon EDS operation. Therefore, for the ACC it is assumed that the full dewaxing and hydrotreating of the distillate recycle solvent will improve MAF coal conversion by 3 percentage points(95% vs 92% in Base Case).

Such an improvement further increases the potential product yield and reduces the IOM recycle rate.

Results

The results of the ACC are shown in Figures 1A & 2A and Tables 2A to 13A.

In Figure 1A, the results of reduced feed ash and improved coal conversion are evident. While the solids concentration in the ash concentrate remains the same, organic rejection is reduced to 8.5% on MF coal. At the same time, recycle solvent rate is reduced by 20% because of wax removal and lower feed ash and IOM recirculating rates. Moly catalyst recirculation enhancement remains at the same 3.3 factor as in the Base Case. In order to achieve the higher product yield, the required per pass resid plus IOM conversion increases in both reaction stages. As reaction temperatures are not changed, this increased conversion is achieved by a space velocity reduction (predicted by first order kinetics) of approximately 15% versus the Base Case. Tables 4A and 5A show that although reactor space velocities are lower, reactor weights are only slightly higher due to the offsetting effect of lower recycle solvent rates.

Figure 2A shows the overall effect of the advanced concepts. Gasoline product rate increases by 4.5% while a significant quantity of the valuable wax byproduct is also produced. As shown in Table 2A, C_4+ product yield increases to greater than 65 wt.% on MF coal.

Hydrogen consumption increases in proportion to the increased product rate. With the significant decrease in organic rejection, additional gasification of coal is required to close the hydrogen balance.

The total electrical power requirement for the ACC increases by approximately 12% due to increased gasification quantities and the requirements of the added units.

Capital costs for the ACC are shown in Tables 10A thru 12A. Process unit investment increases by $432 million due to the added units and the increased gasification requirements. The total capital required increases by $ 520 million over the Base Case.

However, net operating costs drop by approximately $140 million/year due to the lower liquefaction system additive costs and the significant impact of byproduct wax revenue.

If a 15% capital charge factor is used, the required gasoline product selling price is $41.82/Bbl. or $4.64/Bbl. less than in the Base Case.

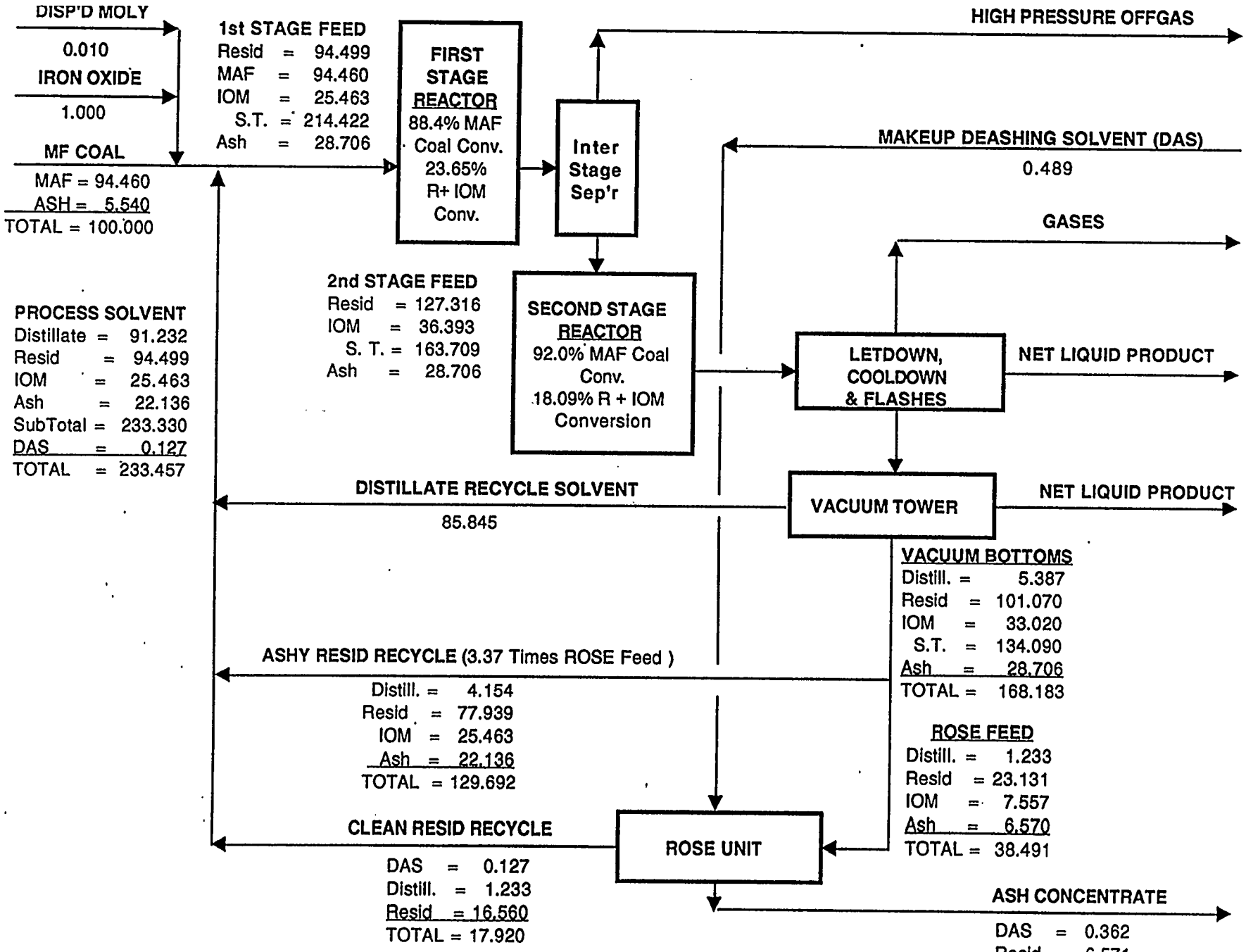


FIGURE 1 SIMPLIFIED RESID, IOM & ASH BALANCE
BASE CASE (SO_3- Free ash basis, WR#263J)

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5/24/94

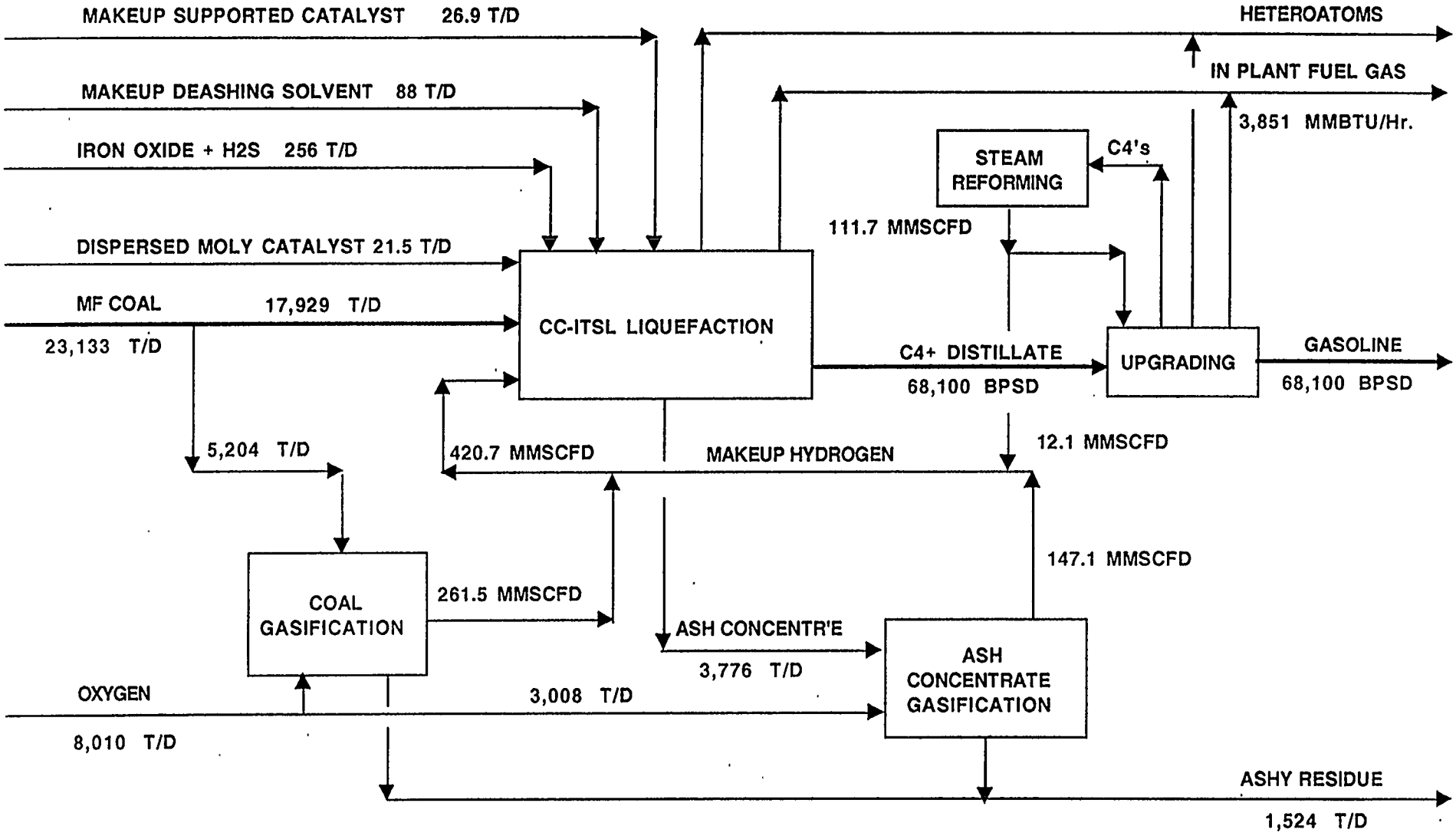

FIGURE 2
BLACK THUNDER LIQUEFACTION STUDY - HYBRID MODE
SIMPLIFIED BLOCK FLOW DIAGRAM - CONCEPTUAL COMMERCIAL PLANT
BASE CASE (SO_3-Free Ash, Wilsonville Run # 263J)

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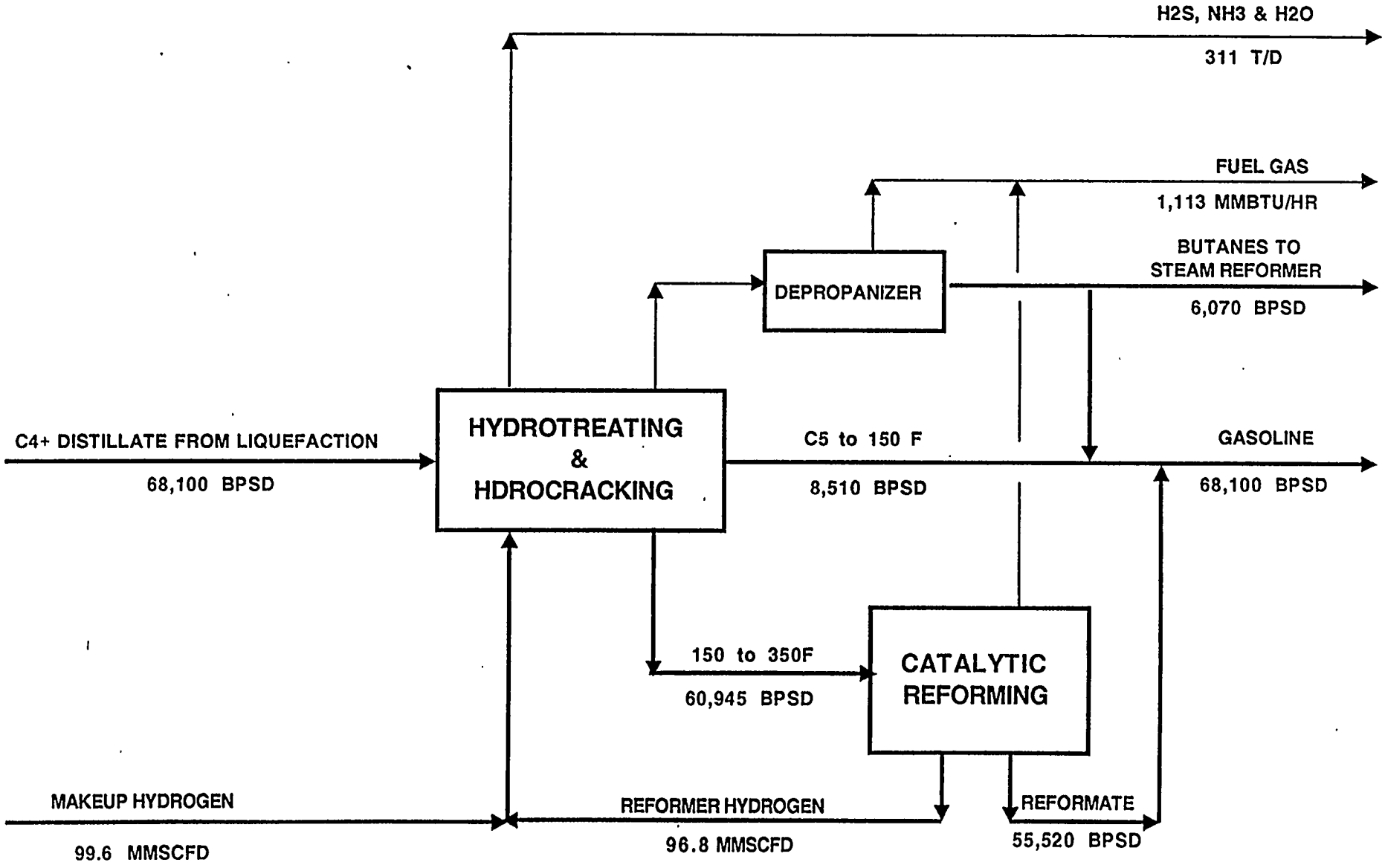

FIGURE 3
BLACK THUNDER LIQUEFACTION STUDY
UPGRADING UNITS SIMPLIFIED BLOCK FLOW DIAGRAM
BASE CASED (WILSONVILLE RUN # 263J)

mp 2/28/95

TABLE 1
BASELINE CASE STUDY : BLACK THUNDER COAL
COAL PROPERTIES

ELEMENTALS, WT% MF

• CARBON	70.32
• HYDROGEN	4.68
• OXYGEN	17.92
• NITROGEN	1.04
• SULFUR	0.50
• SO_3 Free ASH	5.54
Total	100.00

MOISTURE, AS-RECEIVED 30%

HEATING VALUE, Btu/lb.

•LHV, As-Rec'd	7,939
•HHV, MF	11,760

TABLE 2
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
LIQUEFACTION SYSTEM YIELDS

INPUTS:

• MF COAL	100.000	
• DISPERSED MOLY CATALYST	0.120	(Molyvan L)
• IRON OXIDE	1.000	
• SULFIDING AGENT (H_2S)	0.430	
• MAKEUP DAS	0.489	
• HYDROGEN	5.906	
Total =	107.945	

OUTPUTS:

• WATER	12.450
• HYDROGEN SULFIDE	0.310
• AMMONIA	0.630
• CARBON MONOXIDE	0.970
• CARBON DIOXIDE	5.150
• C1 to C3 GASES	7.830
• C4+ DISTILLATE	59.545
• ASH CONCENTRATE	21.060
Total =	107.945

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TABLE 3
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED C4+ DISTILLATE PRODUCT PROPERTIES

• YIELD, Wt% on MF COAL	59.545
• PRODUCTION RATE, BPSD	68,100
• DENSITY, Degrees API	26.5
• HIGHER HEATING VALUE, Btu/lb.	19,424
• ELEMENTALS, Wt.%:	
- CARBON	86.08
- HYDROGEN	11.37
- OXYGEN	1.93
- NITROGEN	0.58
- SULFUR	0.04
Total =	100.00
• CUTS, Wt.% :	
- IBP to 350 F	20.5
- 350 to 450 F	13.1
- 450 to 650 F	38.0
- 650 to EP (800F)	28.4
Total =	100.0

TABLE 4
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED FIRST STAGE REACTOR PARAMETERS

- Four Once-Thru Refractory lined Reactors in Parallel, 13.2 Feet ID. (10.7" Wall Thk. & 6" Ref. Thk.) x 81 Feet Height

- 1,184 Tons Each, 4,736 Tons Total

- MF Coal Feedrate, 17,929 T/D

- MF Coal Concentration in Slurry = 30%

- Process Solvent Composition :
  - Distillate 39.10%
  - Resid 40.50%
  - UC 10.91%
  - Ash 9.49%

- Liquefaction Additives :
  - Dispersed Moly (Molyvan L) @ 100 ppm on MF Coal
  - Iron Oxide + H_2S @ 0.7% Fe on MF Coal & H_2S/Fe 1/1, molar

- Temperatures :
  - Preheater Outlet = 757° F
  - Reactor Inlet / Outlet = 762° F / 873° F
  - Reactor Effective = 840° F
  - Reactor Design = 650° F (Refractory Lined)

- Operating/ Design Pressure = 2,910 / 3,200 psig

- Average Hydrogen Partial Pressure = 2,185 psig

- Inlet / Outlet Hydrogen Purity = 89.0 / 61.4 Vol. %

- H_2 Consumed / Available = 199.3 / 515.6 MMSCFD

- Actual / Nominal Slurry Residence Time = 17.6 / 34.7 Min.

- MAF Coal Conversion = 88.4%

- Resid + IOM Conversion = 23.65%

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TABLE 5
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMAT'D SECOND STAGE REACTOR PARAMETERS

- Four Ebullated Reactors in Parallel, 14 Feet ID. (11.4" Wall Thk.) x 52 Feet Height
- 648 Tons Each, 2,592 Tons Total
- Criterion (Shell) 324 Ni-Moly Catalyst
- Slurry Feedrate = 52,564 T/D
- MAF Coal Conversion In / Out = 88.4 / 92.0 %
- Resid + UC Conversion = 18.09%
- Space Velocity = 312.9 lb. Feed / Hr.- ft^3 Catalyst
- Temperatures:
  - Slurry @ Reactor Inlet = 680°F
  - Gas @ Reactor Inlet = 800°F
  - Reactor Inlet = 790°F
  - Reactor Outlet = 825°F
  - Reactor Effective = 810°F
  - Reactor Design = 850°F
- Operating / Design Pressure = 2,760 / 3,200 psig
- Average Hydrogen Partial Pressure = 2,220 psig
- Inlet / Outlet Hydrogen Purity = 89.5 / 71.6 Vol. %
- H_2 Cons'd / Available = 199.3 / 572.5 MMSCFD.
- Total Catalyst Inventory = 756,000 lbs.
- Catalyst Replace't Rate = 26.9 T/D, (3 lb./ton MF)

TABLE 6
BASELINE CASE STUDY : BLACK THUNDER COAL HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED DEASHING UNIT PARAMETERS

- MAF Coal Conversion = 92.0%

- Flowrates,T/SD :
  - Vacuum Bottoms Feed = 6,901
  - Makeup DAS = 88
  - Clean Resid Product = 3,213
  - Ash Concentrate = 3,776

- Organic Rejection = 14.5% of MF Coal

- Energy Rejection = 17.3% of Coal HHV

TABLE 7
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
OVERALL UPGRADING YIELDS

INPUTS (Wt.% on C_4+ Distillate):

• C_4+ DISTILLATE	100.00
• HYDROGEN	2.22
Total =	102.22

OUTPUTS:

• WATER	2.17
• HYDROGEN SULFIDE	0.04
• AMMONIA	0.71
• C_1 to C_3 GASES	3.78
• C_4's	11.79
• LIGHT NAPHTHA	9.06
• REFORMATE	74.67
Total =	102.22

TABLE 8
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
HYDROGEN AND FUEL GAS BALANCES

HYDROGEN BALANCE (MMSCFD):

• CONSUMPTION	
- LIQUEFACTION UNIT	420.7
- UPGRADING	196.4
Total =	617.1
• PRODUCTION	
- GASIFICATION OF COAL	261.5
- GASIFICATION OF ASH CONC.	147.1
- STEAM REFORMING OF HC GASES	111.7
- PRODUCED IN CAT. REFORMING	96.8
Total =	617.1

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

• CONSUMPTION	
- SLURRY PREHEATER	1,323
- CATALYTIC REFORMER	900
- STEAM REFORMER	707
- DISTILLATE HYDROPROCESSING	296
- DRYING COAL GASIFICATION	229
- VACUUM UNIT	203
- ROSE UNIT	132
- SULFUR RECOVERY UNIT	61
Total =	3,851
• PRODUCTION	
- LIQUEFACTION OFF GAS	2,738
- DISTILLATE HYDRO. OFF GAS	2,115
- CAT. REFORMING OFF GAS	78
Sub-Total =	4,931
- STEAM REFORMING FEED	- 1,080
Total =	3,851

TABLE 9
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - RUN# 263J
ELECTRICAL POWER REQUIREMENTS

UNIT	MEGAWATTS
COAL GRINDING	21.4
COAL SLURRY PREPARATION & DRYING	2.7
FIRST STAGE REACTION SYSTEM	21.1
SECOND STAGE REACTION, LETDOWN & VACUUM FRACTIONATION SYSTEMS	3.8
ROSE UNIT	2.3
GAS PLANT HYDROGEN RECOVERY & RECYCLE	32.6
GASIFICATION	31.8
OXYGEN PLANT	153.0
STEAM REFORMER	2.3
MAKEUP HYDROGEN COMPRESSION	42.1
UPGRADING UNITS	16.3
OFFSITES & UTILITIES	38.4
DISTRIBUTION LOSSES @ 3%	11.0
TOTAL =	**378.8**

TABLE 10
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - RUN# 263J
PROCESS UNIT INVESTMENT

UNIT	INVESTMENT (Millions of Mid '94 $:Wyoming Location)
COAL SLURRY PREPARATION & DRYING	84
FIRST STAGE REACTION SYSTEM	355
SECOND STAGE REACTION SYSTEM	116
LETDOWN SYSTEM	50
VACUUM FRACTIONATION	189
ROSE UNIT	62
GAS PLANT HYDROGEN RECOVERY & RECYCLE	218
ASH CONCENTRATE & COAL GASIFICATION	491
OXYGEN PLANT	196
STEAM REFORMER	82
MAKEUP HYDROGEN COMPRESSION	136
UPGRADING UNITS	584
TOTAL **PUI** =	**2,563**

TABLE 11
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - RUN# 263J
OFFSITE UNITS INVESTMENT

UNIT	INVESTMENT (Millions of Mid '94 $:Wyoming Location)
LIQUID TANKAGE	140
COAL HANDLING & STORAGE	102
SITE DEVELOPMENT	92
BUILDINGS & CONTROL SYSTEMS	88
ELECTRICAL POWER DISTRIBUTION	85
SOUR WATER TREATING, AMMONIA & PHENOL RECOVERY	84
INTERCONNECTING PIPING	69
WASTEWATER TREATMENT	50
WATER SYSTEMS	39
ASH DISPOSAL	32
RAILROAD & TRUCK FACILITIES	27
STEAM SYSTEM	25
FIRE PROTECTION SYSTEM	22
SULFUR PLANT	13
OTHER UNITS (3)	35
TOTAL OFFSITES =	**903**

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TABLE 12
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - RUN# 263J
TOTAL CAPITAL REQUIREMENT

	INVESTMENT (Millions of Mid '94 $: Wyoming Location)
PROCESS UNITS	2,563
OFFSITE UNITS	903
WORKING CAPITAL	125
START-UP COSTS	160
INITIAL CATALYSTS & CHEMICALS	91
Total Capital Required =	**3,842**

TABLE 13
BASELINE CASE STUDY : BLACK THUNDER COAL
HYBRID CONFIGURATION - RUN# 263J
ANNUAL OPERATING COSTS

	COST ($ Millions/Yr.)	($ / Bbl. Gasoline)
TOTAL MF COAL: 23,133 T/D @ $7.14/T	52.85	2.425
PURCHASED ELECTRICAL POWER, MW @ 4¢/ Kw-hr.	116.43	5.343
LIQUEFACTION SYSTEM ADDITIVES :		
- Iron Oxide @ 12¢/lb. & H_2S @ 7.5¢/lb.	17.47	0.802
- Dispersed Molyvan L @ $3.20/ lb.	44.03	2.021
- Supported Ni-Moly @ $3/lb.	51.64	2.370
MAKEUP DEASHING UNIT SOLVENT	14.30	0.656
OTHER LIQ'N CATALYSTS & CHEMICALS	13.72	0.630
UPGRADING UNITS CATALYSTS & CHEM.	16.35	0.750
RAW WATER @ $ 2.50/1,000 Gallons	7.71	0.354
ASH DISPOSAL @ $5/Ton	2.44	0.112
OPERATING LABOR	20.00	0.918
ADMINISTRA'N & OPERATIONS SUPPORT	13.00	0.597
MAINTENANCE @ 1.5% of TIC + ICC	53.36	2.449
INSURANCE & LOCAL TAXES @ 1% of TPC + ICC	35.57	1.632
BYPRODUCT(NH_3, Sulf., Phenols)CREDITS	- 22.84	- 1.048
Total =	**436.03**	**20.011**

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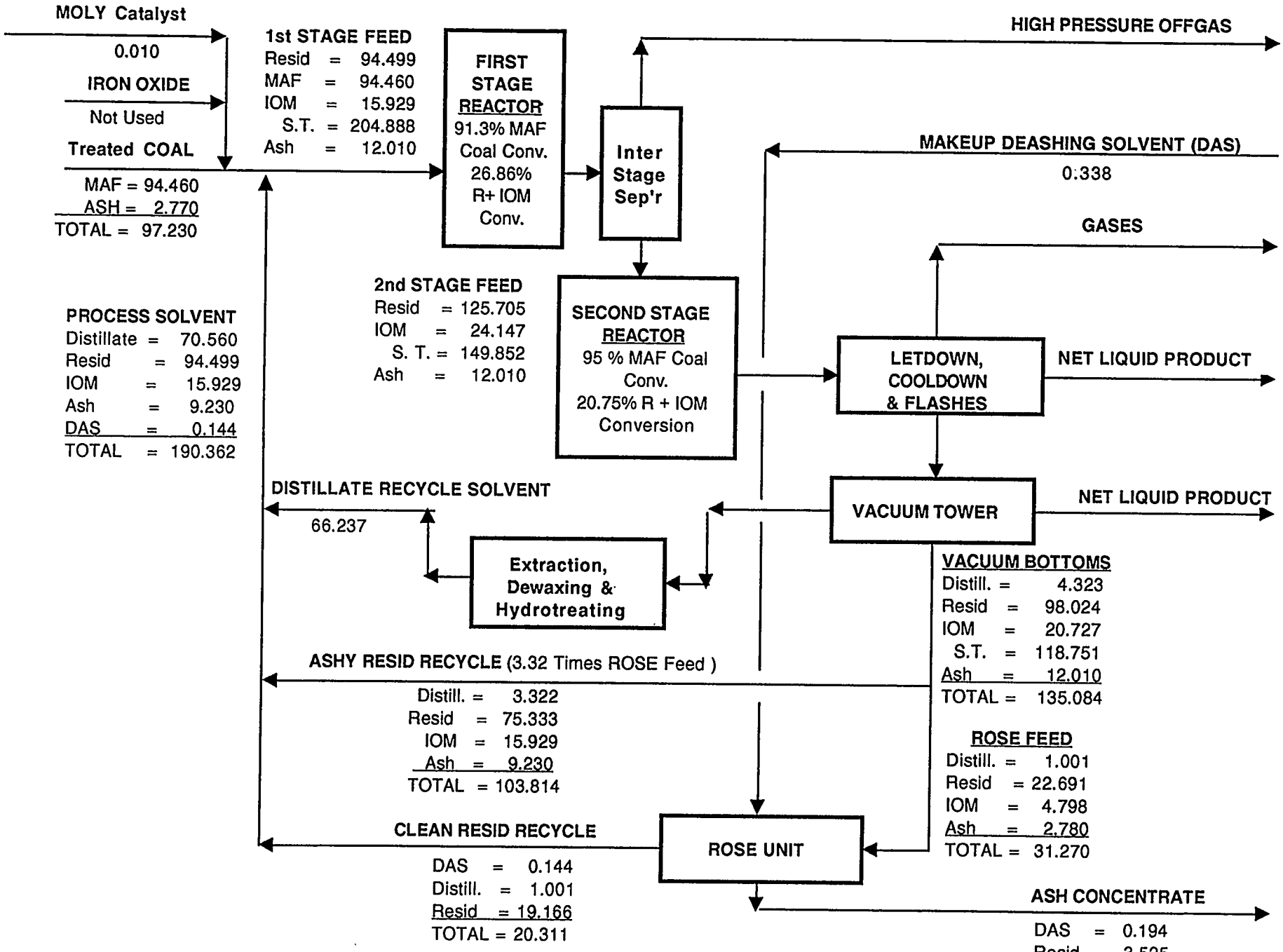

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FIGURE 1A SIMPLIFIED RESID, IOM & ASH BALANCE
ADVANCED CONCEPTS CASE (SO_3- Free ash basis, WR#263J)

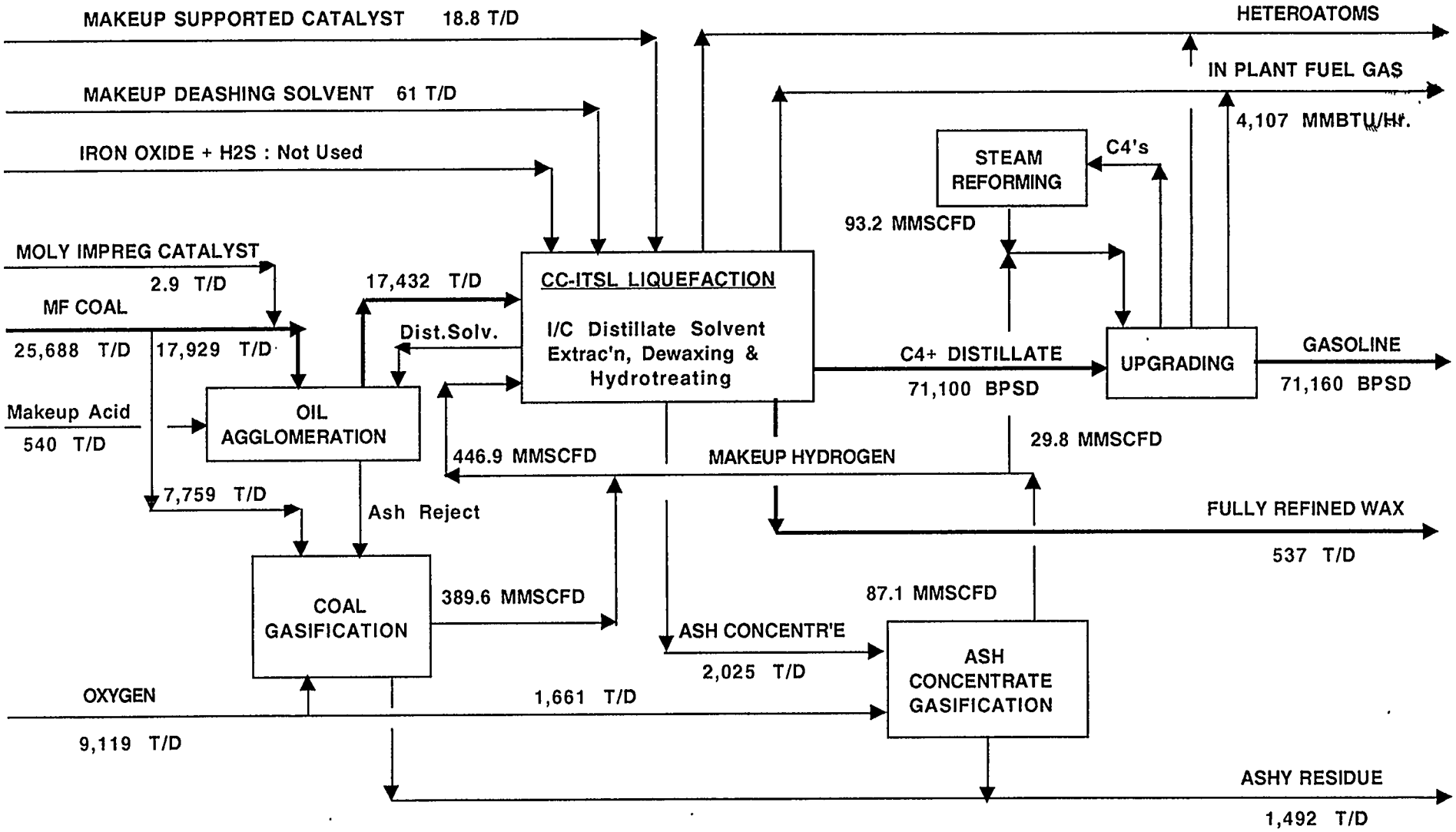

FIGURE 2A
BLACK THUNDER LIQUEFACTION STUDY - HYBRID MODE
SIMPLIFIED BLOCK FLOW DIAGRAM - CONCEPTUAL COMMERCIAL PLANT
ADVANCED CONCEPTS CASE (SO_3-Free Ash, W'ville Run # 263J)

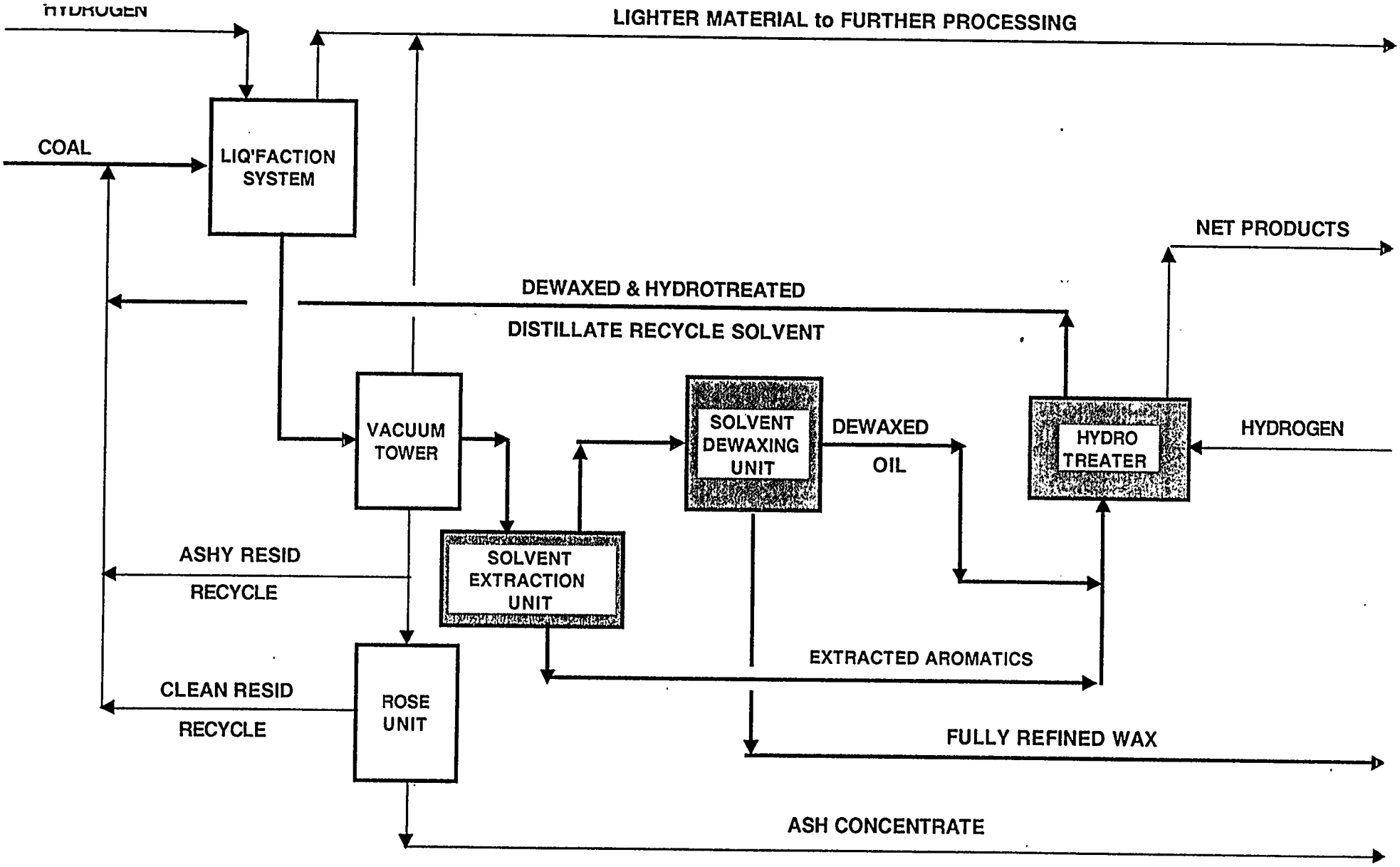

FIGURE 4
ADVANCED CONCEPTS CASE SIMPLIFIED BLOCK FLOW DIAGRAM
SOLVENT EXTRACTION, SOLVENT DEWAXING & HYDROTREATING
OF THE DISTILLATE RECYCLE SOLVENT

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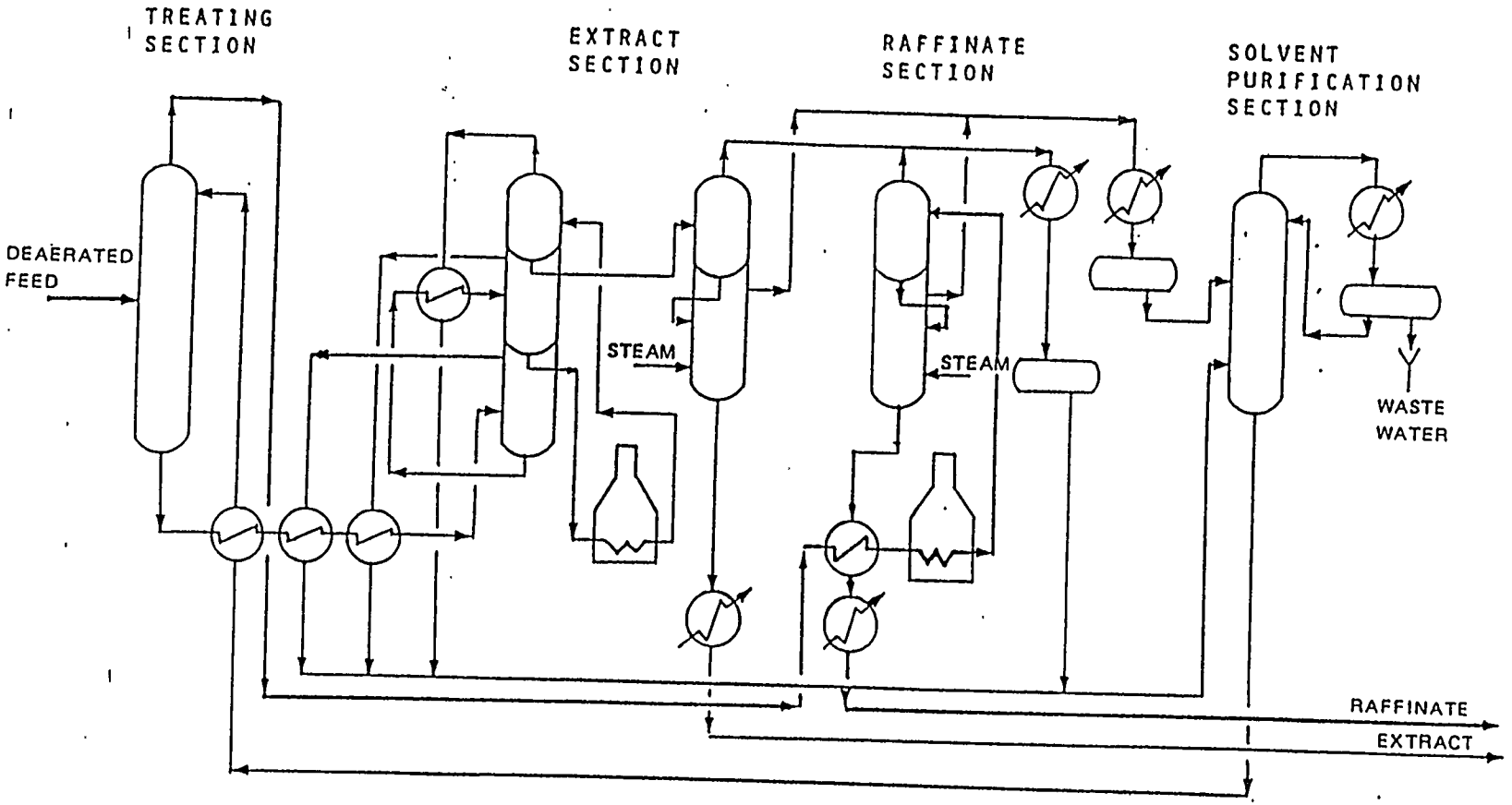

FIGURE 5
SIMPLIFIED PROCESS FLOW DIAGRAM
TEXACO MP SOLVENT EXTRACTION PROCESS

TEXACO DEVELOPMENT CORPORATION

THREE STAGE SOLVENT DEWAXING-WAX FRACTIONATION UNIT WITH INCREMENTAL DILUTION AND WARM UP DEOILING

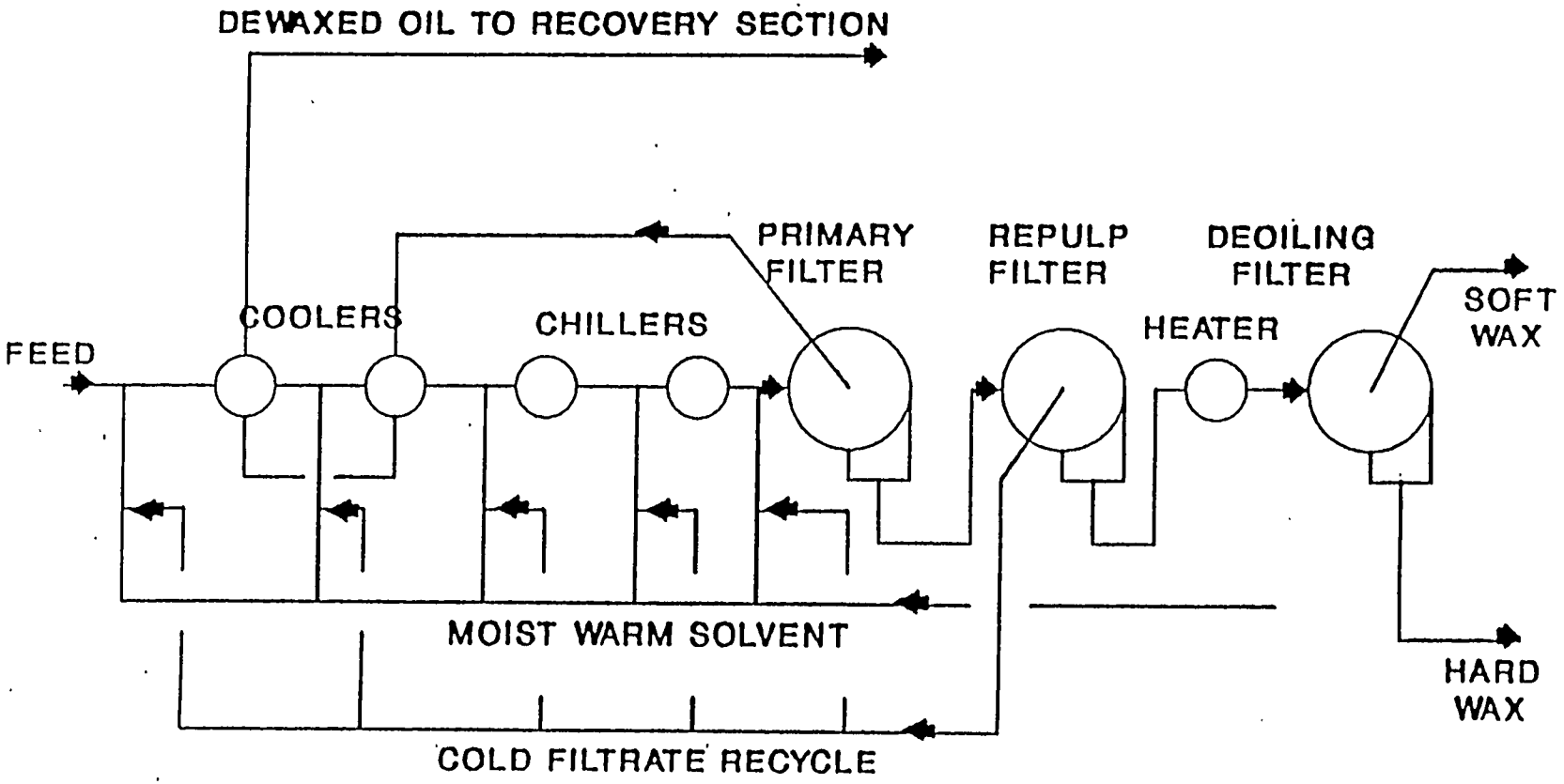

FIGURE 6

TABLE 2A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
LIQUEFACTION SYSTEM YIELDS

INPUTS:

• MF COAL	100.000
• MOLY CATALYST	0.010
• IRON CATALYST	Not Used
• SULFIDING AGENT (H_2S)	0.007
• MAKEUP DAS	0.338
• HYDROGEN	6.276
Total =	106.631

OUTPUTS:

• WATER	12.900
• HYDROGEN SULFIDE	0.276
• AMMONIA	0.677
• CARBON MONOXIDE	0.970
• CARBON DIOXIDE	5.150
• C1 to C3 GASES	7.408
• C4+ DISTILLATE	62.187
• WAX BYPRODUCT	2.996
• ASH CONCENTRATE	11.297
• ASH (OIL AGGLOMERATION)	2.770
Total =	106.631

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TABLE 3A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED C4+ DISTILLATE PRODUCT PROPERTIES

• YIELD, Wt% on MF COAL	62.187
• PRODUCTION RATE, BPSD	71,100
• DENSITY, Degrees API	26.4
• HIGHER HEATING VALUE, Btu/lb.	19,334
• ELEMENTALS, Wt.%:	
- CARBON	86.14
- HYDROGEN	11.22
- OXYGEN	2.00
- NITROGEN	0.60
- SULFUR	0.04
Total =	100.00
• CUTS, Wt.% :	
- IBP to 350 F	20.5
- 350 to 450 F	13.1
- 450 to 650 F	38.0
- 650 to EP (800F)	28.4
Total =	100.0

TABLE 4A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED FIRST STAGE REACTOR PARAMETERS

- Four Once-Thru Refractory lined Reactors in Parallel, 13.2 Feet ID. (10.7" Wall Thk. & 6" Ref. Thk.) x 84 Feet Height
- 1,225 Tons Each, 4,900 Tons Total
- MF Coal Feedrate, 17,432 T/D
- MF Coal Concentration in Slurry = 33.8%
- Process Solvent Composition :
  - Distillate 37.07%
  - Resid 49.64%
  - UC 8.37%
  - Ash 4.85%
- Liquefaction Additives :
  - Coal is Impregnated with Moly @ 100 ppm on MF Coal
- Temperatures :
  - Preheater Outlet = 750° F
  - Reactor Inlet / Outlet = 756° F / 875° F
  - Reactor Effective = 840° F
  - Reactor Design = 650° F (Refractory Lined)
- Operating/ Design Pressure = 2,910 / 3,200 psig
- Average Hydrogen Partial Pressure = 2,185 psig
- Inlet / Outlet Hydrogen Purity = 88.9 / 61.6 Vol. %
- H_2 Consumed / Available = 188.0 / 504.3 MMSCFD
- Actual / Nominal Slurry Residence Time = 20.9 / 42.0 Min.
- MAF Coal Conversion = 91.3%
- Resid + IOM Conversion = 26.86%

TABLE 5A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMAT'D SECOND STAGE REACTOR PARAMETERS

- Four Ebullated Reactors in Parallel, 13.5 Feet ID. (11.0" Wall Thk.) x 58 Feet Height
- 650 Tons Each, 2,600 Tons Total
- Criterion (Shell) 324 Ni-Moly Catalyst
- Slurry Feedrate = 44,221 T/D
- MAF Coal Conversion In / Out = 91.3 / 95.0 %
- Resid + UC Conversion = 20.75%
- Space Velocity = 263.9 lb. Feed / Hr.- ft^3 Catalyst
- Temperatures:
  - Slurry @ Reactor Inlet = 680°F
  - Gas @ Reactor Inlet = 800°F
  - Reactor Inlet = 790°F
  - Reactor Outlet = 825°F
  - Reactor Effective = 810°F
  - Reactor Design = 850°F
- Operating / Design Pressure = 2,760 / 3,200 psig
- Average Hydrogen Partial Pressure = 2,220 psig
- Inlet / Outlet Hydrogen Purity = 89.3 / 71.8 Vol. %
- H_2 Cons'd / Available = 188.0 / 559.2 MMSCFD
- Total Catalyst Inventory = 754,000 lbs.
- Catalyst Replace't Rate = 18.8 T/D, (3 lb./ton MF)

TABLE 6A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
ESTIMATED DEASHING UNIT PARAMETERS

- MAF Coal Conversion = 95.0%

- Flowrates,T/SD :
  - Vacuum Bottoms Feed = 5,606
  - Makeup DAS = 61
  - Clean Resid Product = 3,642
  - Ash Concentrate = 2,025

- Organic Rejection = 8.5% of MF Coal

- Energy Rejection = 10.1% of Coal HHV

TABLE 7A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL HYBRID CONFIGURATION - W'VILLE RUN# 263J
OVERALL UPGRADING YIELDS

INPUTS (Wt.% on C_4+ Distillate):

• C_4+ DISTILLATE	100.00
• HYDROGEN	2.39
Total =	102.39

OUTPUTS:

• WATER	2.25
• HYDROGEN SULFIDE	0.04
• AMMONIA	0.73
• C_1 to C_3 GASES	3.79
• C_4's	7.89
• GASOLINE	87.69
Total =	102.39

TABLE 8A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL
HYBRID CONFIGURATION - W'VILLE RUN# 263J
HYDROGEN AND FUEL GAS BALANCES

HYDROGEN BALANCE (MMSCFD):

• CONSUMPTION	
- LIQUEFACTION REACTORS	396.7
- DISTILLATE SOLVENT HYDROT'R	50.2
- UPGRADING	224.1
Total =	671.0
• PRODUCTION	
- GASIFICATION OF COAL	389.6
- GASIFICATION OF ASH CONC.	87.1
- STEAM REFORMING OF HC GASES	93.2
- PRODUCED IN CAT. REFORMING	101.1
Total =	671.0

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

• CONSUMPTION	
- SLURRY PREHEATER	1,115
- CATALYTIC REFORMER	941
- STEAM REFORMER	590
- DISTILLATE HYDROPROCESSING	320
- DRYING, COAL GASIFICATION	340
- VACUUM UNIT	171
- ROSE UNIT	108
- DISTILLATE SOLVENT EXTRACT'N	227
- DISTILLATE SOLVENT DEWAXING	113
- DISTILLATE SOLVENT HYDROT'G	116
- SULFUR RECOVERY UNIT	66
Total =	4,107
• PRODUCTION	
- LIQUEFACTION OFF GAS	2,704
- DISTILLATE HYDRO. OFF GAS	2,224
- CAT. REFORMING OFF GAS	80
Sub-Total =	5,008
- STEAM REFORMING FEED -	901
Total =	4,107

TABLE 9A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL HYBRID CONFIGURATION - RUN# 263J
ELECTRICAL POWER REQUIREMENTS

UNIT	MEGAWATTS
COAL GRINDING	21.4
OIL AGGLOMERATION	5.0
COAL SLURRY PREPARATION & DRYING	2.3
FIRST STAGE REACTION SYSTEM	18.2
SECOND STAGE REACTION, LETDOWN & VACUUM FRACTIONATION SYSTEMS	3.2
ROSE UNIT	1.9
GAS PLANT HYDROGEN RECOVERY & RECYCLE	32.9
GASIFICATION	36.8
OXYGEN PLANT	174.0
STEAM REFORMER	1.9
MAKEUP HYDROGEN COMPRESSION	42.0
UPGRADING UNITS	17.0
OFFSITES & UTILITIES	41.0
DISTILLATE SOLVENT EXTRACTION	2.3
DISTILLATE SOLVENT DEWAXING	5.9
DISTILLATE SOLVENT HYDROTREATING	4.7
DISTRIBUTION LOSSES @ 3%	12.3
TOTAL =	**422.8**

LDP ASSOCIATES 3/21/95

TABLE 10A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL HYBRID CONFIGURATION - RUN# 263J
PROCESS UNIT INVESTMENT

UNIT	INVESTMENT (Millions of Mid '94 $:Wyoming Location)
OIL AGGLOMERATION	60
COAL SLURRY PREPARATION & DRYING	78
FIRST STAGE REACTION SYSTEM	332
SECOND STAGE REACTION SYSTEM	112
LETDOWN SYSTEM	47
VACUUM FRACTIONATION	175
ROSE UNIT	55
DISTILLATE SOLVENT EXTRACTION	74
DISTILLATE SOLVENT DEWAXING	207
DISTILLATE SOLVENT HYDROTREATING	95
GAS PLANT HYDROGEN RECOVERY & RECYCLE	218
ASH CONCENTRATE & COAL GASIFICATION	540
OXYGEN PLANT	213
STEAM REFORMER	74
MAKEUP HYDROGEN COMPRESSION	136
UPGRADING UNITS	599
TOTAL **PUI** =	**3,015**

LDP ASSOCIATES 3/21/95

TABLE 11A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL
HYBRID CONFIGURATION - RUN# 263J
OFFSITE UNITS INVESTMENT

UNIT	INVESTMENT (Millions of Mid '94 $:Wyoming Location)
LIQUID TANKAGE	153
COAL HANDLING & STORAGE	112
SITE DEVELOPMENT	96
BUILDINGS & CONTROL SYSTEMS	92
ELECTRICAL POWER DISTRIBUTION	91
SOUR WATER TREATING, AMMONIA & PHENOL RECOVERY	88
INTERCONNECTING PIPING	72
WASTEWATER TREATMENT	52
WATER SYSTEMS	43
ASH DISPOSAL	31
RAILROAD & TRUCK FACILITIES	28
STEAM SYSTEM	26
FIRE PROTECTION SYSTEM	23
SULFUR PLANT	14
OTHER UNITS (3)	36
TOTAL OFFSITES =	**957**

LDP ASSOCIATES 3/21/95

TABLE 12A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL
HYBRID CONFIGURATION - RUN# 263J
TOTAL CAPITAL REQUIREMENT

	INVESTMENT (Millions of Mid '94 $: Wyoming Location)
PROCESS UNITS	3,015
OFFSITE UNITS	957
WORKING CAPITAL	125
START-UP COSTS	168
INITIAL CATALYSTS & CHEMICALS	99
Total Capital Required =	**4,364**

TABLE 13A
ADVANCED CONCEPTS CASE : BLACK THUNDER COAL
HYBRID CONFIGURATION - RUN# 263J
ANNUAL OPERATING COSTS

	COST ($ Millions/Yr.)	($ / Bbl. Gasoline)
TOTAL MF COAL: 25,688 T/D @ $7.14/T	58.69	2.577
PURCHASED ELECTRICAL POWER, MW @ 4¢/ Kw-hr.	129.95	5.707
LIQUEFACTION SYSTEM ADDITIVES :		
- Iron Oxide @ 12¢/lb. & H_2S @ 7.5¢/lb.	NOT USED	
- Moly Impregnating Catalyst	10.00	0.439
- Supported Ni-Moly @ $3/lb.	36.15	1.588
MAKEUP DEASHING UNIT SOLVENT	9.88	0.434
OTHER LIQ'N CATALYSTS & CHEMICALS	27.49	1.207
UPGRADING UNITS CATALYSTS & CHEM.	17.08	0.750
RAW WATER @ $ 2.50/1,000 Gallons	8.87	0.389
ASH DISPOSAL @ $5/Ton	2.39	0.105
OPERATING LABOR	22.61	0.993
ADMINISTRA'N & OPERATIONS SUPPORT	13.90	0.610
MAINTENANCE @ 1.5% of TIC + ICC	61.07	2.682
INSURANCE & LOCAL TAXES @ 1% of TPC + ICC	40.71	1.788
BYPRODUCT CREDITS:		
• Ammonia, Sulfur & Phenols	- 24.31	- 1.067
• Fully Refined Paraffin Wax	-116.89	- 5.133
Total =	**297.59**	**13.069**

LDP ASSOCIATES 3/21/95

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SECTION FOUR

Sandia National Laboratories

Advanced Concepts for Direct Coal Liquefaction Final Report

INTRODUCTION

This report describes Sandia National Laboratories' portion of a research program performed by the University of Kentucky Center for Applied Energy Research (CAER), the Consolidation Coal Company (CONSOL), Sandia National Laboratories (SANDIA) and LDP Associates to develop advanced, integrated process concepts to reduce the cost of liquid fuels produced by direct coal liquefaction. Sandia has developed and evaluated approaches to allow better control of initial coal dissolution reactions by producing a better hydrogen donor solvent. Hydrogen donor improvements have been attained through solvent dewaxing (CONSOL) and a variety of hydrotreating reactions (Sandia). Another component of Sandia's research has been synthesis and testing of hydrotreating catalysts for solvent pretreatment reactors. The goal of the Advanced Concepts for Direct Coal Liquefaction Program research is to advance to bench-scale testing those concepts that have the potential for making reductions in process costs by improving coal conversion and distillate yields. Figure 1 shows a current direct coal liquefaction process and a new integrated liquefaction process scheme incorporating solvent pretreatment steps. Hydrogen donors have been extensively studied in direct coal liquefaction research and have been used effectively to stabilize thermolysis products in the first stage of liquefaction as shown stylistically in Figure 2, where pyrene (a hydrogen donor precursor) is hydrogenated to 4,5 dihydropyrene, which can donate two hydrogens to stabilize reaction products. The bulk of this report discusses hydrogenation of liquefaction solvent, including dewaxed solvents and solvents selectively chosen to increase hydrogen donating ability. The following table can be used as a guide.

Section	Subtask	Topic
A	2.3.3	Catalyst Screening with a Model Compound Mixture
B	2.1.3/2.3.3	Heavy Distillate Solvent Pretreatment Studies*
B.1	2.1.3/2.3.3	Synthesis Gas/Steam - Lower Temp. Experiments
B.2	2.1.3	Hydrogen Only - Higher Temperature Experiments
B.3	2.1.3	Process Simulation Testing
B.4	2.1.3	Batch Hydrogenation to Evaluate Maximum Hyd. Uptake
B.5	2.1.3	Distillation Pretreatment and Batch Testing
B.6	2.1.3	Evaluation of Donor Solvent Precursors

* The bulk of this project involved heavy distillate solvent pretreatment.

Section A. Catalyst Screening with a Model Compound Mixture [Subtask 2.3.3]

Background

Initial solvent pretreatment work at Sandia consisted of solvent hydrogenation using the water-gas shift reaction as the source of hydrogen. A recent study used the combined water-gas shift/hydrogenation reaction to hydrotreat petroleum fractions [1]. The aim of Sandia's work is to reduce reaction temperature and pressure for donor solvent

hydrogenation and to remove the requirement for purified hydrogen. The use of water and CO mixtures involves two classes of coupled catalytic reactions:

Water-gas shift:

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2\,(g)}$$

Hydrogenation of donor species, for example:

$$\text{Pyrene} + H_{2\,(g)} \leftrightarrow \text{4,5 Dihydropyrene } (H_2Py)$$

Hydrogenation of a donor solvent species is illustrated here by the hydrogenation of pyrene, a donor solvent precursor. Equilibrium concentrations of hydrogen and H_2Py are greatly increased at lower temperatures due to the greater K_p for the above reactions. The ability to lower the coupled reaction temperature allows the total system pressure to be reduced and still achieve adequate solvent hydrogenation.

Solvent pretreatment using hydrogen from an in situ water-gas shift reaction is very efficient at low temperatures. For this reason, a catalyst that is active at low temperatures (<300°C) for both water-gas shift and solvent hydrogenation is very desirable. Catalyst testing at Sandia has involved hydrogenation of a synthetic solvent containing 9.5 wt% aromatic compounds in hexadecane. A 1:1:1 equimolar mixture of CO, H_2, and steam is reacted with the solvent in a trickle-bed reactor to produce hydrogen and hydrogenate the solvent in one step.

Experimental: Apparatus and Procedure

Solvent hydrogenation tests were conducted with model compounds mixed in hexadecane. The model compound tests give an indication of the relative activity of a variety of catalyst formulations for use as supported catalysts in a fixed-bed hydrotreating reactor. The model compound mixture contained 3.9% phenanthrene, 2.3% pyrene, and 3.3% fluoranthene (total aromatic concentration 9.5%). This mixture was catalytically hydrogenated in a fixed-bed reactor operated in a trickle-bed mode. Reactant gases (CO/H_2/steam) and liquids were pumped concurrently with a downward flow. Figure 3 shows a schematic diagram of the trickle-bed reactor.

A microflow reactor consisting of a 0.25" O.D. type 316 stainless steel tube was fixed in a convectively heated oven to hydrogenate the model compound mixture. Solvent was pumped into the reactor with an Eldex A-30 liquid chromatography pump and the synthesis gas (CO and H_2) was metered into the microflow reactor with two Brooks 5850 flowmeters. Water was added to the reactor with a Beckman 114M microflow liquid chromatography pump. Flow reactor pressure was maintained with a Circle Seal BPR-7A back pressure regulator.

All catalysts were packed in the trickle-bed reactor after they were crushed and sieved to a -30+40 mesh particle size (unless specified otherwise). Nickel molybdenum (NiMo) and cobalt molybdenum (CoMo) catalysts were sulfided in situ for 2 hours at 390°C with a 10%

H_2S in hydrogen mixture. A platinum hydrous titanium oxide (HTO) catalyst was first calcined and then reduced in situ with hydrogen. After appropriate catalyst pretreatment, reactions were performed using a 1:1:1 equimolar mixture of CO, H_2, and steam to hydrogenate the concurrently flowing synthetic solvent using the water-gas shift reaction. Weight Hourly Space Velocities (WHSV) for the model compound experiments were calculated on a weight aromatic feed/weight catalyst/hour basis. Gas chromatography was used to evaluate CO conversions and capillary gas/liquid chromatography was used to measure hydrogenation of the aromatic feed components. Examples of the feed and product chromatograms are shown in Figures 4 and 5. Tables 1 to 7 list the results of the model compound screening tests.

Results and Discussion

Cobalt Molybdenum Catalyst Results

A commercially available CoMo catalyst (5.8% Mo, 1.65% Co supported on alumina, surface area = 300 m^2/g) was tested using the in situ water-gas shift reaction. All reactants were fed downward over the catalyst bed concurrently, and total reaction pressure was maintained at 1000 psig. WHSV was 0.5 hr^{-1}. This catalyst gave a 60% CO conversion at 275°C compared to average conversions of ~95% for NiMo catalysts. The lower activity for this catalyst could be due to the lack of an alkali promoter (potassium or cesium). Potassium analysis of this catalyst showed less than 100 ppm by weight. Therefore, potassium was added to this catalyst to test the effect on the combined reactions. Comparative results for the potassium loaded and potassium free catalysts are shown in Table 1.

Table 1. CoMo Catalyst Comparison With and Without Potassium Promotion (Total System Pressure = 1000 psig, WHSV = 0.5 hr^{-1})

Catalyst	TEMP (°C)	%CO Conv.	Phen. Conv. (%)	Fluor. Conv. (%)	Pyrene Conv. (%)
CoMo	275	60	21	38	34
CoMo/potassium	275	94	0	6	4
CoMo	300	76	12	33	26
CoMo/potassium	300	94	0	14	9

At 275°C, the addition of potassium increased the carbon monoxide conversion to 94%, but greatly reduced the aromatic hydrogenation reaction. For example, fluoranthene hydrogenation decreased from 38% to 6%. The water-gas shift results are in general agreement with studies that report alkali metal promotion of sulfided CoMo catalysts [2,3]. The high potassium concentration (8 wt%) on the potassium loaded catalyst inhibited the hydrogenation reaction, and the low potassium concentration (0.1%, tested previously) proved ineffective in enhancing the shift reaction. The optimum potassium/molybdenum ratio for water-gas shift promotion should be approximately 0.4; this would equal approximately 1 wt% potassium for this catalyst [2,3]. However, potassium inhibition of the hydrogenation reaction made further study of this catalyst unprofitable.

Platinum Catalyst Results

An HTO catalyst was prepared with platinum as the active metal. The HTO was prepared from tetraisopropyl titanate and tetraethyl orthosilicate in a sodium hydroxide methanol solution. The solution was hydrolyzed with acetone and water to precipitate the sodium form of the HTO [4]. This platinum catalyst was made by exchanging platinum ammonium nitrate onto the bulk HTO support.

Solvent pretreatment tests were run using this synthesized Pt HTO catalyst. Two initial flow reactor experiments were carried out. Results for solvent hydrogenation and water-gas shift CO conversion for the first experiment were obtained using a mild catalyst calcining temperature of 200°C and a reduction temperature of 250°C. Results from this test (Table 2) gave only 27% CO conversion and showed no hydrogenation of the aromatic compounds.

Table 2. Pt HTO Catalyst (Total System Pressure = 1400 psig, WHSV = 0.5 hr^{-1})

Calcining Temp. (°C)	Reaction Temp. (°C)	CO Conv. (%)	Phen. Conv. (%)	Fluor. Conv. (%)	Pyrene Conv. (%)
200	275	27	0	0	0
500	275 (day 1)	95	35	56	58
500	275 (day 2)*	96	15	25	22
500	300 (day 1)	95	68	97	80

* Second day of operation showed catalyst deactivation.

The second experiment used catalyst calcined at 500°C and reduced at 250°C. The 500°C calcining step activates the catalyst and drives off troublesome nitrogen compounds before the catalyst is reduced in the reactor with flowing hydrogen. Results from this second test (Table 2) showed that calcining at 500°C greatly increased catalyst performance. The catalyst showed a marked gain in activity, but hydrogenation activity decreased during the run at 275°C as seen by the day 2 results. Deactivation was most likely due to sulfur in the pyrene feed. Sulfur poisoning of platinum catalysts is known to be somewhat reversible, and thus activity might be maintained at higher temperatures. For this reason, a reaction was performed at 300°C to check temperature effects. This higher temperature gave significant improvements in hydrogenation activity. Therefore, a catalyst stability test was performed at 315°C to test for deactivation due to sulfur in the feed. This 315°C temperature should allow for desorption of sulfur from the catalyst during hydrotreating. The catalyst was first calcined at 500°C in air, packed in the 0.25" O.D. reactor tube, and reduced at 200°C with hydrogen. WHSV was maintained at 0.85 hr^{-1} on an aromatic feed basis for over six hours. Results from this catalyst stability test are shown in Table 3. This catalyst showed high activity for the water-gas shift reaction (96% CO conversion) and the solvent hydrogenation reaction (60% phenanthrene conversion, 93% fluoranthene conversion, 71% pyrene conversion). In addition, the catalyst did not show any measurable deactivation, indicating that sulfur poisoning at these conditions was not a problem. The platinum catalyst also removed much of the sulfur in the feed. The feed had over 250 ppm sulfur and the product had less than 30 ppm sulfur. An odor of H_2S was present throughout the experiment, indicating that the sulfur

was at least partially removed by hydrodesulfurization. The Pt HTO catalyst became a candidate for further testing with the heavy distillate feeds.

Table 3. Pt HTO Catalyst (Total System Pressure = 1400 psig, WHSV = 0.85 hr^{-1})

Elapsed Time (min)	Reaction Temp. (°C)	CO Conv. (%)	Phen. Conv. (%)	Fluor. Conv. (%)	Pyrene Conv. (%)
104	315	NA	63	93	74
200	315	95	61	92	71
287	315	95	61	93	72
366*	315	96	60	93	71

* Reactor system pressure = 1000 psig.

Nickel Molybdenum Catalyst Testing

Combined water-gas shift solvent hydrogenation tests were conducted with three NiMo catalysts to evaluate each catalyst's ability to perform both the water-gas shift reaction and the aromatic solvent hydrogenation reaction. The three catalysts included a commercially available NiMo on alumina (Shell 324M, 12.4 wt% Mo, 2.8 wt% Ni) and two Sandia catalysts: a NiMo HTO thin film catalyst coated onto a large pore silica bead (CHTO) and a bulk NiMo HTO catalyst (BHTO). Table 4 shows the data from the trickle-bed hydrogenation tests. Results from these tests showed that the Shell 324M and BHTO performed well. However, questions remain about the expense of raw materials for BHTO catalysts for heavy distillate feedstock hydrotreating. The thin film NiMo HTO catalyst showed significantly lower hydrogenation activity than the BHTO or Shell 324M. These results led us to try a thicker NiMo coating for the supported HTO catalysts.

Table 4. NiMo Catalyst Comparison (Total System Pressure 1000 psig)

Catalyst	Mo (Wt%)	WHSV (hr^{-1})	Temp. (°C)	Phen. Conv. (%)	Fluor. Conv. (%)	Pyrene Conv. (%)
CHTO*	0.68	0.17	275	8	29	13
CHTO	0.68	0.17	300	20	71	37
BHTO**	10.4	0.5	250	17	88	32
BHTO	10.4	0.5	275	50	98	69
BHTO	10.4	0.5	300	68	99	70
Shell 324M	12.4	0.5	275	56	98	71
Shell 324M	12.4	0.5	300	73	96	69

* CHTO = Coated (**thin film**) Hydrous Titanium Oxide on Silica Bead

** BHTO = Bulk Hydrous Titanium Oxide

Two additional flow reactor experiments were conducted to evaluate two of the more active catalyst formulations in larger reactors (0.4" O.D.,12 cm^3), which will be used for coal-derived

solvent hydrogenation experiments. The first catalyst tested was an HTO **thick film** catalyst that had been coated multiple times with nickel and molybdenum. This coated HTO (CHTO) catalyst was prepared by first coating a porous silica bead with a film of hydrous titanate, then loading molybdenum by ion exchange, and finally adding the nickel by incipient wetness. The second catalyst was Shell 324M. Both catalysts were used in their engineered forms: extrudates for Shell 324M and beads for the thick film HTO.

For each test the reactor was packed with catalyst and diluent (low surface area α alumina), then sulfided. Catalyst activity results are shown in Table 5 along with data showing the effect of gas treat rates on CO conversion and solvent hydrogenation. The gas treat rates are listed as Gas Hourly Space Velocity (GHSV = cubic centimeters gas/cubic centimeters reactor/hour at 1 atm).

Table 5. NiMo Catalyst Comparison - Gas Feed Rate Effects (Total System Pressure = 1000 psig)

Catalyst	Mo (Wt%)	Temp (°C)	WHSV (hr^{-1})	GHSV (hr^{-1}) CO/H_2	%CO Conv	Phen. Conv. (%)	Fluor. Conv. (%)	Pyrene Conv. (%)
Shell 324M	12.4	275	.44	300/300	78	47	95	67
Shell 324M	12.4	275	.44	200/200	86	48	96	68
Shell 324M	12.4	275	.44	100/100	93	48	96	68
CHTO*	5.6	275	.44	300/300	78	42	89	53
CHTO	5.6	275	.44	200/200	88	45	88	57
CHTO	5.6	275	.44	100/100	95	43	85	55
Shell 324M	12.4	275	.89	100/100	95	27	84	54
CHTO	5.6	275	.89	100/100	95	25	65	36
CHTO	5.6	300	.89	100/100	95	45	82	49

* CHTO = Coated (**thick film**) Hydrous Titanium Oxide on Silica Beads

The effect of gas treat rate on the solvent hydrogenation reaction was negligible. However the gas velocity did affect the water-gas shift reaction. The carbon monoxide conversion decreased with increasing gas treat rate, showing a kinetic effect for this reaction under these conditions. In addition, on a weight of catalyst basis the Shell 324M catalyst proved to be somewhat more active for solvent hydrogenation. On a catalyst metal basis, however, the coated HTO catalyst showed greater activity.

After some catalyst deactivation, the CHTO catalyst from tests described in Table 5 was used to test the effects of feed rate on solvent hydrogenation rate. The WHSV of the synthetic solvent was varied between 0.44 and 1.11 hr^{-1}. Feed rate effects are shown in Table 6. The water-gas shift reaction was unaffected by the increase in aromatic feed rate to the reactor. Preliminary analysis of the liquid products, however, indicates that fluoranthene hydrogenation rates are much faster than those for either phenanthrene or pyrene. Table 6 shows the dramatic differences among these rates. Indeed, the high initial rate for fluoranthene hydrogenation seems to repress the other two hydrogenation reactions, possibly by competing for the available hydrogen.

Table 6. Aromatic Feed Rate Effects, NiMo CHTO/Silica Catalyst (5.6 wt% Mo (thick film)), 1000 psig, used catalyst from Table 5 experiments)

WHSV (hr^{-1})	Temp. (°C)	%CO Conv.	Phen. Conv. (%)	Flour. Conv. (%)	Pyrene Conv. (%)
0.44	275	94	31	80	46
0.67	275	94	29	76	44
1.11	275	96	14	57	23

Coated NiMo HTO on Alumina Extrudates

Further tests were performed with a catalyst synthesized by coating HTO on 1/32" alumina extrudates and then exchanging in NiMo. An alumina support was used to achieve more favorable reactor packing densities. The catalyst was used as extrudates and mixed with low surface area α alumina as a diluent in the 0.4" O.D. reactor tube. WHSV effects were measured at 0.87 hr^{-1} and 0.43 hr^{-1} on an aromatic feed basis. Comparative results from this catalyst and previous NiMo catalysts are shown in Table 7.

All three catalysts showed high activity for the water-gas shift reaction. The NiMo HTO on alumina showed somewhat higher hydrogenation activities than the silica supported catalyst and had comparable hydrogenation activities to the Shell 324M. In addition, the NiMo HTO on alumina has 7.2% molybdenum compared to 12.4% molybdenum for the Shell 324M catalyst. The improved activity on an active metals basis is most likely due to increased metal dispersion using the coating technology, which also gives increased flexibility in catalyst metal loading.

Table 7. NiMo Catalyst Comparison (Total System Pressure = 1000 psig) GHSV = 100/100 hr^{-1} for CO/H_2

Catalyst	Mo (Wt%)	Temp (°C)	WHSV (hr^{-1})	%CO conv.	Phen. Conv. (%)	Fluor. Conv. (%)	Pyrene Conv. (%)
CHTO on alumina	7.2	275	0.43	93	44	96	62
CHTO on alumina	7.2	275	0.87	97	22	81	43
CHTO on silica	5.6	275	0.44	95	43	85	55
CHTO on silica	5.6	275	0.89	95	25	65	36
Shell 324M	12.4	275	0.44	93	48	96	68
Shell 324M	12.4	275	0.89	95	27	84	54

Catalyst Screening Conclusions

Catalyst testing experiments were performed with a combination of a mixture of three aromatic compounds to evaluate hydrogenation activity and a 1:1:1 equimolar mixture of CO, H_2, and steam to evaluate hydrogen production using the water-gas shift reaction. Results have identified several candidate supported catalysts for use in hydrotreating heavy distillate solvents. Supported NiMo HTO and Pt HTO catalysts have shown excellent activity for hydrogenating polynuclear aromatic compounds, which are key hydrogen donor precursors. A NiMo HTO catalyst coated on an alumina support has shown comparable hydrogenation activity to commercially available Shell 324M. The NiMo coated catalyst had 7.2 wt% Mo versus 12.4 wt% Mo for Shell 324M. A Pt HTO catalyst showed no evidence of deactivation after 6 hours of processing a mixture of aromatic model compounds with the water-gas shift reaction at 315°C. In most reactions performed at temperatures between 300 and 325°C, the water-gas shift reaction effectively produced hydrogen as evidenced by carbon monoxide conversions greater than 93%.

Section B. Heavy Distillate Solvent Pretreatment Studies [Subtask 2.1.3]

Background and Experimental

Preliminary Testing with V1074 Feed and Dewaxed V1074 Feed

The previous model compound tests included testing of NiMo coated HTO and Pt HTO catalysts as well as various commercial catalysts. The following tests used V1074 heavy distillate solvent (Sample 1621-22-5) from Wilsonville run 262E and two samples of V1074 that had been dewaxed at -5°C and -35°C by CONSOL. All tests using heavy distillate solvents required reactor modifications to increase the catalyst volume. For this purpose a larger catalyst bed was used. The larger reactor has 22cm^3 of internal volume and consists of two 0.4" I.D by 7" long stainless steel tubes connected in series. This configuration allows

for adequate reactor volume to achieve suitable liquid space velocities. A "day" of processing in this reactor equals eight hours of reaction time because this reactor cannot be operated unattended. Sample numbers consist of the month (first two digits) and day (middle two digits) the reaction was performed followed by the sample number (last two digits).

Section B.1 Synthesis Gas / Steam - Lower Temperature Experiments

Three sets of tests were performed with Shell 324M (12.4 wt% Mo, 2.8 wt% Ni on alumina) as the baseline catalyst to evaluate the response of V1074 heavy distillate to low severity hydrogenation using the water-gas shift reaction. Additional tests were performed using the -5°C dewaxed V1074 with a Pt HTO (5.4 wt% Pt) catalyst and a NiMo coated HTO (8.1 wt% Mo, 2.7 wt% Ni) catalyst, both of which had been synthesized at Sandia. The water-gas shift reaction used 1:1:1 equimolar amounts of CO:H_2:steam to hydrogenate the concurrently flowing heavy distillate solvent. Liquid Hourly Space Velocity (LHSV = volume feed/volume catalyst/hour) effects were tested from about 0.2 hr^{-1} to 1.1 hr^{-1}. The reactor system pressure was 1000 psig (unless specified otherwise) and the tests were performed at two temperatures, 300°C and 325°C. Several modifications were made to the reactor to ensure smooth operations. Since the V1074 solvent is a semisolid at room temperature it was necessary to heat the feed reservoir and to heat-trace feed lines to keep the waxy V1074 from freezing and stopping flow

Results and Discussion

Shell 324M Testing

Shell 324M was used in the form of extrudates and packed in the 0.4" I.D. reactor tube without a diluent. The catalyst bed was then sulfided at 390°C for four hours with a 9% H_2S in hydrogen mixture. A fresh batch of catalyst was used whenever the feed was changed to enable comparisons under similar conditions. Elemental analyses of products from these runs are presented in Table 8.

Some decrease in hydrogenation activity was noticed during the first day of catalyst testing. This can be attributed to catalyst deactivation that seems to take place during the first several hours on-line. Hydrogen content was increased from 9.9% to 10.7% using the V1074 feed and an LHSV of about 0.4 hr^{-1}. Hydrogen content increased from 8.5% to 9.3% using -5°C dewaxed solvent and an LHSV of about 0.25 hr^{-1}. Overall, the maximum hydrogen increase was approximately 0.8 wt%. These increases should be sufficient to make notable improvements in coal liquefaction runs. By way of comparison 4,5 dihydropyrene, a known hydrogen donor compound, has 1.0 wt% donatable hydrogen content.

Hydrogen content increased from 8.0 wt% to 8.9 wt% using the -35°C dewaxed solvent as feed with an LHSV of about 0.44 hr^{-1}. In general, the -35°C dewaxed solvent performed like the -5°C dewaxed solvent, except that the -35°C feed was more difficult to pump. Overall the maximum hydrogen content increase was about 0.8 to 0.9 wt%. Samples 110603, 110605, and 110607 were taken on the third day of operation and were hydrotreated with hydrogen as the sole gas reactant to test the effect of hydrogen partial pressure. Reducing hydrogen

pressure did not have a significant effect on product hydrogen content. This result could be due in part to catalyst deactivation during previous testing.

Table 8. Carbon and Hydrogen Content of Solvent (V1074, -5°C and -35°C dewaxed V1074), Shell 324M Catalyst, Combined WGS Reaction

Feed Sample	LHSV (hr^{-1})	Temperature (°C)	Carbon (wt%)	Hydrogen (wt%)
V1074	NA*	NA	89.5	9.9
092803	0.41	300	88.2	10.4
092804	0.38	300	88.6	10.7
092906	0.72	325	87.3	10.2
-5°C Dewaxed V1074	NA	NA	89.1	8.5
102203	0.25	300	89.3	8.9
102206	0.25	300	88.8	8.9
102208	0.24	325	89.1	9.3
102306	0.64	325	88.9	8.8
102307	0.62	325	89.1	8.9
-35°C Dewaxed V1074	NA	NA	90.6	8.0
110404	0.40	300	90.4	8.9
110405	0.44	300	90.9	8.5
110502	0.24	325	88.9	8.7
110508	0.63	325	91.4	8.1
110603**	0.57	325	91.1	8.4 (1000 psig)
110605**	0.58	325	91.2	8.3 (670 psig)
110607**	0.53	325	90.4	8.3 (330 psig)

* NA = Not Applicable

** Hydrogen only for these experiments. Assume feed density is 1.0 g/cc for V1074, 1.05 g/cc for -5°C Dewaxed, 1.1 g/cc for -35°C Dewaxed, packed catalyst density is 0.86 g/cc.

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

Platinum HTO Catalyst Testing

A batch of platinum HTO catalyst was prepared for use in the water-gas shift solvent hydrogenation reaction using -5°C dewaxed feed. Pretreatment of the catalyst consisted of pressing into pellets, sizing to -10+20 mesh, and calcining in air at 500°C to remove residual

amine compounds from catalyst synthesis. The catalyst was next packed in the trickle-bed reactor and the platinum was reduced in flowing hydrogen gas for two hours at 200°C. LHSV was varied from about 0.3 hr^{-1} to 0.8 hr^{-1}. The reactor system pressure was 1000 psig and temperatures were 300°C and 325°C.

Results in Table 9 show that hydrogen content of the solvent increases by a moderate 0.5% using the combined water-gas shift solvent hydrogenation reaction (samples 111707, 111804 and 111806). The less-than-expected hydrogen contents of these samples were due to lower hydrogen partial pressures since some of the carbon monoxide formed methane under these conditions. This side reaction reduces hydrogen partial pressure in the trickle-bed reactor. Previous tests using the model compound mixture and the Pt HTO catalyst showed very little methane formation. The current tests showed as much as 14 vol% methane in the exit gas at 325°C. The most plausible explanation for the high methane production in these runs was the lower GHSV in this larger reactor (150 hr^{-1} compared to 400 hr^{-1} for the model compound runs).

Table 9. Carbon and Hydrogen Content of Solvent (-5°C dewaxed V1074, Pt catalyst)

Feed Sample	LHSV (hr^{-1})	Temperature (°C)	Carbon (wt%)	Hydrogen (wt%)
-5°C Dewaxed V1074	NA*	NA*	89.1	8.5
111707	0.32	300	90.5	9.0
111804	0.32	325	90.4	9.0
111806	0.82	325	90.6	8.9
111903**	0.78	325	89.9	9.6 (1000 psig)
111905**	0.73	325	90.5	9.0 (670 psig)
111907**	0.74	325	90.9	8.6 (330 psig)

* Not applicable

** Hydrogen only for these experiments. Assume feed density is 1.05 g/cc for -5°C Dewaxed V1074; packed catalyst density is 1.1 g/cc.

The product from the hydrogen only tests (samples 111903, 111905, and 111907) showed a marked hydrogen concentration effect (unlike the tests using Shell 324M). An increase of 1.1% hydrogen was noted for the sample produced at 1000 psig hydrogen. Although good hydrogenation activity is typical of noble metal catalysts, it is notable that this high activity was achieved after two days of operation with a rather dirty feed. The good performance after two days suggests that Pt HTO catalysts may not deactivate as rapidly as the Shell 324M catalyst at these conditions and may be a good candidate for other upgrading applications.

Coated HTO Nickel Molybdenum Catalyst Testing

Experiments with coated HTO catalysts used -5°C dewaxed solvent from CONSOL in the microflow trickle-bed reactor. The catalyst used in these tests was a hydrous titanium oxide coated onto an alumina substrate. It contained 2.7 wt% nickel and 8.1 wt% molybdenum. The catalyst was used as -10+20 mesh size and was packed in the 0.4" I.D. reactor tube.

The catalyst bed was sulfided at 390°C for four hours with a 9% H_2S in hydrogen mixture. Testing was performed at LHSVs of 0.4 hr^{-1} or 1.1 hr^{-1}. These LHSV values are slightly higher for this catalyst than for the Shell 324M tests because the packing density was approximately 72% as large as that for the Shell 324M tests. Carbon and hydrogen contents of the starting and hydrogenated solvents are shown in Table 10.

Table 10. Carbon and Hydrogen Contents of Solvent (-5°C dewaxed solvent, NiMo HTO catalyst coated on alumina)

Sample	LHSV (hr^{-1})	Temperature (°C)	Carbon (wt%)	Hydrogen (wt%)
-5°C Dewaxed V1074	NA*	NA	89.1	8.5
121503	0.37	300	90.4	9.4
121504	0.41	300	89.9	9.6
121603	0.42	325	90.4	9.6
121604	0.96	325	90.5	9.0
121802**	1.0	325	89.8	9.3 (1000 psig)
121804**	1.0	325	90.5	8.9 (670 psig)
121806**	1.1	325	90.5	9.1 (330 psig)

* Not Applicable

** Hydrogen only for these experiments

Hydrogen content of the dewaxed feed was increased from 8.5 wt% to 9.6 wt% for the -5°C dewaxed solvent hydrotreated with an LHSV of about 0.4 hr^{-1}. At an LHSV of 1.0 hr^{-1}, the maximum hydrogen content increase was 0.8 wt%. Gas samples taken during this combined water-gas shift solvent hydrogenation experiment showed that CO conversions were 95% at 300°C. Samples 121802, 121804, and 121806 were taken on the third day of operation and were hydrotreated with hydrogen as the sole gas reactant to test the effect of hydrogen partial pressure. Results show there was no apparent hydrogen concentration effect.

Bulk NiMo HTO Tests

Solvent pretreatment reactions were performed with a bulk NiMo HTO (9.8 wt% molybdenum and 3.2 wt% nickel) catalyst to hydrogenate -5°C dewaxed V1074 heavy distillate (Table 11). At 300°C, the maximum hydrogen increase was 1.1 wt%, which was higher than obtained with Shell 324M. Hydrotreating took place in a series of experiments performed over three days. The third day was used to test the effects of using hydrogen instead of the water-gas shift reaction for hydrogenation. Therefore, the gas phase of the reactor was changed to 1000 psig H_2 only. After testing was completed with just hydrogen, the gas phase was changed to 330 psig H_2. The system pressure was kept at 1000 psig; nitrogen was added to adjust the hydrogen partial pressure.

Proton NMR characterization of products indicated that hydrogenation with the water-gas shift reaction resulted in decreased condensed aromatic protons and increased cyclic α and cyclic β protons. Samples 020302 and 020303 (first day of reaction) were hydrogenated at 300°C using the water-gas shift reaction. These samples showed that the condensed

aromatic concentration was reduced from 16% to 7.7% and 9.5% respectively. Samples 020403, 020405, and 020407 (second day of reaction) were hydrogenated at 325°C. These samples show an increase in hydrogen content of about 0.5 wt% and a decrease in condensed aromatic hydrogens from 16% to about 12%. The second day samples showed that the catalyst had deactivated somewhat compared to the first day. Hydroaromatic hydrogen concentration (cyclic α + cyclic β) increased from 36% to near 40% for most of the samples.

Table 11. Carbon and Hydrogen Content of Feed and Hydrogenated Solvent Using a Bulk NiMo HTO Catalyst

Sample	LHSV (hr^{-1})	Temperature (°C)	Carbon (wt%)	Hydrogen (wt%)
-5°C Dewaxed V1074	NA	NA	89.1	8.5
020302	0.28	300	89.0	9.6
020303	0.27	300	88.7	9.2
020403	0.38	325	88.9	9.1
020405	0.72	325	88.9	9.1
020407	0.78	325	87.8	8.8
020502*	0.75	325	88.4	8.9
020506**	0.72	325	89.2	8.3

* 1000 psig hydrogen only

** 330 psig hydrogen plus 670 psig nitrogen

Catalyst Deactivation

The solvent pretreatment reactor is a fixed-bed reactor consisting of two 0.4" I.D. tubes that are packed with catalyst and connected in series by a short 0.125" O.D. connecting tube. The two-reactor configuration is necessary to achieve the desired LHSVs for the liquid feed. Post-test carbon content was measured for catalyst at the feed end of reactor tube one as well as the exit ends of reactor tubes one and two. Table 12 shows the carbon contents of the catalysts that were removed from the trickle-bed reactor after the three days of reaction. All catalysts were washed with copious amounts of tetrahydrofuran before carbon contents were determined.

Table 12. Carbon contents (wt%) of used catalysts

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

Results in Table 12 show that the more aromatic dewaxed feeds deposited more carbon on the alumina supported Shell 324M than did the more paraffinic V1074. This is to be expected since the more aromatic feeds have higher concentrations of coke forming compounds. The used NiMo coated HTO catalyst's carbon contents were similar to the Shell 324M post-test carbon contents for the -5°C dewaxed feed. This is not surprising since both catalysts have alumina supports, which are acidic and would yield carbon deposition under these conditions. The Pt catalyst, however, had a relatively low amount of carbon possibly because of the less acidic bulk HTO support. This may be an important consideration in long term catalyst testing.

Catalyst deactivation can also be measured using a model compound hydrogenation test on the used catalyst [5]. Table 13 presents results from pyrene hydrogenation tests with fresh presulfided NiMo coated HTO catalyst and the aged catalyst and the fresh and aged bulk Pt HTO catalyst. Results from these tests show that both the NiMo coated HTO and the Pt HTO showed catalyst deactivation. Residual activity on the Pt HTO is slightly better than the NiMo coated HTO, although the initial Pt HTO activity was higher ($k=0.26$ sec^{-1} for Pt HTO and $k=0.19$ sec^{-1} for the NiMo coated HTO). Carbon contents of the Shell 324M commercial alumina supported catalyst (see Table 12) were high indicating that residual hydrogenation activity may be very low in these catalysts as well.

Table 13. Pyrene hydrogenation results for fresh and used catalysts

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

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

Conclusions

Results from catalyst screening experiments using heavy distillate solvents and the water-gas shift reaction at low temperatures (300-325°C) with NiMo catalysts showed that the V1074 and dewaxed V1074 heavy distillate solvents picked up between 0.8 and 1.1 wt % hydrogen while the catalyst was still fresh. This value dropped to approximately 0.3 to 0.5 wt% hydrogen uptake after the catalyst was aged for one day. The platinum catalyst gave a hydrogen uptake of about 0.4 to 0.5 wt% during the first two days of reaction with the water-gas shift reaction. On the third day with the use of 1000 psig hydrogen only, the hydrogen uptake was 1.1 wt%. The platinum catalyst showed a significant hydrogen concentration effect that was not observed with the NiMo catalysts. In addition, both the NiMo and platinum catalysts showed extensive catalyst activity losses when measured with a pyrene screening test. The lower catalyst activity was somewhat compensated for when the gas

phase was switched to hydrogen only and when the reaction temperature was raised from 300°C to 325°C. These results show a kinetic rather than a thermodynamic limitation on the solvent hydrogenation reaction. For these reasons, subsequent testing used somewhat higher temperatures and only hydrogen as the gas phase to enhance the hydrogenation of aromatics to hydroaromatics in the heavy distillate solvent.

Section B.2 Hydrogen Only - Higher Temperature Hydrogenation

Background

In addition to the comments in the conclusions section of B.1, analysis by LDP Associates showed that the overall hydrogen requirements by the liquefaction plant would necessitate purified high pressure hydrogen in the second stage of the process (assuming that only half of the hydrogen needed for liquefaction (about 3 wt%) could be transferred in the first stage). This requirement would not allow the in situ water-gas shift reaction to displace the separate water-gas shift reactor and attendant purification train from the overall process. Therefore hydrogen was selected as the reductant for the following tests. Figures 6 and 7 show chromatograms of representative samples of feed and hydrotreated product from the higher temperature hydrogenations.

Results and Discussion

Analysis of Hydrotreating Run Using -35°C Dewaxed V1074

Proton NMR spectroscopy was used to evaluate the -35°C dewaxed heavy distillate samples that were hydrotreated at 360°C with the trickle-bed reactor packed with Shell 324M catalyst. Proton assignments were the same as those prescribed by CONSOL [6]. Table 14 presents the results from proton NMR spectroscopy along with analytical and process data from the run. The samples were hydrotreated at different LHSVs to evaluate the effects of increasing flow on the degree of hydrogenation. Increasing liquid flow would allow the process to utilize smaller or fewer hydrotreating reactors for the proposed solvent hydrogenation step in the Advanced Concepts Program.

Table 14. Proton NMR Results for -35°C Dewaxed V1074 Hydrotreated with Shell 324M, at 360°C, 1300 psig H_2

Sample	LHSV* (hr^{-1})	% H	Cond. Arom.	Uncond. Arom.	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
V1074	NA**	9.9	11.3	3.6	14.7	7.6	15.8	34.6	12.3
Dewaxed V1074	NA	8.1	17.3	6.2	20	10.3	17.1	17.9	11.2
090303	0.7	9.3	9.9	6.8	17.2	9.7	21.5	20.6	14.3
090304	0.9	ND**	8.3	5.7	17.0	10.0	20.4	23.0	15.5
090307	1.1	9.0	12.8	5.0	18.8	10.1	21.7	19.6	12.0
090308	1.1	ND	11.9	6.9	18.4	10.6	21.0	18.9	12.2

* Assume density for packed catalyst = 0.86 g/cm^3 and feed = 1.10 g/cm^3.

** NA = Not Applicable, ND = Not Determined.

The trickle-bed reactor system pressure was maintained at 1300 psig H_2 during the reaction. Liquid samples were taken at one hour intervals. Results of proton NMR analyses, displayed in Table 14, show that the level of paraffinic hydrogen (alkyl α, alkyl β and γ) was higher at the lower space velocities (44.6% at LHSV=0.7 hr^{-1}, 41.7% at LHSV=1.1 hr^{-1}). This could be due to hydrocracking of solvent at the lower LHSV. The level of hydroaromatic hydrogen was relatively unchanged when the LHSV was increased to 1.1 hr^{-1} from 0.7 hr^{-1}. This indicates that there appears to be no penalty to increasing space velocity from ~0.7 to 1.1 hr^{-1} under these conditions (360°C, 1300 psig), at least as far as the proton distributions are concerned. Samples produced at the higher LHSV also have somewhat lower overall hydrogen contents. Analyses of two samples (090303 and 090307) indicate that hydrogen content increased 1.2% and 0.9%, respectively. Overall these hydrogenated samples were very effectively hydrogenated at 360°C. Samples 090303 and 090307 were sent to CONSOL for microautoclave testing.

Gas Analyses of Test Using -35°C Dewaxed V1074

Hydrogenation at 360°C is favored thermodynamically over hydrogenation at 400°C since higher equilibrium concentrations of hydroaromatic compounds are favored at the lower temperature for any given hydrogen pressure. Another reason for using milder hydrogenation temperatures is to avoid temperatures at which the solvent can be hydrocracked. Previous hydrotreating tests with the trickle-bed reactor did not include measurement of the effluent gases. Such analyses would indicate the amount of hydrocarbon gases produced during the reaction and also help to estimate hydrogen consumption by gas forming reactions. Hydrogenation testing of -35°C dewaxed V1074 at 360°C is reported in Table 14 and analyses for the effluent gases from this test and a similar test at 320°C are presented in Table 15. The hydrogen treatment rate for these experiments was 330 sccm H_2/cm^3 liquid (1850 scf/Bbl). Hydrocarbon gases account for less than 0.3 vol% of the gases in the effluent at 360°C and less than 0.1 vol% at 320°C. Therefore hydrogen consumption due to hydrocarbon gas formation is approximately 0.4% of the feed hydrogen (total hydrocarbon hydrogen/feed hydrogen) at 360°C.

Table 15. Gas Analyses of Trickle-Bed Hydrogenation Reactor Products for Hydrotreating -35°C Dewaxed V1074 (Effluent Stream)

	H_2*	CH_4	C_2H_6	C_3H_8
Temp 320°C				
Volume (%)	99.90	0.059	0.025	0.014
sccm**	NA***	0.081	0.034	0.019
Temp 360°C				
Volume %	99.71	0.163	0.080	0.050
sccm**	137	0.222	0.110	0.068

* Hydrogen by difference.

** Hydrogen feed to the reactor was 165 sccm (GHSV= 430 hr^{-1} assuming 23 cm^3 reactor volume).

*** NA = not analyzed.

The hydrogen flow rate at 360°C was measured to be 165 sccm in the feed and 137 sccm in the product gases. The difference in measured gas flow rate indicates a hydrogen consumption of 28 sccm, or 1.25 millimoles of hydrogen per minute (2.52 mg H/min). This gas measurement was made when the liquid flow rate was 0.5 g/min. Therefore, the hydrogen consumption was 28 sccm/0.45 cm^3 of feed or 62 sccm/cm^3 (460 scf/Bbl), which is approximately 0.5 wt% hydrogen on a liquid feed basis. The liquid elemental analyses showed approximately 0.6 wt% increase in hydrogen for this period. The gas data are in general agreement with the hydrogen content of the liquids.

Preparative Hydrotreating Run Using V1074

In preparation for the solvent hydrotreating experiments with the dewaxed materials in the Process Simulation Testing (PST, see Section B.3), a run was made with Wilsonville run 262E V1074 heavy distillate (sample 1621-22-5) and Shell 324M catalyst. Table 16 displays the hydrotreating conditions and product analyses for the V1074 hydrotreating experiments. Two temperatures were used for these experiments, 367°C and 384°C. In general, the aromatic hydrogen content decreases and the percentage of γ protons increases with hydrotreating. Sample 122307, taken at 384°C, shows a significant increase in cyclic α protons and a marked decrease in alkyl β protons. It is possible that hydrocracking reactions at 384°C are contributing to this. This run used a higher hydrogen gas treatment rate than the previous tests. Previous tests with heavy distillate samples used hydrogen treatment rates of 330 sccm H_2/cm^3 liquid (1850 scf/Bbl). These tests used hydrogen treatment rates of 600 sccm/cm^3 liquid (3350 scf/Bbl). Overall, the hydrotreated samples showed extensive hydrogenation and indicate that a nominal starting point for the PST could be the following: LHSV = 1 hr^{-1}, temperature ≈ 365°C, hydrogen pressure ≈ 1400 psig and a hydrogen gas treatment rate > 3000 scf/Bbl.

Table 16. Proton NMR Results for V1074 Heavy Distillate Hydrotreated with Shell 324M

Sample	LHSV* (hr^{-1})	Temp. (°C)	Cond. Arom.	Uncond. Arom.	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
V1074	NA**	NA	11.3	3.6	14.7	7.6	15.8	34.6	12.3
122205	1.2	367	3.2	2.4	15.6	7.8	17.6	36.1	17.4
122303	1.3	367	3.8	0.8	13.5	7.4	17.3	38.9	18.3
122307	1.4	384	2.9	3.8	20.0	8.5	16.9	30.7	17.2

* Assume density : packed catalyst = 0.86 g/cm^3; feed = 1.0 g/cm^3.

** Not Applicable

Gas Analyses of Test Using V1074

Table 17 shows the gas analysis of the effluent stream from the trickle-bed reactor. As was noted for the previous hydrotreating run, very little hydrocarbon gas formation takes place at these conditions. Approximately 0.2% of the feed hydrogen was consumed to form hydrocarbon gas. The hydrogen flow rate was 332 sccm in the feed and 288 sccm and 305 sccm in the effluent at 367°C and 384°C respectively. The hydrogen consumption measured at 367°C was 44 sccm at a liquid flow rate of 0.41 cm^3/min or 107 sccm/cm^3 (605 scf/Bbl). The hydrogen consumption for the 384°C test was 27 sccm at a liquid flow rate of 0.51

cm^3/min or 53 sccm/cm^3 (297 scf/Bbl). The rather large differences in hydrogen consumption are caused in part by catalyst deactivation (the catalyst for the 367°C tests was on stream for approximately 3 hours compared to approximately 12 hours for the 384°C test. In addition, hydrogen consumption at 384°C (sample 122307) was lower, because the LHSV was higher for this sample and the equilibrium constant for aromatic hydrogenation is smaller at higher temperatures.

Table 17. Gas Analyses of Trickle-Bed Hydrogenation Reactor Products for Hydrotreating V1074 Heavy Distillate (Effluent Stream)

	H_2*	CH_4	C_2H_6	C_3H_8
Temp 367°C				
Volume %	99.87	0.068	0.037	0.025
sccm**	288	0.185	0.100	0.068
Temp 384°C				
Volume %	99.77	0.115	0.070	0.049
sccm**	305	0.351	0.214	0.149

* Hydrogen by difference.

** Hydrogen feed to the reactor was 332 sccm (GHSV= 860 hr^{-1} assuming 23cm^3 reactor volume).

Conclusions

The -35°C dewaxed V1074 was hydrotreated at different LHSVs to evaluate the effects of increasing flow on hydrogenation at a higher temperature of 360°C. Results of proton NMR analyses show that the paraffinic hydrogen was higher at the lower space velocities, which could be due to hydrocracking of the solvent. Based on proton NMR analyses, there was no apparent penalty for increasing the space velocity from 0.7 to 1.1 hr^{-1}. However, samples obtained at the higher space velocities showed somewhat lower hydrogen contents. Samples from this experiment were sent to CONSOL for microautoclave testing. Analyses showed that hydrocarbon gases accounted for less than 0.3 vol% of the effluent gases, and hydrogen consumption due to hydrocarbon gas formation was about 0.4% of the feed hydrogen. At a liquid flow rate of 0.5 g/min, the hydrogen consumption was 460 scf/Bbl or about 0.5 wt% hydrogen on a liquid feed basis, which is close to the elemental analysis result of 0.6 wt%.

A trickle-bed hydrotreating experiment was done with V1074, Shell 324M, LHSVs from 1.2 to 1.4 hr^{-1}, and temperatures of 367°C and 384°C to identify a nominal starting point for future PST runs. Proton NMR analyses suggested that some hydrocracking may have occurred at the higher temperature. The hydrogen consumption at 367°C with a flow rate of 0.41 cm^3/min was 605 scf/Bbl, whereas the hydrogen consumption at 384°C with a flow rate of 0.51 cm^3/min was 297 scf/Bbl. About 0.2 vol% of the feed hydrogen was consumed to form hydrocarbon gases at 367°C. The hydrotreated samples showed extensive hydrogenation and indicate that a good starting point for Process Simulation Testing could be as follows:

LHSV = 1 hr^{-1}, temperature = 365°C, hydrogen pressure about 1400 psig, and a hydrogen gas treatment rate > 3000 scf/Bbl.

Section B.3 Process Simulation Testing (PST)

Background

PST is designed to use the most favorable process improvements from the Advanced Concepts Program and integrate them in an experimental plan that will use the products from one operation as feed for a subsequent step. A large-scale dewaxing (1000g) test performed at -5°C produced feeds from V1074 for hydrotreating experiments at Sandia. These included two dewaxed materials: a fully dewaxed sample (1621-22-5I) and a 25% dewaxed slipstream sample (1621-22-5K). Dewaxing the recycle stream is expensive in regard to both energy and capital costs. An analysis of the technical and economic factors associated with dewaxing was performed by CONSOL and LDP Associates. Results suggested that using 25% dewaxing was attractive because capital and processing costs could be decreased without much loss of the benefits of dewaxing. Therefore, a 25% dewaxed sample was evaluated along with the 100% dewaxed sample. Two trickle-bed hydrotreating runs were made with these PST samples and the products were used for the oil agglomeration and coal liquefaction testing at CAER and CONSOL.

Hydrotreating of PST Samples

Experimental conditions were closely controlled and duplicated for the two experiments. The reactors consisted of four packed bed tubes connected in series and fastened in a convectively heated oven. Each of the four reactors is 6.6 inches long with a 0.4 inch internal diameter. Sulfided Shell 324M catalyst at a -10+40 mesh size was used. LHSV was maintained at 1.0 to 1.1 hr^{-1}. Both experiments used hydrogen gas treatment rates of 3800 scf/Bbl. Table 18 presents the process conditions and elemental analyses for the products from the two PST hydrotreating runs. Table 19 lists the proton NMR results for the feeds and hydrogenated distillates from the PST runs. The hydrotreated fully dewaxed sample (1621-22-5I) showed a decrease in aromatic hydrogen content from 19.8% to 17.1% with a gain in cyclic β protons of 0.7%. This sample showed a 0.32 wt% hydrogen increase. The hydrotreated 25% dewaxed slipstream sample (1621-22-5K HYD) showed a decrease in aromatic hydrogen content from 18% to 14.9% with a gain in cyclic β protons of 1.2%. This sample showed a 0.21 wt% hydrogen increase. Overall the hydrogen increases in the two hydrotreated distillate samples are lower than expected.

Table 20 shows the results of the gas analyses from the hydrotreating tests. As previously shown, the hydrogen consumption due to hydrocarbon gas formation was less than 0.3 vol% of the total feed hydrogen (total hydrocarbon hydrogen/feed hydrogen). The hydrogen gas treat rate was 3800 scf/Bbl and the hydrogen consumption was 420 scf/Bbl and 290 scf/Bbl for tests with 1621-22-5I and 1621-22-5K respectively. On a weight basis, the hydrogen consumption was approximately 0.6% and 0.44% for the 1621-22-5I and 1621-22-5K samples respectively. The consumption on a weight basis is the weight of hydrogen consumed divided by the weight of liquid processed in a given time. It would appear that the hydrogen treat rate is eight to ten times the consumption for these tests.

Table 18. Elemental analyses for PST Samples

SAMPLE	LHSV* (hr^{-1})	%C	%H*	%N	%S	%O (diff)
1621-22-5I	NA**	89.53	9.09	0.49	0.03	0.86
1621-22-5I HYD	1.07	89.96	9.41	0.40	0.01	0.22
1621-22-5K	NA	89.68	9.53	0.46	0.03	0.30
1621-22-5K HYD	1.09	89.23	9.74	0.37	0.01	0.65

* Assume feed density is 1.035 g/cc for 1621-22-5I, 1.02 g/cc for 1621-22-5K, packed catalyst density is 0.86 g/cc.

** Not Applicable

Table 19. Proton NMR Analyses of PST Distillate Samples

Sample	% H	Cond. Arom.	Uncond. Arom.	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
1621-22-5I	9.09	15.0	4.8	18.5	8.5	18.4	23.1	11.8
1621-22-5I Hyd	9.41	11.9	5.2	17.8	8.6	19.1	24.1	13.2
1621-22-5K	9.53	14.1	3.9	17.2	7.6	17.3	28.1	11.9
1621-22-5K Hyd	9.74	10.2	4.7	17.5	8.1	18.5	27.7	13.3

Table 20. Gas Analyses of Trickle-bed Hydrogenation Reactor Products (Effluent Stream)

	H_2	CH_4	C_2H_6	C_3H_8
Sample 1621-22-5I				
Volume %	99.83	0.073	0.038	0.054
sccm*	566	0.413	0.215	0.306
Sample 1621-22-5K				
Volume %	99.77	0.068	0.037	0.037
sccm*	588	0.400	0.217	0.217

* Hydrogen feed to the reactor was 635 sccm.

Coal Liquefaction Tests with PST Distillates

Table 21 gives the results from coal liquefaction batch microautoclave tests using the original Process Simulation Test (PST) distillate samples and the distillates hydrotreated at Sandia. These experiments were performed using both 1:1 and 2:1 solvent to coal ratios, at 400°C, with nitrogen overpressure. Table 21 also includes experiments performed under the same conditions with the original Wilsonville run 262E V1074 heavy distillate (1621-22-5) and hydrotreated V1074. Although the coal conversions are low, owing to the mild liquefaction conditions, the yields of liquefaction products illustrate the benefit of

hydrotreating. The pentane soluble oil yield was negative for all the tests using unhydrogenated samples and for the tests with hydrotreated V1074. The hydrotreated dewaxed solvent and the hydrotreated slipstream solvent gave slightly positive pentane soluble oil yields. The negative oil yield numbers indicate possible solvent adduction due to insufficient solvent hydrogen for oil formation. This is consistent with the observation by CONSOL that hydrogenating the distillate portion of the recycle solvent leads to increased conversion of coal to THF soluble material that boils above ~1050°F. The pentane insoluble material was weighed and a subsample was dissolved in pyridine to be evaluated for molecular weight with a vapor pressure osmometer.

Table 21. Coal Liquefaction Results for PST Samples. (Black Thunder Coal, 400°C, 30 min., N_2)

Solvent	H(%) (dist)*	Solv/ Coal	IOM (%)	PA+A** (%)	Oil (%)	Gas (%)	Conv. (%)***	M_n**** (PA+A)
Dewaxed[a]	9.09	1:1	41.9	69.3	-16.2	5.0	58.1	600
Dewaxed	9.09	2:1	31.2	76.8	-12.9	4.9	68.8	460
Dewaxed Hyd[b]	9.41	1:1	36.0	57.7	1.3	5.0	64.0	600
Dewaxed Hyd	9.41	2:1	31.9	62.8	0.1	5.2	68.1	450
Slipstream[c]	9.53	1:1	44.3	60.0	-9.2	4.9	55.7	600
Slipstream	9.53	2:1	34.9	80.9	-20.8	5.0	65.1	470
Slipstream Hyd[d]	9.74	1:1	39.5	53.0	2.6	4.9	60.5	600
Slipstream Hyd	9.74	2:1	35.8	57.9	1.4	4.9	64.2	460
V1074	9.79	1:1	57.5	47.5	-13.1	8.1	42.5	610
V1074	9.79	2:1	45.1	65.7	-18.0	7.1	54.9	480
V1074 Hyd	10.20	1:1	52.8	42.7	-1.6	6.1	47.2	620
V1074 Hyd	10.20	2:1	43.4	51.2	-1.0	6.4	56.6	480

* Percent hydrogen in reaction solvent.
** Preasphaltenes & Asphaltenes
*** %Conversion = 100 - %IOM
**** Number average molecular weight

a Fully dewaxed V1074 (1621-22-5I)
b Hydrogenated 1621-22-5I
c 25% dewaxed V1074 (1621-22-5K)
d Hydrogenated 1621-22-5K

Vapor Pressure Osmometer Results of Pentane Insoluble Material

A Knauer vapor pressure osmometer was used to estimate the molecular weights of the pentane insoluble materials (often referred to as preasphaltenes plus asphaltenes, PA+A) from the donor solvent tests described in Table 21. Pyridine was used as the solvent. The analysis temperature was 60°C, and pyrene (MW = 202) was used for a four point calibration. The number average molecular weights (M_n) are reported in the last column of Table 21. Results from the liquefaction tests indicate that pentane insoluble materials from the liquefaction tests using a 2:1 solvent to coal ratio have a M_n of approximately 450-480 g/mol. The pentane insoluble material from the liquefaction tests performed with solvent to coal ratios of 1:1 have a M_n of approximately 600-620 g/mol. The decreased molecular weight of the PA+A fractions for the 2:1 solvent to coal tests indicates that these materials could have incorporated more of the lower molecular weight solvent into them during

liquefaction. It does not appear that the increased yields of PA+A in tests that used unhydrogenated solvent necessarily correlates with a higher molecular weight asphaltene since the molecular weight of the PA+A produced from hydrotreated solvents is nearly the same as that produced with the unhydrotreated solvent. However, the PA+A samples from the unhydrogenated tests are noticeably darker in color and are somewhat glassy in texture (especially at solvent to coal ratios of 1:1). Further characterization by field ionization mass spectrometry could possibly help interpretation of these results.

Experiments using solvent to coal ratios of 2:1 gave higher conversions than similar experiments using solvent to coal ratios of 1:1. In all tests, the more aromatic fully dewaxed solvent (1621-22-5I) gave improved conversions over similar experiments using the slipstream sample (1621-22-5K). This was true irrespective of whether the solvent was the hydrogenated or the unhydrogenated type.

Catalyst Sulfiding for PST Testing

Elemental analyses of the catalysts from the PST trickle-bed reactor solvent hydrogenation experiments included nitrogen and carbon analyses to determine the effects of the distillate upon coke formation and catalyst deactivation. Sulfur contents of the used catalysts have not usually been measured since it was assumed that complete sulfidation had occurred in the catalyst pretreatment step (based on gas flow measurements). However, sulfur analyses were performed on the used catalysts from the PST experiments to determine catalyst activity relative to sulfur content.

Four reactor tubes were connected in series for each of the PST runs. Three catalyst samples were removed from the reactor tubes and analyzed for carbon, nitrogen and sulfur content. Table 22 shows the bed position for each analyzed sample and the carbon, nitrogen and sulfur contents of the used catalysts. Although the carbon and nitrogen contents of the catalyst samples showed only small differences, the sulfur contents of the samples varied significantly. Results in Table 22 indicate that sulfur content of the catalyst decreased dramatically from the top of the first reactor tube to the middle of the first reactor tube. It is clear that the catalyst beds were insufficiently sulfided. This would have contributed to only obtaining the moderate (0.2-0.3 wt%) hydrogen increase observed for the PST product distillates. The source of the insufficient sulfiding was found to be a defective gas mass flow meter, which was replaced for subsequent trickle-bed reactor tests.

Since the PST samples were produced using an inadequately sulfided catalyst bed, batch hydrotreating experiments were performed with fully sulfided catalysts to show the practical upper limit of hydrogen increase for the dewaxed heavy distillate. (See Section B.4 for results of using batch microautoclave tests to determine the maximum hydrogen uptake for these feeds).

Table 22. Post Reaction Catalyst Analysis for Hydrotreating Tests

PST Feed	Bed Position	% Carbon	Nitrogen (ppm)	% Sulfur*
1621-22-5I	Reactor 1 (top)	7.1	2620	5.0
1621-22-5I	Reactor 1 (mid)	7.0	3200	2.4
1621-22-5I	Reactor 4 (bot)	6.6	3460	0.1
1621-22-5K	Reactor 1 (top)	7.2	2670	5.3
1621-22-5K	Reactor 1 (mid)	7.1	3500	2.0
1621-22-5K	Reactor 4 (bot)	6.7	3420	0.1

* Completely sulfided Shell 324M should have ~8 wt% sulfur.

Conclusions

CONSOL produced large batches of dewaxed materials for hydrotreating experiments at Sandia. This included fully dewaxed solvent and a 25% dewaxed slipstream solvent. These solvents were each hydrotreated in trickle-bed reactor runs with Shell 324M catalyst. Characterization of the reaction products showed that the increases in hydrogen contents were very low: 0.32 wt% for the fully dewaxed material and 0.21 wt% for the 25% dewaxed material. Subsequent analyses of the catalysts used in these reactions showed that the sulfur contents at the top of the first catalyst bed for each run were about 5 wt% and in the middle of the first bed for each run the sulfur contents were about 2.2 wt%. Catalyst from the bottom of the fourth reactor bed for each run only had 0.1 wt% sulfur. These results show that the catalyst was not adequately sulfided. This would have contributed to the low increases in hydrogen contents observed in the hydrotreated products.

Section B.4 Batch Hydrogenation Test to Evaluate Maximum Hydrogen Uptake

Background

Previous hydrogenation tests show that the maximum uptake of hydrogen by the heavy distillate is about 1wt %. Temperatures from 300 to 385°C have been tested with the trickle-bed reactor. Due to catalyst aging and the complex nature of the trickle-bed reactor, it was decided that batch hydrogenation tests would be a simpler way to evaluate the maximum hydrogen uptake of the heavy distillate solvents. Therefore, batch hydrogenation tests were performed with dewaxed heavy distillate. Table 23 presents the results of batch hydrogenation experiments using the -5°C dewaxed heavy distillate (1621-22-5I). Results in Table 23 show that the maximum hydrogen increase was obtained for the sample that was hydrotreated at 396°C. This sample had a 0.9 wt% increase in hydrogen as compared to the starting -5°C dewaxed heavy distillate. Proton NMR results show decreases in aromatic protons with hydrotreatment at 355°C, 372°C, and 396°C. Proton NMR results and elemental hydrogen content of the sample hydrogenated at 421°C indicated that this sample was poorly hydrogenated showing relatively high aromaticity and low hydrogen uptake. This observation is consistent with model compound experiments that show the reverse (dehydrogenation) reaction becomes more favored with increasing temperature at a given

hydrogen pressure. In any event, the optimum temperature for hydrogenation for the batch hydrogenation experiments is around 400°C.

Table 23. Batch Hydrotreating of -5°C Dewaxed Heavy Distillate (1621-22-5I), 1400 psig H_2, 60 minutes, Solvent : Catalyst = 2:1.

Temp	%H	Cond. Arom.	Uncond. Arom.	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
Feed	9.1	15.0	4.8	18.5	8.5	18.4	23.1	11.8
355°C	9.2	11.7	4.8	19.3	8.7	20.3	23.4	11.7
372°C	9.8	12.0	4.6	18.7	8.5	20.5	23.6	11.9
396°C	10.0	13.3	4.5	18.4	8.2	20.0	23.6	12.0
421°C	9.2	15.5	4.5	18.7	8.1	19.0	22.9	11.3

Four preparatory runs were performed at ~396°C to generate enough material for testing at CONSOL. The runs were 60 minutes long, with a solvent to catalyst ratio of 3:1, and the initial hydrogen pressure was 1400 psig. Hydrogen consumption from the preparatory runs indicated that the solvent should have picked up approximately 0.9 wt% hydrogen. Elemental analyses indicated an increase from 9.1 wt% (for the 1621-22-5I) to 9.7 wt% for the hydrotreated material. Approximately 20g of this sample was shipped to CONSOL to be tested and compared to the PST samples.

Conclusions

Batch microautoclave experiments were performed to identify conditions that give the maximum hydrogen uptake for the -5°C fully dewaxed V1074 solvent. Hydrotreating temperatures ranged from 355°C to 421°C. Results show that the maximum uptake (0.9 wt%) was obtained for the sample hydrotreated at 396°C. Proton NMR results showed that this product as well as those produced at lower temperatures had decreased amounts of aromatic protons, whereas product from the 421°C reaction was poorly hydrogenated. Based on these results, four reactions were performed to generate material for additional testing. Elemental analysis of the product from these reactions showed a 0.6 wt% hydrogen increase. A sample was sent to CONSOL to be tested and compared to the previous PST samples.

Section B.5 Distillation Pretreatment and Batch Testing

Background

Much discussion on the nature of donor solvents has involved the concentration and accumulation or depletion of aromatic molecules in recycle solvents. This work used preliminary tests to evaluate the concept of staging the ROSE unit at Wilsonville to produce a recycle solvent enriched with donor precursors. To test the effects of the recycle distillation cutpoint upon donor solvent quality, CONSOL performed a distillation on run 262E heavy distillate (V1074). The products from the distillation were split and portions of the light (-833°F cut) and heavy (+833°F cut) distillate were dewaxed in 45/55 (vol%)

MEK/Acetone at -35°C. The distillations were done to supply Sandia with light and heavy distillate solvents for hydrogenation with a supported catalyst in microautoclave tests. Table 24 gives a description of the samples. The dewaxed oil yields from the dewaxing process were 84.5% and 82.5% for the light fraction and the heavy fraction respectively.

Table 24. Run 262E V1074 Distillation Samples from CONSOL

Sample	Wt% on distillation	Sample Description
1621-22-5G	46.1	Light distillate from V1074 distillation
1621-22-5H	53.4	Heavy distillate from V1074 distillation
1621-22-5G-1	NA*	Dewaxed (1621-22-5G) light distillate
1621-22-5H-1	NA	Dewaxed (1621-22-5H) heavy distillate

* Not Applicable

Experimental Results

Each of six samples (original V1074, each of the two distillate fractions, and each of the dewaxed materials from these three samples) was hydrogenated in batch microautoclaves using 1400 psig hydrogen for 60 minutes. Proton NMR results for the original and hydrotreated nondewaxed solvents are shown in Table 25. Column two of Table 25 shows the hydrotreating temperature used with the listed samples. Initial tests at two temperatures (325°C and 375°C) with the whole V1074 indicated more extensive hydrogenation at 375°C. For this reason the distillation samples were hydrotreated only at 375°C. In general, the light distillate (1621-22-5G) had a lower initial aromatic hydrogen concentration than the original V1074, and hydrogenation increased its cyclic α and β hydrogen content from 29.7% to 31.4%. The heavy distillate (1621-22-5H) had a higher initial aromatic hydrogen content than the original V1074, and hydrogenation increased its cyclic α and β protons from 31% to 34.7%.

Table 25. Proton NMR Results for Original and Batch Hydrotreated, Nondewaxed Distillation Products, 1400 psig H_2

Sample	Hyd. Temp (°C)	Cond. Arom.	Uncond. Arom.	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
V1074	Feed	11.3	3.6	14.7	7.6	15.8	34.6	12.3
V1074	325	9.2	2.9	14.8	7.0	17.2	36.0	12.8
V1074	375	8.4	3.4	14.0	6.7	18.3	36.0	13.2
1621-22-5G	Feed	9.4	2.6	13.0	6.6	16.7	37.4	14.3
1621-22-5G	375	8.4	2.8	13.2	6.4	18.2	36.9	14.1
1621-22-5H	Feed	13.1	2.7	15.0	6.7	16.0	34.6	11.9
1621-22-5H	375	10.2	3.1	16.9	7.2	17.8	33.5	11.3

Results from proton NMR spectroscopy analysis of the dewaxed V1074 and the dewaxed distillate cuts from the V1074 are shown in Table 26. The dewaxed light distillate (1621-22-

5G-1) had a lower initial aromaticity (before hydrotreating) than the dewaxed V1074 and therefore had a lower hydroaromatics content after hydrotreating. Hydrogenation increased the cyclic α and β hydrogen content from 35.9% to 37.1%. Hydrotreating the dewaxed V1074 heavy distillate fraction (1621-22-5H-1) increased the cyclic α and β hydrogen content from 38.3% to 42.5%.

Table 26. Proton NMR Results for Hydrotreated Products. (Feeds = Dewaxed V1074, Dewaxed Light Distillate Fraction, Dewaxed Heavy Distillate Fraction, 1400 psig H_2)

Sample	Hyd. Temp. (°C)	Cond. Arom.	Uncond. Arom.	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
-35°C Dewax	Feed	15.3	3.5	18.8	8.3	19.0	23.2	11.8
-35°C Dewax	325	12.8	3.6	19.4	8.8	19.8	23.4	12.2
-35°C Dewax	375	10.3	3.9	18.6	8.8	21.3	24.3	12.8
1621-22-5G-1	Feed	13.2	3.0	16.6	8.4	19.3	25.5	14.1
1621-22-5G-1	375	10.8	4.0	16.7	8.2	20.4	25.8	14.2
1621-22-5H-1	Feed	17.2	3.6	20.2	9.3	18.1	20.9	10.6
1621-22-5H-1	375	14.5	3.0	22.0	8.2	20.5	20.9	10.8

If one looks at the improvement in solvent quality over the original waxy V1074, we can see an increase in cyclic α plus cyclic β hydrogen content from 30.5% to 42.5% (hydrotreated 1621-22-5H-1) after treatment by distillation, dewaxing and hydrotreating. Microautoclave tests will be necessary to see how these proton distribution changes affect dissolution of the Black Thunder coal. These samples were submitted to CONSOL for this purpose.

Conclusions

CONSOL sent Sandia light and heavy distillate fractions of the original V1074 solvent and -35°C dewaxed samples of each fraction. These solvents as well as the original V1074 and the -35°C dewaxed V1074 were hydrotreated in batch microautoclaves to test the effects of the recycle solvent distillation cutpoint on donor solvent quality. There was a significant improvement in solvent quality over the original waxy V1074 as seen by an increase in cyclic α plus cyclic β hydrogen content from 30.5% to 42.5% after treatment by distillation, dewaxing and hydrotreating. CONSOL will perform microautoclave tests with Black Thunder coal to see how these proton distribution changes affect coal dissolution.

Section B.6 Subsequent Trickle-bed Reactor Tests

Background

The maximum amount of donor hydrogen contained in hydrotreated dewaxed distillates from Wilsonville run 262E heavy distillate is ~1 wt% for a sample that has been dewaxed (see section B-4). Recycle distillates that carry as much as 2 wt% donor hydrogen would be very desirable (hexahydropyrene, a good hydrogen donor, has 2.7 wt% donor hydrogen). For this reason three tests were performed using different starting solvents. The three different

feedstocks were chosen to give a variety of feed aromaticities, and hydrogenation tests were designed to evaluate a range of hydrogenated samples for donor solvent potential. Sample 1621-22-5K (25% dewaxed slipstream) was chosen to repeat one of the earlier PST runs, since the catalyst had been inadequately sulfided. Post-run analyses of the catalysts from these more recent experiments showed > 8% sulfur for all of the used catalyst samples, indicating that the catalyst beds were adequately sulfided.

Experimental Procedure

The trickle-bed reactor consisted of two 0.4" ID reactor tubes fastened together in series. Fresh catalyst was crushed to -20+40 mesh and packed in the reactor tubes, which were subsequently installed in a convectively heated oven where the catalyst beds were sulfided in situ with a 10% H_2S in H_2 mixture. Shell 324M was used as the catalyst at the following conditions: 1400 psig H_2, 365 and 380°C, and LHSV approximately 1 hr^{-1}. As has been shown previously, sample analyses indicated a loss of catalyst activity with time on stream.

Results and Discussion

Table 27 shows samples, operating conditions, and hydrogen contents for the starting feeds and products from the trickle-bed reactor tests. Hydrogen increases for the Wilsonville 258K distillate, Lummus pasting solvent, and the PST slipstream solvent (1621-22-5K) were approximately 1.0, 2.5 and 0.3 wt% respectively. The starting Lummus pasting solvent approximates the aromaticity of an anthracene oil and therefore represents an upper limit for solvent hydrogenation. The hydrotreated 258K distillate and hydrotreated Lummus pasting solvent show excellent increases in solvent hydrogen, whereas the hydrotreated slipstream shows only a moderate increase of 0.3 wt%, which is similar to results observed previously in the PST run where the catalyst was poorly sulfided (see Table 18). In this case, however, the catalyst was adequately sulfided.

Table 27. Trickle-bed Hydrogenation Samples and Related Reaction Conditions

Sample	Temp. (°C)	H_2 Pressure (psig)	LHSV (hr^{-1})	% H
Run 258K dist	-	-	-	8.7
060207	365	1400	1.1	9.7
060210	380	1400	1.1	9.6
Lummus Paste	-	-	-	5.5
060905	365	1400	0.9	8.0
060909	380	1400	1.0	8.2
Slipstream*	-	-	-	9.5
062205	365	1400	1.2	9.8
062208	380	1400	1.2	9.8

* Slipstream (1621-22-5K, 25% dewaxed)

Table 28 shows the proton NMR results for the slipstream sample, the hydrotreated slipstream sample, the previous (PST) hydrotreated slipstream sample (for comparison purposes), the Lummus pasting solvent, and the hydrotreated pasting solvent. Comparison of these results shows that sample 062205 has less aromatic protons (13.5% vs 14.9%) and increased cyclic α plus cyclic β protons (37.5% vs 36.0%) compared to the previously hydrotreated PST sample. Both of these parameters indicate sample 062205 is a better donor solvent than the PST sample, even though the hydrogen contents are similar. A portion of this newly hydrotreated slipstream sample was shipped to CAER for testing.

Table 28. Proton NMR Results for Trickle-bed Hydrogenation Tests

Sample	%H	Cond. Arom.	Uncond. Arom.	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
Slipstream	9.5	14.1	3.9	17.2	7.6	17.3	28.1	11.9
062205*	9.8	9.7	3.8	16.1	7.6	21.4	29.0	12.3
Hyd. Slip. **	9.7	10.2	4.7	17.5	8.1	18.5	27.7	13.3
Lummus	5.5	71.4	3.1	11.7	3.4	4.9	3.9	1.6
060905***	8.0	23.0	5.7	24.0	8.9	23.5	11.0	3.9

* See Table 27
** PST 1621-22-5K Hydrotreated (see Table 19)
*** See Table 27

The unhydrogenated Lummus pasting solvent has the highest amount of aromatic protons (74.5%). After hydrogenation, there is only 28.7% aromatic protons and the cyclic α plus cyclic β protons have increased from 16.6 to 47.5%. Both of these parameters indicate the Lummus pasting solvent would be excellent for coal liquefaction, which is substantiated by results in Table 29.

Table 29. Black Thunder Coal Conversions with Hydrogenated Solvents

Solvent	Sample Number	%H in Solvent	Liquefaction Temp (°C)	Conversion (%MAF)*
Lummus Paste	NA**	5.5	400	25
Hyd. Lummus Paste	060905	8.0	400	78
Lummus Paste	NA	5.5	450	4
Hyd. Lummus Paste	060905	8.0	450	93
Slipstream	1621-22-5K	9.5	400	65
Hyd. Slipstream	062205	9.8	400	64
Hyd. Slipstream	PST run	9.7	400	64
Slipstream	1621-22-5K	9.5	450	66
Hyd. Slipstream	062205	9.8	450	88

* Conversion to THF soluble material.
** Not Applicable

Table 29 shows the results of Black Thunder Coal liquefaction tests with the hydrogenated Lummus pasting solvent and the hydrogenated slipstream sample (062205). All of the tests were performed non-catalytically, with no hydrogen overpressure so the effect of the hydrogen donor solvent could be determined. The unhydrogenated Lummus pasting solvent gave a very low coal conversion (25%) at 400°C and an even lower conversion (4%) at 450°C. The higher temperature placed higher demands on the solvent leading to coke formation in the microautoclave under these conditions. When the hydrogenated Lummus pasting solvent was used, coal conversions increased from 25% to 78% at 400°C and from 4% to 93% at 450°C. These results agree with the proton NMR data that shows the hydrogenated Lummus pasting solvent is an excellent hydrogen donor.

For comparison purposes, Table 29 includes results from a previous microautoclave test with the hydrotreated slipstream from the PST run. The slipstream solvent gave essentially the same coal conversions at 400°C whether it was hydrogenated (sample from PST run and 062205) or not. At 450°C, however, the hydrogenated slipstream sample gave 88% conversion compared to 66% conversion for the test using the unhydrogenated slipstream solvent. At both 400°C and 450°C, the hydrogenated Lummus pasting solvent gave significantly higher conversions than the hydrotreated slipstream solvent.

Conclusions

Three solvents with varying aromaticities were hydrotreated in the trickle-bed reactor to evaluate their donor solvent potentials. Wilsonville run 258K distillate, Lummus pasting solvent, and a newly hydrogenated slipstream solvent (sample 062205 obtained with a well sulfided catalyst) gave hydrogen increases of 1.0, 2.5, and 0.3 wt% respectively. These three solvents were evaluated in coal liquefaction experiments with Black Thunder coal. The hydrotreated Lummus pasting solvent had the highest amount of cyclic α plus cyclic β protons and gave the highest THF conversions, 78% and 93%, with experiments performed at 400°C and 450°C respectively. The unhydrotreated and hydrotreated slipstream samples from 400°C experiments and the unhydrotreated slipstream sample from a 450°C experiment all gave the same THF conversions (about 64%). An experiment at 450°C with the hydrotreated slipstream sample gave 88% conversion. These results show that the hydrogenated Lummus pasting solvent was the best coal liquefaction solvent of the three samples tested. A sample of the newly hydrotreated slipstream solvent was sent to CAER for testing.

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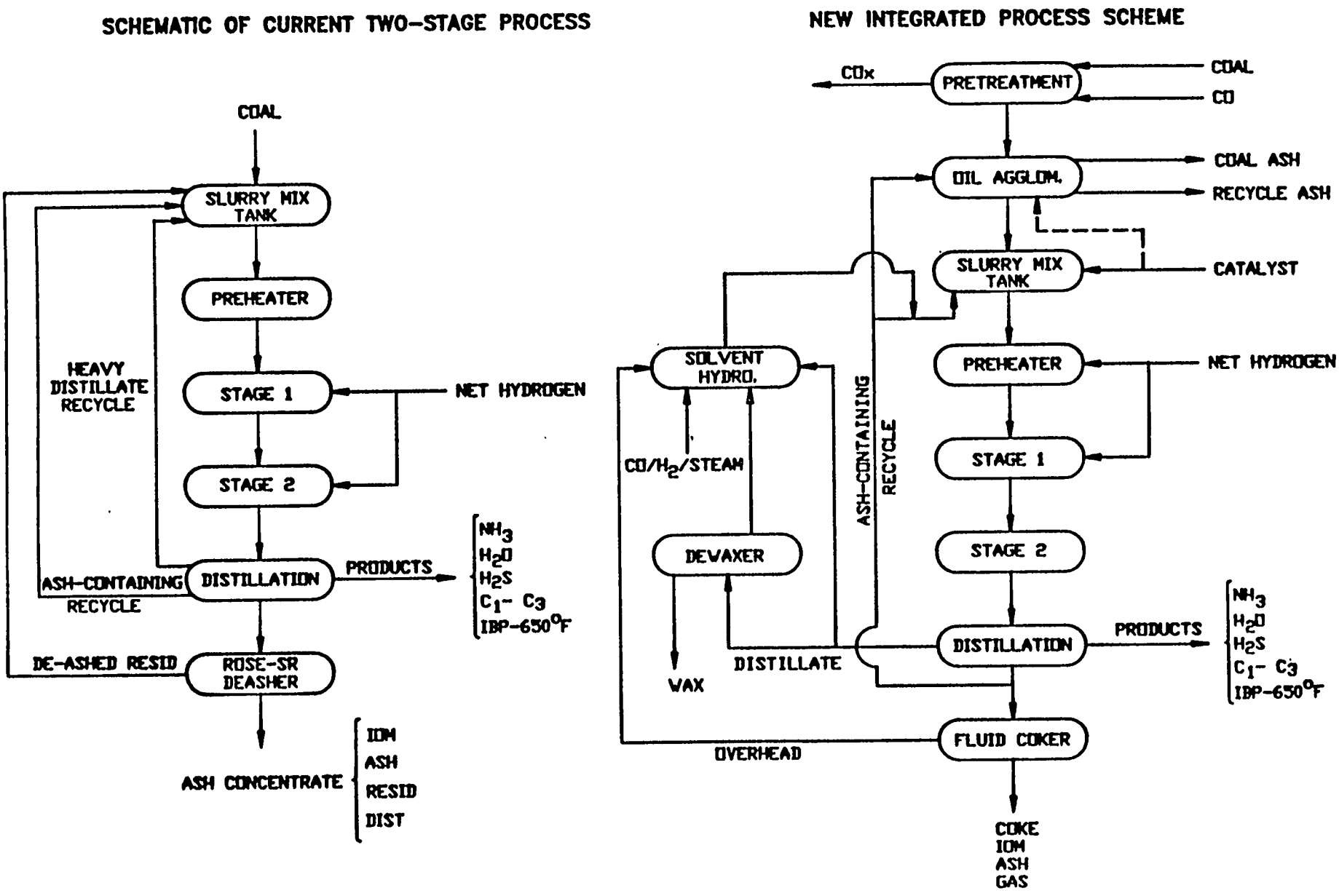
Figure 1. Proposed Advanced Concepts Schematic Diagrams



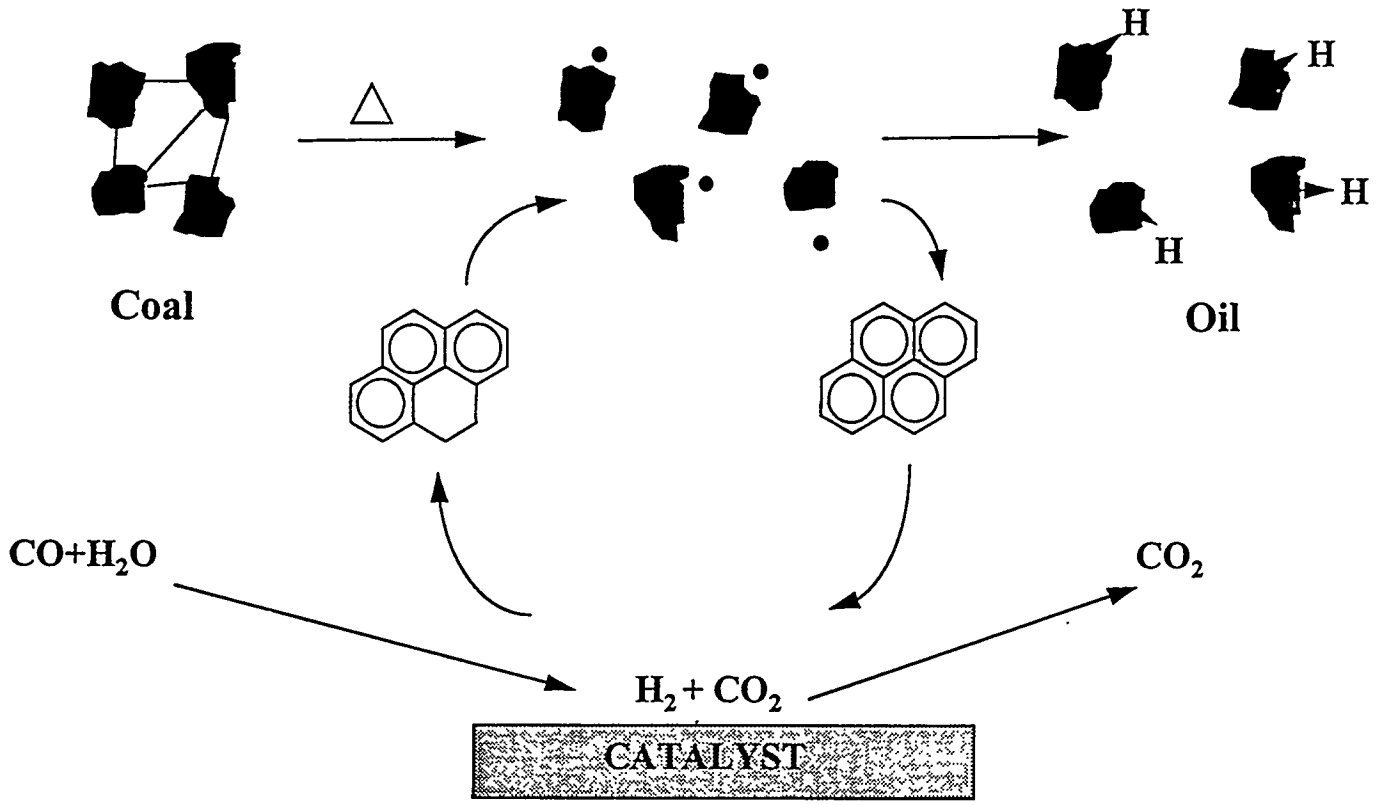
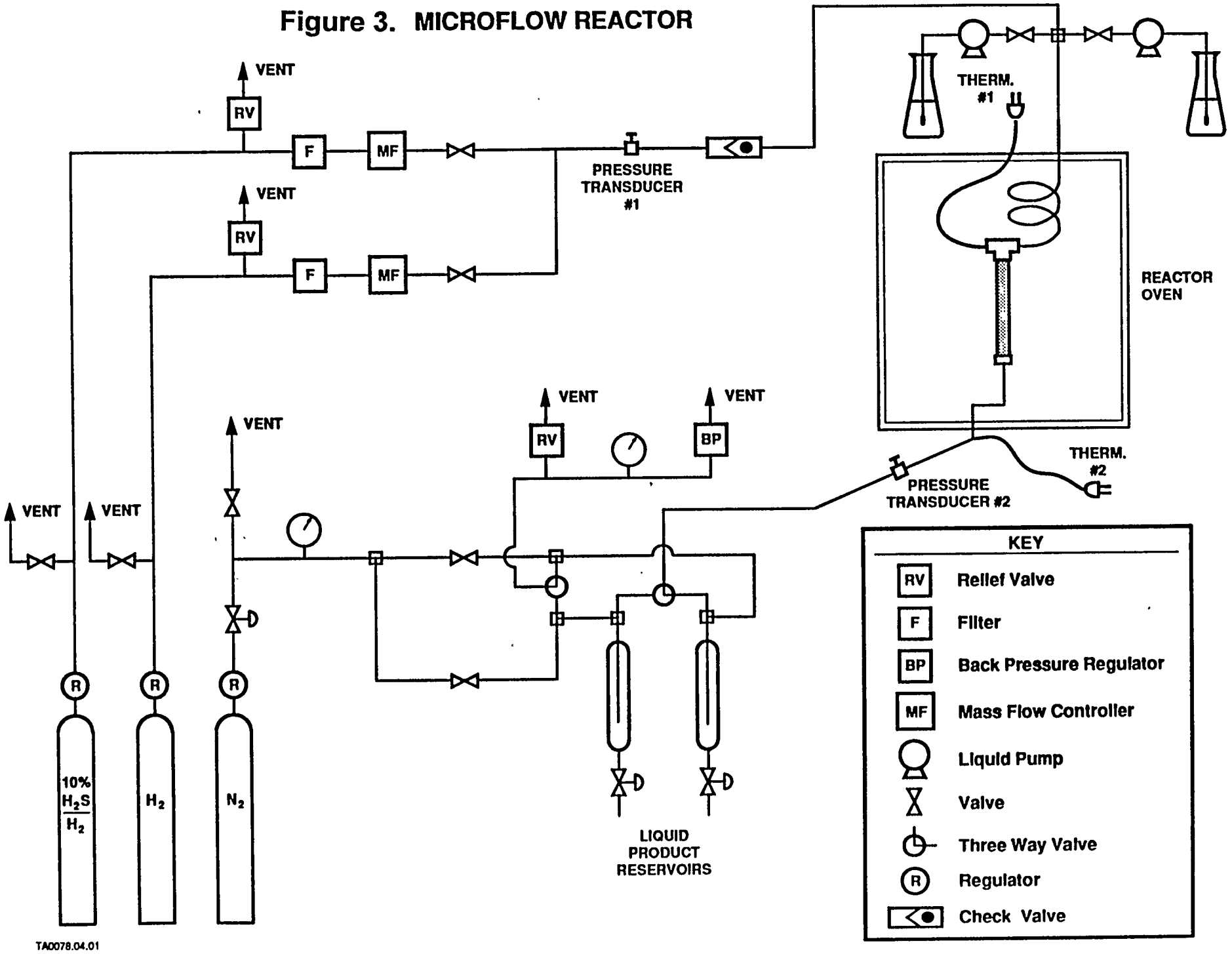


Figure 2. Stylistic Donor Solvent Coal Liquefaction

Figure 3. MICROFLOW REACTOR



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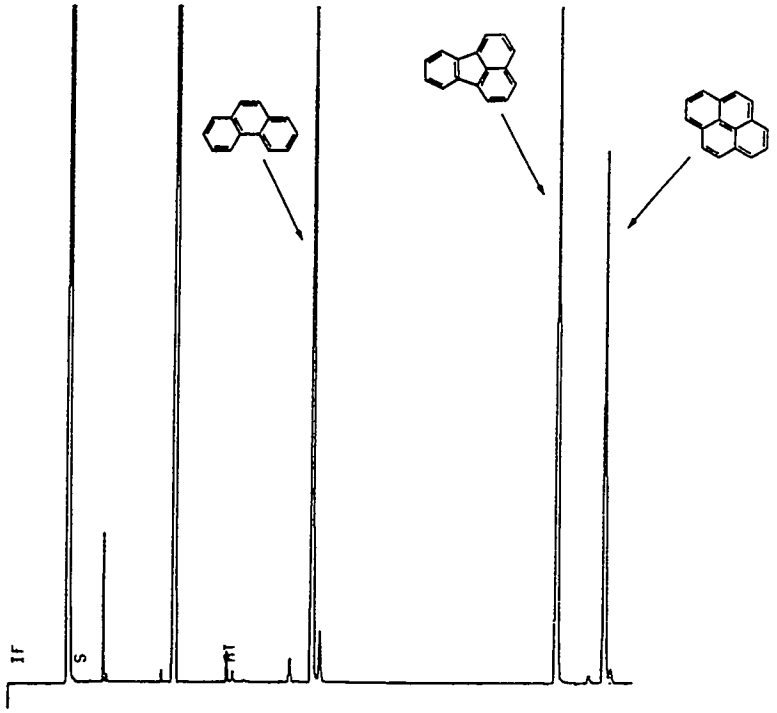

Figure 4. Model Compound Feed

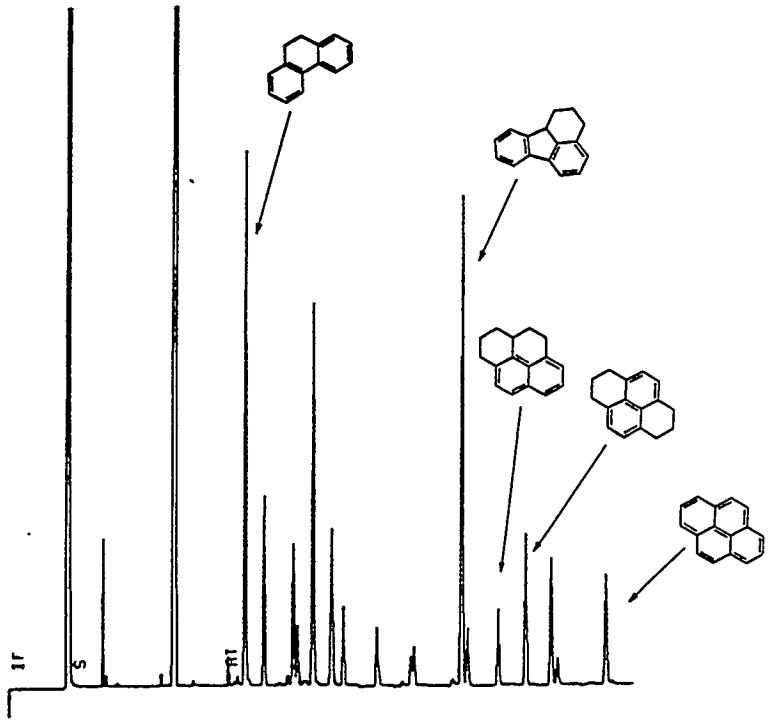

Figure 5. Hydrogenated Model Compound Mix

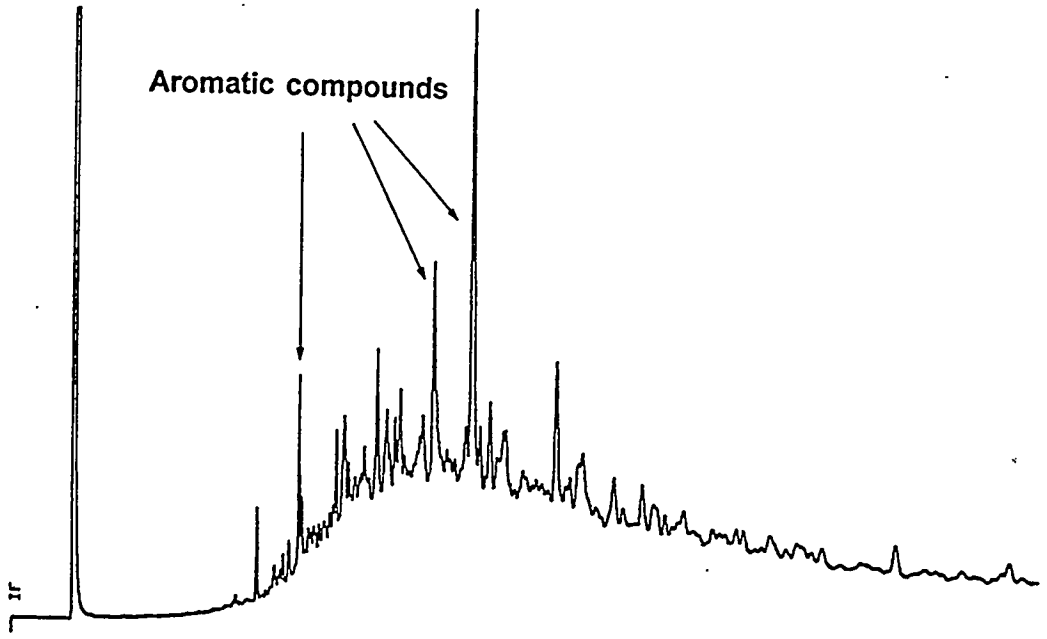

Figure 6. Heavy Distillate Feed

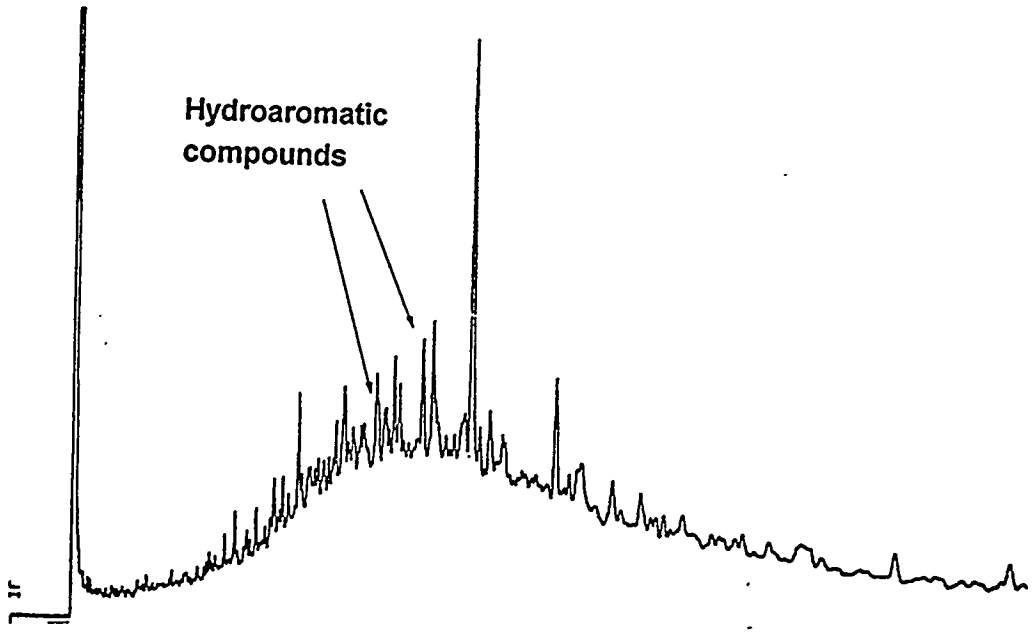

Figure 7. Hydrogenated Heavy Distillate