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EVALUATION OF THE EFFECT OF SOLVENT MODIFICATION AND COAL PRETREATMENT AND BENEFICIATION ON LIQUEFACTION

Final Report

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March 1985

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For
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Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Air Products and Chemicals, Inc.
Allentown, Pennsylvania

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ABSTRACT

An extensive research program was conducted to ascertain ways to improve oil yields and process economics of direct coal liquefaction. The effects of removing heteroatoms from the solvent, pretreating coal by several techniques (including solvent extraction, oxidation, grinding, and ion exchange), and beneficiating coal by removing mineral species were investigated in both catalytic and noncatalytic coal liquefaction reactions. Additionally, fundamental studies were carried out to explain the role of heteroatoms in catalytic coal liquefaction. The effects of process variables, catalysts and mode of catalyst addition, solvent properties, and recycle of SRC on oil production and coal conversion were also studied.

In both catalytic and noncatalytic coal liquefaction, oil production improved significantly when basic nitrogen compounds, phenols, or both types of compounds were removed. Adding model nitrogen compounds and heteroatoms that had been previously removed from the solvent back to modified solvent significantly reduced oil yield in catalytic coal liquefaction.

Several metal catalysts like iron, nickel, and molybdenum catalyzed the coal liquefaction reaction, whereas lead, zinc, and copper were detrimental. Combinations of catalysts like iron and molybdenum yielded more oils than individual metals alone.

In both catalytic and noncatalytic liquefaction experiments, coals that had been pretreated by extraction with a mixture of benzene and ethanol yielded significantly more oil than nonextracted coals. Grinding of coal in air and preoxidation of coal were extremely detrimental to coal liquefaction in original solvent, but the severity of negative effects was reduced considerably by using modified solvent. Ion exchange of raw and preoxidized coal did enhance oil yield, but the enhancement was much more pronounced with the raw coal. Deep cleaning of coal was extremely detrimental to noncatalytic

coal liquefaction, whereas it did not cause any change in catalytic liquefaction. However, when compared on the same-weight basis, deep-cleaned (beneficiated) coal showed higher oil yield and recovery of products than raw coal in catalytic coal liquefaction.

Recycle of SRC significantly increased oil yield in noncatalytic coal liquefaction, but it dramatically decreased coal conversion. In catalytic coal liquefaction, recycle of SRC significantly increased oil yield without severely hurting coal conversion.

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SUMMARY

This is the final report on work conducted for the Department of Energy under Contract No. DE-AC22-82PC50003, entitled "Evaluation of the Effect of Solvent Modification and Coal Pretreatment and Beneficiation on Liquefaction." This contract with Air Products and Chemicals, Inc. included subcontracts with Auburn and Pennsylvania State Universities to provide technical support in understanding how the heteroatoms present in coal liquefaction solvent, the catalysts, and pretreatment and beneficiation of coal affect coal liquefaction. The contract covered the period 1 October 1982 through 31 March 1985.

The overall objective of this program was to investigate options to enhance oil yields as well as process economics in coal liquefaction. Studies yielded significant results in the areas of the effects of solvent modification, catalyst selection, and coal pretreatment and beneficiation upon oil yield and coal conversion. Because of the extensive amount of work conducted under this contract, the overall conclusions of the program are discussed in greater detail in the Program Synopsis. Some of the major findings of the program are highlighted below.

- Treatment of process solvent with either anhydrous HCl gas or silica gel removed almost all the basic nitrogen compounds. However, the removal of basic nitrogen compounds was also accompanied by more than 50% removal of phenols.

- Treatment of process solvent with aqueous NaOH, basic alumina, and zeolite removed more than 50% phenols. Removal of phenolic compounds was surprisingly not accompanied by the removal of basic nitrogen compounds. However, it did affect removal of some neutral nitrogen compounds.

- Sequential treatment of process solvent with anhydrous HCl gas followed by silica gel practically removed all the nitrogen compounds (basic as well as nonbasic). It also resulted in removal of more than 75% phenolic compounds.

- During noncatalytic liquefaction, solvent from which either basic nitrogen compounds or phenols had been removed showed significantly increased oil yields in the tubing-bomb reactor. In addition, oil yield increased with an increase in the degree of heteroatoms removal. However, no changes were noted in the larger scale autoclave reactor.

- In catalytic liquefaction of coal, removal of basic nitrogen compounds or phenols or both significantly increased oil yield both in small tubing-bomb and large autoclave reactors.

- The highest oil yield was noted with the removal of maximum amounts of both nitrogen bases and phenols from the solvent, in both catalytic and noncatalytic coal liquefaction.

- Although coal conversion decreased considerably with the removal of heteroatomic compounds in noncatalytic coal liquefaction, no decrease was noted in catalytic coal liquefaction.

- Use of hydrotreater solvent in noncatalytic liquefaction of coal resulted in a significantly higher oil yield compared to original and treated solvents derived from SRC-I operation. This information shows the importance of solvent properties in coal liquefaction.

- Addition of a catalyst to the reaction mixture containing hydrotreater solvent did not show any marked improvement over noncatalytic liquefaction.

- Under noncatalytic coal liquefaction, treatment of a hydrotreater solvent to remove heteroatomic compounds did not show any beneficial effects, but the addition of a catalyst did improve oil yield.

- Fundamental studies showed that the addition of model nitrogen compounds to modified solvent significantly decreased oil yield in catalytic coal liquefaction. Addition of a phenolic compound (ß-naphthol), however, did not show any negative effect.

- Fundamental studies also showed that the readdition of heteroatomic compounds that had been previously removed from the modified solvent significantly reduced oil yield.

- Several metals like iron, nickel, and molybdenum increased oil yield in the presence of original (untreated) solvent. However, the increase in oil yield was considerably higher with treated solvent, indicating hindrance of the catalytic activity of these metals by the heteroatomic compounds.

- Several inexpensive metals such as zinc, lead, copper, and cobalt were detrimental to coal liquefaction.

- Simultaneous use of an inexpensive metal like iron and zinc and an expensive one like molybdenum significantly increased oil yield both with original (untreated) and treated solvents.

- In the presence of original (untreated) solvent, the activity of iron catalyst was independent of its concentration, provided it was above 0.5% based on coal. However, its activity was very sensitive to its concentration in the presence of modified solvent.

- Molybdenum catalyst showed significantly higher oil yield and coal conversion when dispersed in the reaction mixture than when it was impregnated on coal.

- Although the extraction of small molecules from coal by benzene and ethanol prior to liquefaction did not show any beneficial effects, extraction with a mixture of benzene and ethanol significantly increased oil yield in catalytic and noncatalytic liquefaction in the presence of both original (untreated) and treated solvents.

- Extraction of coal with both citric acid and coal-derived middle distillate prior to liquefaction did not change oil yield in subsequent coal liquefaction.

- Mild oxidation of coal (oxygen uptake of up to 3%) was very detrimental to both oil yield and coal conversion in the presence of original (untreated) solvent, but it did not alter either oil yield or conversion in the presence of modified solvent. Severe oxidation of coal, however, was very detrimental to coal liquefaction irregardless of solvent used.

- Ion exchange of both raw and preoxidized coals significantly increased oil yield. However, ion-exchange treatment of oxidized coal was not as effective in increasing oil yield as was ion exchange of raw coal.

- Grinding of coal in air or original (untreated) solvent before liquefaction with original solvent was detrimental to coal liquefaction. Grinding in modified solvent followed by liquefaction in the presence of modified solvent had little effect--either in noncatalytic or catalytic liquefaction.

- Grinding in the presence of ethanol was extremely detrimental, but grinding in toluene did enhance oil yield.

- In noncatalytic coal liquefaction, removal of iron-bearing species from coal was extremely detrimental to liquefaction in the presence of both original (untreated) and modified solvents.

- In catalytic liquefaction, removal of iron-bearing species showed no clear advantage over raw coal in both tubing-bomb and autoclave reactors.

- Beneficiated coal showed considerably higher oil yield and recovery of net production in catalytic liquefaction than raw coal when the data were compared on the same-weight basis.

- Recycling SRC in noncatalytic coal liquefaction significantly increased oil yield with both original and treated solvents, but overall coal conversion decreased dramatically.

- Increasing the concentration of SRC recycled to the reaction mixture further increased oil yield and decreased coal conversion, indicating the limitations of SRC recycle in noncatalytic liquefaction.

- Recycling SRC in catalytic coal liquefaction significantly increased oil yield with both original and treated solvents without severely hurting the level of coal conversion. An increase in oil yield, however, was higher with treated solvent than original solvent.

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OBJECTIVES

The objective of this research program was to investigate various ways to enhance coal liquefaction oil yields as well as overall process economics. Various new approaches such as removal of heteroatoms from the process solvent, selection of the optimal catalyst or catalyst combination, and coal pretreatment and beneficiation were studied to determine their effect on oil yield and coal conversion. In addition, fundamental studies were performed to explore the role of heteroatoms in coal liquefaction.

The research program was divided into six major tasks, each consisting of several subtasks. An outline of the program is given below:

1. Prepare detailed program plan for Department of Energy's review and approval.

2. Review existing published papers and patents in related areas.

3. Select method for the removal of heteroatoms and prepare modified solvent samples.

4. Evaluate the effect of solvent modification on catalytic and noncatalytic coal liquefaction.

5. Pretreat and beneficiate various coal samples, and evaluate the effect of coal pretreatment and beneficiation on liquefaction.

6. Select the most promising results from tasks 3 to 5 and verify them in a large-scale 300-mL semicontinuous autoclave system.

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DEFINITIONS OF VARIOUS LIQUEFACTION SOLVENTS

Various terms used throughout this report to describe the different liquefaction solvents used are defined below:

- Starting liquefaction solvent: Liquefaction solvent generated from Kentucky #9 coal at the Wilsonville Advanced Coal Liquefaction Facility (WACLF) under standard SRC-I process conditions; used to establish baseline data for Kentucky #9 coal.

- Base liquefaction solvent: Liquefaction solvent generated from Illinois #6 coal at the WACLF under standard SRC-I conditions, and from which pentane-insoluble material was extracted; used to establish baseline data for Illinois #6 coal.

- Treated or modified liquefaction solvent: Liquefaction solvent samples prepared by treating either the starting or base liquefaction solvent to remove nitrogen bases or phenols or both.

- Hydrotreater solvent: Liquefaction solvent generated by hydrotreating SRC in a catalytic hydrocracker at the WACLF.

- Modified hydrotreater solvent: Liquefaction solvent prepared by treating the hydrotreater solvent to remove nitrogen bases and phenols.

I. PROGRAM SYNOPSIS

Extensive research has been conducted on a variety of coal liquefaction processes, both noncatalytic and catalytic, to develop the design data base needed for future commercialization. The primary goal of all the liquefaction processes is production of high oil yield with minimum hydrogen consumption. High oil yield has generally been achieved by using either severe reaction conditions, supported catalysts like Co-Mo-Al, or a two-stage liquefaction concept. When severe reaction conditions are used, high oil yield is obtained at the expense of high hydrocarbon gas production and, concomitantly, high hydrogen consumption, which makes the liquefaction process economically unattractive. Supported catalysts also enhance oil yield, but in addition to being expensive these catalysts are deactivated very rapidly by minerals present in the coal and by coke formed during the liquefaction reaction. Therefore, to maintain both high catalyst activity and oil production, fresh catalyst has to be added and the spent catalyst withdrawn at an alarming rate, making the use of supported catalysts also uneconomical.

In an attempt to solve the problem of high catalyst replacement rate and thereby high catalyst cost, some researchers proposed a two-stage coal liquefaction concept in which coal was liquefied in the absence of a catalyst in the first stage. The liquefied product was then deashed before being subjected to further conversion in the second stage in the presence of a supported catalyst. The processing of deashed coal was supposed to reduce the catalyst deactivation rate; unfortunately, it did not make a significant difference.

A number of other alternatives have also been proposed to enhance oil yield without causing catalyst deactivation and increasing process economics. Several inexpensive coal minerals such as pyrite and expensive metal catalysts like molybdenum at very low concentrations have been reported to increase oil yield, and to be active even at less severe reaction conditions. However, the increase in oil yield with both inexpensive mineral catalysts and expensive metal catalysts is nowhere near that reported in the literature with supported catalysts.

In a coal liquefaction reaction, the molecules of coal are believed to rupture thermally, producing free radicals. These free radicals are either quenched by the hydrogen donated by the process solvent or polymerized to produce coke. Therefore, liquefaction performance depends greatly on the nature and type of solvent used in the process. If the solvent has enough capacity to quickly supply all the hydrogen needed to the free radicals, the process will be very efficient. Sufficient capacity can be achieved in two ways: by using either an excessive amount of solvent or a very high solvent-to-coal ratio (using high internal recycle of process solvent).

The use of a high solvent-to-coal ratio necessitates large reactors and provides low throughput, which is undesirable. However, this problem can be resolved by using a solvent that can be rehydrogenated within the liquefaction reactor, which allows it to donate more hydrogen. Therefore, the function of an efficient process solvent is twofold: (1) to donate hydrogen to coal free radicals and (2) to pick up hydrogen from the gas phase. In other words, in any coal liquefaction process, hydrogen is transferred from gas phase to liquid phase and then from liquid phase to coal free radicals.

Research has shown that transfer of hydrogen between these phases and ultimately to free radicals can be enhanced by adding the inexpensive mineral catalysts and expensive metal catalysts mentioned previously. Also, the presence of heteroatoms such as nitrogen and oxygen compounds in the liquid phase (solvent) has been shown to hinder the transfer of hydrogen from gas to liquid phase even in the presence of a catalyst. Therefore, hydrogen transfe could conceivably be significantly enhanced by removing the heteroatomic compounds from the solvent. This would undoubtedly improve the overall liquefaction reaction. Furthermore, other literature reports indicate that pretreating and cleaning coals before liquefaction will influence their liquefaction behavior to varying degrees.

The experimental program conducted by Air Products and Chemicals, Inc. and reported on herein was designed to corroborate some of these reported claims in an attempt to definitively identify ways to improve coal liquefaction yields. The main objective of our research was to investigate how heteroatom affect oil yield in catalytic and noncatalytic coal liquefaction. In addition, we examined other options to improve yields such as coal pretreatment and beneficiation.

Before beginning any experimental work, a detailed program plan was prepared and submitted to the Department of Energy for their approval. In addition, an extensive literature search encompassing published papers and patents was performed in the areas of (1) treatment of process solvent to remove heteroatomic constituents, (2) effect of removal of heteroatomic constituents from process solvent upon coal liquefaction, (3) effect of catalysts and their forms upon liquefaction, (4) techniques to pretreat and beneficiate coal, and (5) effect of coal pretreatment and beneficiation on coal liquefaction. Details on both the program plan and literature review can be found in reports submitted earlier under this program (see references 1 and 2).

Because the programs encompassed three different but equally significant areas of coal liquefaction, Air Products subcontracted some of the research to Auburn University in Auburn, Alabama and to Pennsylvania State University, University Park, Pennsylvania. Auburn assisted Air Products in determining the role of heteroatoms and selecting the optimal catalyst or catalyst combination for liquefaction, while Penn State studied coal benefication, and beneficiated a number of coal samples for liquefaction testing.

Most of the work during this program was conducted using Illinois #6 coal from the Burning Star mine and SRC-I process solvent derived from the same coal during runs at the Wilsonville Advanced Coal Liquefaction Facility (WACLF) in Wilsonville, Alabama. Some tests were also conducted on Kentucky #9 coal from the Fies mine, again with process solvent derived from the same type of coal. Both coals are from the Western Kentucky Region and are low in ash and pyrite, but high in organic sulfur. They were selected primarily because they have been extensively examined at the Wilsonville plant and because corresponding solvents were available.

Research focused on six major areas, and the results reported herein are structured correspondingly. The studies are as follows:

- Solvent Modification: Process solvents derived from both Illinois #6 and Kentucky #9 coals and from the WACLF hydrotreater were modified in several ways to remove heteroatoms.
- Effect of Solvent Modification on Liquefaction: The effects of modified process solvents on catalytic and noncatalytic liquefaction of Illinois #6 and Kentucky #9 coals were studied. Before studying the effects of the modified solvents, extensive baseline data were established, both with and without catalysts.
- Catalyst Selection: Various metal catalysts in several forms (dispersed or impregnated) were tested to compare their effect on the coal liquefaction reaction.
- Coal Pretreatment and Beneficiation: Illinois #6 coals were pretreated by four different methods (solvent extraction, oxidation, ion exchange, or pulverization) or deep-washed (beneficiated) and then liquefied with both original (untreated) and modified solvents, with and without catalyst, to determine the effect of coal pretreatment and beneficiation upon liquefaction.
- Scale-up Studies: Since all the experiments conducted in the preceding portions of the program were carried out in a small tubing-bomb reactor, a scaled-up 300-mL semicontinuous autoclave reactor was constructed and used in liquefaction testing to verify the earlier findings.
- Exploratory Studies: Finally, a series of tests was performed to ascertain the optimal reaction conditions and catalyst for coal liquefaction, and to determine the effects of recycling SRC during reaction.

A brief synopsis of each study is presented below.

SOLVENT MODIFICATION

Since the presence of heteroatoms in solvents can hinder their effectiveness during liquefaction, extensive experiments were conducted to remove such compounds and then test the modified solvents during liquefaction.

Two process solvents derived from the liquefaction of Illinois #6 and Kentucky #9 coals in the SRC-I mode at the WACLF were selected for the study. Process solvent from the SRC hydrotreater was also studied because of its high hydrogen and low heteroatom content.

Treatment of Solvent Derived from Illinois #6 Coal

Since the starting liquefaction solvent derived from Illinois #6 coal at Wilsonville was produced when light SRC was recycled in the plant, it contained some SRC. Therefore, this solvent was extracted with pentane to separate out the SRC. The pentane-soluble portion, called base liquefaction solvent, was used for the treatment (heteroatom removal) and subsequent liquefaction studies.

The base liquefaction solvent was treated in several ways to remove nitrogen bases and/or phenols to evaluate the effect of heteroatom removal. Nitrogen compounds were significantly removed (>75% removal of total nitrogen content) by treatment with anhydrous hydrochloric acid or silica gel, but this was accompanied by 25-40% removal of oxygen. These figures correspond to almost complete removal of nitrogen as basic nitrogen compounds and more than 50% oxygen as phenolic compounds. Significant amounts of phenolic components (>50%) were removed by treatment with aqueous NaOH, basic alumina, and zeolite. The removal of oxygen compounds (phenolics) was also accompanied by partial removal of neutral nitrogen compounds, in the form of NH_2.

Some samples were also treated sequentially, to remove both basic nitrogen and phenolic compounds. A sample pretreated with HCl to remove nitrogen bases was further treated with silica gel, and the NaOH-treated sample was further treated with HCl. In both cases, nitrogen compounds, basic and nonbasic, were completely removed. In addition, the removal of oxygen as phenols was more than 75% in both cases.

Other experiments that treated base liquefaction solvent with various clays and solid adsorbents such as bentonite, kaolin, and porocel removed almost none of the nitrogen and oxygen compounds. Attapulgus clay and syloid were marginally effective in removing heteroatom compounds. In contrast, sepiolite removed approximately 25 and 20% of the total nitrogen and oxygen content, respectively. Both acid washing and acid washing followed by activation by heat treatment enhanced sepiolite's ability to remove heteroatoms. Treatment of base liquefaction solvent with acidic alumina removed approximately 17% of the total oxygen. Interestingly, no removal of nitrogen compounds was noted with acidic alumina.

Treatment of Solvent Derived From Kentucky #9 Coal

Like the treatment of Illinois #6 coal derived solvent, samples of starting liquefaction solvent derived from Kentucky #9 coal were treated with both silica gel and basic alumina to remove nitrogen bases and phenols. Treatment with basic alumina removed 39 and 16% of the total oxygen and nitrogen, respectively. Silica gel, however, adsorbed more material, and removed much more oxygen and nitrogen -- 48 and 73%, respectively.

Treatment of Hydrotreater Solvent

Hydrotreater solvent was generated by hydrotreating a mixture of process solvent and SRC generated from Illinois #6 coal in a catalytic hydrocracker at the WACLF. This solvent sample was treated with silica gel, which removed only 30 and 50%, respectively, of the total oxygen and nitrogen compounds, much less than that noted for silica gel treatment of SRC-I process solvent derived from Illinois #6 and Kentucky #9 coals.

EFFECT OF SOLVENT MODIFICATION ON LIQUEFACTION

Before determining the effect of solvent modification, extensive baseline data were generated with original, modified, and hydrotreater solvents. These results were compared with data from the solvent modification liquefaction experiments.

Establishing Baseline Data

The liquefaction behavior of Illinois #6 and Kentucky #9 coals was studied both in the presence and absence of a catalyst to establish baseline data. Solvent derived from the liquefaction of Illinois #6 coal in the SRC-I mode of operation at the WACLF was used for the liquefaction testing of Illinois #6 coal to avoid any mismatch of coal and solvent. In some cases both low-severity (solvent-to-coal ratio of 2:1, reaction time of 60 minutes, initial hydrogen pressure of 850 psig at 25°C, reaction temperature of 425°C, and agitation of 1,000 strokes per minute) and high-severity (solvent-to-coal ratio of 1:1, reaction time of 60 minutes, initial hydrogen pressure of 1,200 psig at 25°C, reaction temperature of 440°C, and agitation of 1,000 strokes per minute) reaction conditions were used to generate baseline date.

Liquefaction of Illinois #6 Coal with Base Liquefaction Solvent. Noncatalytic Liquefaction: Base liquefaction solvent was used in noncatalytic liquefaction of Illinois #6 coal under both low- and high-severity reaction conditions in a 50-mL tubing-bomb reactor to generate baseline data. Under low-severity conditions, the oil yield was 12.5 wt %. Overall coal conversion, defined as the material soluble in a mixture of 10% methanol in methylene chloride, was 82%. This value is low compared to over 90% reported at the WACLF. The coal conversion values differ because we used a weak solvent (a mixture of 10% methanol in methylene chloride) to determine conversion, whereas Wilsonville used a strong (pyridine or cresol oil) solvent.

When the liquefaction conditions were changed from low severity to high severity, oil yield increased from 12.5 to 29.2%, which was a remarkable improvement. However, overall coal conversion decreased from 82 to 76.7%, indicating an onset of retrograde reactions at high severity. The onset of retrograde reactions was also evidenced by a significant increase in gas production.

Catalytic Liquefaction: Base liquefaction solvent was also used in catalytic liquefaction of Illinois #6 coal to establish baseline data. A catalyst concentration of 500 ppm of molybdenum based on coal, added as molybdenum octoate, was used for low-severity reaction, whereas only 250 ppm of molybdenum was used for high-severity reaction. Molybdenum catalyst was selected because we had experience with it, and we did not want to delay the program by waiting until the best catalyst was identified. Instead, catalyst selection studies were initiated concurrently, the results of which are discussed later in a separate section.

Under low-severity conditions, the addition of molybdenum catalyst increased the oil yield from 12.5 to 25.4%. Overall coal conversion also increased from 82 to 92%. SRC production decreased slightly with the addition of a catalyst. Apparently, the primary function of the catalyst is to increase conversion of coal to SRC and of SRC to oil. Most interestingly, the production of gases did not increase with catalyst addition.

Use of high-severity reaction conditions increased the oil yield from 29 to 45%. In addition, overall coal conversion increased from 77 to 94% with the addition of a catalyst, contrary to the onset of retrograde reactions in noncatalytic liquefaction of Illinois #6 coal at high-severity conditions. The high coal conversion value indicates that retrograde reactions were literally absent, confirming the importance of catalysts in coal liquefaction reaction.

Liquefaction of Illinois #6 Coal with Hydrotreater Solvent. Noncatalytic Liquefaction: A hydrotreater solvent generated by hydroprocessing SRC derived from Illinois #6 coal at WACLF was used to generate the baseline data. Only high-severity reaction conditions were studied. Liquefaction resulted in an oil yield of 45%, considerably higher than that noted with base liquefaction solvent under similar conditions. Overall conversion (≈90%) was also considerably higher. These increased yields were probably due to one of two reasons: either much more hydrogen was available for reaction because the hydrotreater solvent contained more hydrogen than base liquefaction solvent, or the hydrotreater solvent contained much fewer heteroatomic compounds than base liquefaction solvent. The latter reason tends to support our hypothesis that liquefaction performance can be improved by removing heteroatomic compounds from the solvent. Although the data do not pinpoint the true cause for improved liquefaction performance, they do clearly indicate the strong influence of solvent properties on the liquefaction reaction.

Catalytic Liquefaction: Addition of a catalyst to the reaction mixture containing Illinois #6 coal and hydrotreater solvent did not show any marked improvements over noncatalytic liquefaction experiments. This was very surprising because we had always noticed markedly improved liquefaction performance previously upon catalyst addition.

Liquefaction of Kentucky #9 Coal with Starting Liquefaction Solvent.

Noncatalytic Liquefaction: Starting liquefaction solvent derived from SRC-I liquefaction of Kentucky #9 coal at WACLF was used to generate baseline data. Only low-severity reaction conditions were studied. Liquefaction resulted in an oil yield of 12.7%, which was very similar to that noted in the case of Illinois #6 coal liquefaction with base liquefaction solvent. Overall coal conversion was 74%, which was once again lower than that noted at WACLF. This low conversion value is due to the use of weaker solvent for determining coal conversion, as explained earlier in the Illinois #6 coal liquefaction section.

Catalytic Liquefaction: As expected, addition of 500 ppm of molybdenum based on coal (as molybdenum octoate) increased the oil yield from 12.7 to 17%. Overall conversion increased from 75 to 85%. Increases in both oil yield and coal conversion were considerably lower than those noted with the addition of catalyst in the liquefaction of Illinois #6 coal. The production of SRC increased from 55 to 64%, which was opposite of that noted with Illinois #6 coal. During Illinois #6 coal liquefaction, catalyst addition increased conversion of both coal and SRC to oil, whereas in Kentucky #9 coal liquefaction, the catalyst increased only the conversion of coal, partly to SRC and partly to oil.

The noncatalytic and catalytic baseline data generated from liquefaction of Illinois #6 coal using base liquefaction and hydrotreater solvents and of Kentucky #9 coal using starting liquefaction solvent were used as benchmarks to compare results from subsequent runs with modified solvents.

Effect of Solvent Treatment on Liquefaction

Liquefaction of Illinois #6 Coal with Treated Base Liquefaction Solvent.

Noncatalytic Liquefaction: Liquefaction experiments were conducted with base liquefaction solvent treated with a mixture of silica gel and neutral alumina under low-severity conditions and with anhydrous HCl followed by silica gel under both low- and high-severity reaction conditions. In all cases, oil production was markedly higher with the treated solvents. It increased by more than 60% at low severity, although, unfortunately, coal conversion also decreased. We also found that the decrease in coal conversion depended on the extent of heteroatoms removal; as more heteroatoms were removed, the coal conversion decreased correspondingly. Interestingly, under high-severity reaction conditions, instead of decreasing with solvent treatment, coal conversion increased. Production of gases decreased with solvent treatment under low-severity reaction conditions, but remained unchanged under high-severity reaction conditions. These observations clearly indicate that the removal of heteroatoms from the solvent enhances noncatalytic liquefaction performance, especially oil yield.

Catalytic Liquefaction: Numerous solvents prepared by treating base liquefaction solvent to remove either nitrogen bases (treatment with anhydrous HCl or silica gel) or phenols (treatment with NaOH, basic alumina, or Y-zeolite) or both nitrogen bases and phenols (treatment with anhydrous HCl followed by silica) were used in catalytic liquefaction experiments to determine the effect of solvent treatment on liquefaction.

Under low-severity reaction conditions and in the presence of 500 ppm of molybdenum catalyst based on coal, the removal of nitrogen bases with either anhydrous HCl or silica gel dramatically increased the oil yield from 25 to 38%. However, overall coal conversion was not greatly affected. Most of the increase in oil yield came from increased conversion of SRC. Gas production either decreased slightly or remained unchanged.

Likewise, under low-severity reaction conditions, the removal of phenols by either basic alumina or Y-zeolite increased the oil yield from 25 to 34%. Again, coal conversion was not greatly affected by phenols removal, and the increase in oil yield came from increased conversion of SRC. Gas yield declined marginally. Base liquefaction solvent treated with NaOH to remove phenols somehow was not as effective in improving liquefaction performance as the other two solvents just discussed.

Removal of both nitrogen bases and phenols from the solvent resulted in the highest production of oil under low-severity reaction conditions. Once again, overall coal conversion was not greatly affected, and the added increase in oil yield came from increased conversion of SRC. Gas production declined slightly. Under high-severity reaction conditions, the removal of both nitrogen bases and phenols from the solvent increased oil yield from 44 to 51%. Coal conversion and gas production, however, were not greatly affected. Again, the increased oil yield came from improved conversion of SRC.

Overall, our data clearly indicate that the removal of heteroatoms significantly enhances catalytic liquefaction performance, especially the oil yield.

Liquefaction of Illinois #6 Coal with Treated Hydrotreater Solvent. When modified hydrotreater solvent was used during noncatalytic liquefaction of Illinois #6 coal under high-severity reaction conditions, yields did not improve noticeably, probably because treatment had only marginally removed the nitrogen compounds and phenols. When used during catalytic liquefaction of Illinois #6 coal, the oil yield did increase and coal conversion improved slightly. However, the magnitude was small.

Liquefaction of Kentucky #9 Coal with Treated Starting Liquefaction Solvent. Liquefaction tests of the modified solvents prepared by treating starting liquefaction solvent with either basic alumina or silica gel were conducted only with a catalyst under low-severity reaction conditions. Removal of heteroatoms from the solvent with basic alumina increased the oil yield from 16 to 31%. However, the oil yield increased further when more heteroatoms were removed (with silica gel). In both cases, coal conversion increased slightly with heteroatoms removal, and the increase in oil yield was attained at the expense of both increased SRC and coal conversion.

Fundamental Studies Related to Solvent Modification. To support our findings about the beneficial effect of removing heteroatoms from process solvent and to better understand the role of the heteroatoms, Auburn University performed several fundamental experiments. Because of differences between the tubing-bomb reactor design, reaction conditions, and solvent separation procedures used at Auburn University and at Air Products, Auburn reestablished the baseline data for catalytic coal liquefaction with both base liquefaction solvent (from Illinois #6 coal) and modified solvent (treated base liquefaction solvent with anhydrous HCl followed by silica gel). As expected, Auburn also reported higher oil yield with modified solvent than with base liquefaction solvent.

Next, Auburn added several model nitrogen compounds typically found in coal-derived solvents (quinoline, phenanthridine, and acridine) to modified solvent to increase its total nitrogen content. In all cases, oil production during catalytic coal liquefaction was inhibited by adding nitrogen compounds and the decrease in oil yield was inversely proportional to increases in the total nitrogen content. Furthermore, Auburn tested the effect of adding a representative oxygen compound (ß-naphthol) to modified solvent to increase its total oxygen content. Liquefaction results indicated no change in oil production by adding ß-naphthol, but more work is needed to determine the effect of phenols (particularly those of high molecular weight).

The final experiment conducted by Auburn involved adding the heteroatomic compounds that had been extracted from the base liquefaction solvent back to the modified solvent. Oil production during subsequent liquefaction with this reconstituted solvent was again reduced, further confirming the detrimental effect of such polar compounds.

To further understand the role of such compounds, researchers studied a simple catalytic hydrogenation reaction system using phenanthrene as a model compound. They surmised that heteroatomic compounds, especially nitrogen compounds, severely limit hydrogen transfer from the gas to liquid phase, resulting in hydrogen starvation.

CATALYST SELECTION

Metal catalysts play an important role during coal liquefaction. Our liquefaction experiments consistently showed that adding molybdenum improved oil yields. However, the cost of the catalyst can strongly influence the economic feasibility of the process, and the form in which it is used can affect its activity. Hence, catalyst selection tests were performed to determine the best catalyst and the form in which it should be used for coal liquefaction.

Auburn University carried out a number of experiments to test the activity of various metals such as molybdenum, cobalt, nickel, copper, lead, zinc, and iron using base liquefaction solvent. These metals were impregnated on coal and tested individually and in combination with other metals.

The experimental data revealed that molybdenum, nickel, and iron catalyzed the coal liquefaction reaction, whereas zinc, lead, copper, and cobalt did not. At a concentration of 250-ppm metal based on coal, molybdenum catalyst was more active than nickel and 1 wt % iron. A combination of a cheap metal like iron or zinc and an expensive metal such as molybdenum resulted in significantly higher oil yields compared to individual metals alone.

Since molybdenum and iron catalysts impregnated on coal displayed good catalytic activity in coal liquefaction with base liquefaction solvent, the catalytic activity of these two metals impregnated on coal was tested at Air Products using modified solvent. Both iron and molybdenum catalysts showed higher oil yield with modified solvent than base liquefaction solvent, indicating that the catalytic activity of the metals was hindered by the heteroatoms present in the base liquefaction solvent. Furthermore, the oil yield increased by increasing the concentration of iron metal, which is contrary to the results noted with base liquefaction solvent.

When molybdenum was dispersed in the reaction mixture by using oil-soluble molybdenum octoate, it showed much higher activity both in terms of oil yield and coal conversion than when it was impregnated on coal. Therefore, the method of applying the catalyst is very important in coal liquefaction. Since dispersed catalysts are more active than impregnated catalysts, the amount of catalyst required could be reduced considerably. However, the relative costs of achieving dispersion (i.e., cost of oil-soluble metal compared to water-soluble catalyst) must be weighed against the total amount of catalyst required for sufficient activity in making a selection for commercial operation.

COAL PRETREATMENT AND BENEFICIATION

Several coal pretreatment and beneficiation methods were also studied during this program to determine their effect on liquefaction yield under varying operating conditions. Most of the pretreatment work was carried out by Air Products, while Pennsylvania State University carried out all the coal beneficiation experiments. All the pretreated coals and raw coal samples were liquefied with base liquefaction and modified solvents, in the presence and absence of a slurry catalyst, to evaluate their liquefaction behavior.

Solvent Extraction

Solvent extraction of coal prior to liquefaction removes either small molecules or moisture from the coal, opening up pore space that can then be filled with process solvent capable of donating hydrogen. Several extraction experiments were conducted: using benzene and ethanol, either separately or as a mixture; treating coal with middle distillate solvent first and then extracting with either methylene chloride or benzene/ethanol; and extracting with citric acid to remove cations and exchangable sodium and calcium metals.

Noncatalytic liquefaction of Illinois #6 coal extracted with a mixture of benzene and ethanol showed a significantly increased overall oil yield. In contrast, treatment with middle distillate and citric acid extraction either did not affect or even detrimentally affected the product distribution from coal liquefaction.

Several solvent-extracted Illinois #6 coal samples were also liquefied at low-severity reaction conditions in the presence of molybdenum catalyst. The coal samples extracted with a mixture of benzene and ethanol showed a noticeable increase in oil production. Extraction may have removed occluded material and replaced it with hydrogen-donor solvent, thus improving coal liquefaction. Also, extraction may have replaced moisture at the surface with alcohol or benzene, which would alter the coal's reactivity. Extraction with citric acid did not affect the liquefaction behavior of coal using 500-ppm Mo catalyst and either base liquefaction solvent or modified solvent.

Oxidation

Several experiments were conducted to determine the effect of natural or induced oxidation, which makes the coal more refractive and increases the amount of oxygen compounds that poison catalysts. Oxidation was achieved by exposing coal samples to air in a fluidized bed reactor or by treatment with hydrogen peroxide or sulfuric acid. Samples were prepared representing several levels of oxidation and weight gain.

As expected, liquefaction of oxidized coal in the presence of original (untreated) solvent resulted in considerable decreases in both oil yield and conversion. On the contrary, the air-oxidation technique, with oxygen uptake of up to 3%, did not alter the product distribution in the presence of modified solvent; the same optimal oil yields obtained with nonoxidized coal and modified solvent were achieved. However, the use of strong oxidizing agents such as sulfuric acid and hydrogen peroxide had a severe detrimental effect on oil production, which dropped by almost 80%.

The air-oxidation results from these experiments are particularly interesting because they suggest that oxidized coal can be liquefied without normal loss of oil production by using modified solvent rather than original or base liquefaction solvent as conventionally used. Use of modified solvent would avoid the need for complicated preparation and coal-handling systems designed to minimize oxidation.

Cation Exchange

Several experiments were conducted to determine whether catalytic activity could be improved by using ion exchange to molecularly disperse catalysts deep within the coal structure. Both raw and preoxidized coal samples were tested. Oxidation was expected to produce the functional groups that are not normally present in bituminous coals needed to complex the metal catalysts.

Selected coals were slurried with dilute salt solutions to effect ion exchange of Ca^{2+}, Na^{+}, Fe^{2+}, or Fe^{3+}. For the most part, we found that mild air oxidation of Illinois #6 coal produced only a minor fraction of metal adsorption sites relative to the large amount of oxygen incorporated.

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Illinois #6 coal was also ground in the presence of coal-derived solvents and liquefied at various temperatures. Grinding in base liquefaction solvent at low temperature decreased oils compared to baseline runs, while use of modified solvent had little effect at all. Grinding also had little effect during catalytic liquefaction.

Increasing the temperature during grinding to 170°C had little effect on oil production or coal conversion in both noncatalytic and catalytic liquefaction runs. Grinding in the presence of hydrogen rather than helium increased oil production from 34 to 40%. Other runs in which 1% Fe was added to a catalyst batch further increased oil yield to about 45%.

Grinding was also performed in the presence of alcohols such as ethanol and toluene. The results were compared with helium baseline experiments. Grinding in alcohol had significant detrimental effects on oil production, but grinding in toluene increased oil production from 34 to about 42%. These improvements were still short of liquefaction of untreated coal in a similar environment.

Finally, the use of toluene to grind coal in the presence of molybdenum hexacarbonyl resulted in significantly higher oil production upon liquefaction using modified solvent compared to the oil yield obtained by grinding coal in modified solvent containing either oil-soluble molybdenum catalyst or molybdenum added as molybdenum hexacarbonyl.

Beneficiation

Pennsylvania State University beneficiated a freshly acquired sample of Illinois #6 coal using float sink and Diester Table techniques to yield samples containing varying amounts of ash, pyritic sulfur, and total iron. Removal of certain detrimental inorganic species was expected to improve coal liquefaction, while removal of catalytic iron-bearing minerals was expected to adversely affect results.

In noncatalytic coal liquefaction, removal of the mineral matter, particularly iron-bearing species, was found to be extremely detrimental to liquefaction. However, the addition of a slurry catalyst nullified the detrimental effects of coal beneficiation -- neither the oil yield nor coal conversion changed significantly. Nevertheless, even though beneficiation by itself does not appear worthwhile in terms of improving the liquefaction yields, it would hel reduce the solids loading during actual plant operation and minimize subsequent solid handling steps.

SCALE-UP STUDIES

The experimental results generated throughout most of this program indicated that solvent modification improved oil production in both noncatalytic and catalytic coal liquefaction. However, these results were obtained in a small tubing-bomb reactor, and researchers were not sure whether the same effects would be noted under scaled-up conditions. Therefore, a larger 300-mL semicontinuous reactor system was designed and used to test liquefaction of Illinois #6 coal with both original and modified solvents, with and without catalyst.

Using modified solvent in noncatalytic liquefaction marginally improved oil yields and coal conversion compared to the base liquefaction solvent, in contrast to the results obtained in the tubing-bomb reactor.

The yields noted during catalytic liquefaction clearly showed the benefit of using modified solvent, substantiating what we had observed with the tubing-bomb reactor.

Deep-cleaned or beneficiated Illinois #6 coal was also liquefied in the autoclave reactor, with and without catalyst and with both original and modified solvents. Noncatalytic liquefaction with base liquefaction (nontreated) solvent resulted in a net loss of oil yield, confirming the results noted in the tubing-bomb reactor. Runs with modified solvent increased oil production and lowered SRC production. Yields from catalyzed liquefaction runs in the scaled up reactor also paralleled the results noted in the tubing-bomb runs.

With regard to oil yield and coal conversion, use of beneficiated coal again showed no clear advantage over raw (untreated) coal. However, advantages of coal beneficiation became clear when the results were compared on the same weight basis. Beneficated coal yielded more oil and net products than raw coal. In addition, coal beneficiation reduced the production of liquefaction residue. This would decrease the load on the solid/liquid separator and improve its efficiency.

EXPLORATORY STUDIES

The final portion of this program consisted of several exploratory experiments designed to increase oil production beyond that already achieved. Studies focused on finding the optimum reaction conditions, finding the best catalyst or combination of catalysts, and studying the effect of recycling unconverted SRC.

Optimum Reaction Conditions

Since we know that the activity of dispersed molybdenum was greater than that of impregnated molybdenum and equivalent to that of iron, we searched for optimum reaction conditions using molybdenum in the dispersed form. Reaction variables studied were reaction temperature, residence time, initial hydrogen pressure, solvent-to-coal ratio, and catalyst concentration. Selection of the best reaction conditions was based on increased oil yield and overall coal conversion and decreased gas yield. Detailed study resulted in selection of the following conditions: 440°C reaction temperature, 60-min residence time, 1,200-psig initial hydrogen pressure, 1,000 strokes per minute agitation rate, solvent-to-coal ratio of 1:1, and molybdenum catalyst concentration of 250 ppm based on coal.

Optimum Catalyst

In an attempt to further increase oil production, the activities of nickel and iron were tested using modified base liquefaction solvent and the optimal reaction conditions. Metal combinations were also examined to see whether oil yield could be increased or catalyst cost reduced.

Results showed that nickel would not be beneficial, but either iron or molybdenum would be suitable and selection should be based on cost. The combination of 125-ppm Mo with 0.5% Fe was as good as 250-ppm Mo alone.

One can conclude that the oil yield and coal conversion obtained with 250-ppm Mo are close to the maximum obtainable. However, combining catalysts can improve oil yield and coal conversion somewhat, so that ultimate selection should be based on the best economics.

Effect of SRC Recycle

Since recycling light SRC had been reported to significantly improve the liquefaction performance of coals at the WACLF, several SRC recycle experiments were performed to evaluate its effects on liquefaction using both base liquefaction and modified solvents in the presence and absence of catalysts.

Recycling SRC in noncatalytic coal liquefaction significantly increased oil yield with both base liquefaction and modified solvents. However, coal conversion decreased considerably. Increasing the level of SRC recycle in the reaction mixture further increased oil yield with both solvents, but the increase in oil yield was much greater with base liquefaction solvent than with modified solvent. However, overall coal conversion further decreased with an increase in the level of SRC recycle; the decrease in conversion was dramatic with modified solvent.

Recycling SRC in catalytic coal liquefaction significantly increased oil yield with both base liquefaction and modified solvents. Unlike the dramatic decrease in coal conversion with SRC recycle in noncatalytic liquefaction, coal conversion decreased marginally in the presence of a catalyst. In fact, an increase in catalyst concentration restored coal conversion to the level noted without SRC recycle.

The benefits of SRC recycle were clearly demonstrated by the dramatic increase in oil yield--to as much as 70% of the product slate. However, this was achieved only in the presence of a catalyst.

Recommendations for Further Investigation

In this program, several novel approaches were identified to increase oil yield in coal liquefaction. However, the following work is needed to fully understand their role and exploit their potential in coal liquefaction:

1. Investigate solvent modification on a large scale, and determine its effect upon steady-state catalytic and noncatalytic liquefaction.

2. Investigate poisoning or hindrance of the catalytic activity of individual metals or combinations of metals by heteroatomic compounds at steady state.

3. Investigate the effect of deep coal cleaning on catalytic liquefaction in a pilot plant. Furthermore, investigate the effect of recycling liquefaction residue containing spent catalyst upon liquefaction.

4. Investigate the effect of SRC recycle in catalytic liquefaction at steady state.

5. Investigate the overall economics of solvent modification, catalyst application, deep coal cleaning, and SRC recycle to identify the best mode of operation.

Patent Activity

A total of nine inventions were disclosed based upon the research conducted under this contract. Appendix 3 provides a compilation of all the Record of Invention forms disclosed to the Department of Energy.

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II. EXPERIMENTAL PROGRAM

COAL FEEDSTOCKS

Coals from western Kentucky and Illinois (Kentucky #9 Fies and Illinois #6 Burning Star mines) were tested in this program. These two coals differ significantly from coals in eastern Kentucky: in their inorganic (mineral) composition; the functionality of elements such as hydrogen, sulfur, and oxygen; the distribution of ion-exchange elements such as calcium and sodium; their petrographic composition; and their coal rank.

Samples of these two coals were supplied by the Wilsonville Advanced Coal Liquefaction Facility. As specified in the program plan, Illinois #6 coal was tested extensively in the program, whereas Kentucky #9 coal was used to provide supporting data. Detailed analyses of the coal samples (Table 1) showed that they contained a significant amount of ash. The pyritic sulfur content in both samples was typical of a western Kentucky coal. The samples were crushed and sieved to -150 mesh before use.

PROCESS SOLVENTS

One of the key factors in the development of a coal liquefaction process is solvent self-sufficiency. Coal liquefaction solvents derived from coal, petroleum, and tar sands can all be used for starting up an operation. During liquefaction, the start-up solvent is then slowly replaced by solvent material generated from the feed coal during the process, so that the concentration of coal-derived process solvent increases with the number of recycle passes. At steady state, the recycle solvent will be completely derived from the coal used in the plant. Because each coal type is unique and has a different liquefaction behavior, it is preferable to study coal liquefaction using a process-derived solvent generated at steady state from the same coal type.

Therefore, in order to avoid a mismatch of solvents and coals, liquefaction testing of the two coals studied in this program was conducted with solvents that had been generated from steady-state operation of the Wilsonville plant

TABLE 1

ANALYSIS OF COAL SAMPLES

	wt %	
	Kentucky #9	Illinois #6
Proximate analysis		
Moisture	2.30	2.54
Ash	8.90	10.46
Volatile	--	37.56
Fixed carbon	--	49.44
Ultimate analysis		
C	71.40	68.43
H	5.09	4.96
O (by difference)	7.63	8.93
N	1.40	1.38
S	3.10	3.23
Cl	0.18	0.07
Distribution of sulfur		
Total sulfur	3.10	3.23
Pyrite sulfur	0.82	1.09
Sulfate sulfur	0.20	0.00
Organic sulfur	2.08	2.14

under standard SRC-I process conditions using either Illinois #6 or Kentucky #9 coal. Detailed analyses of the two starting liquefaction solvents are presented in Table 2. Both samples contained considerable amounts of heteroatom (nitrogen and oxygen) compounds. Starting liquefaction solvent derived from Illinois #6 coal also contained a large amount of pentane-insoluble material such as SRC (13.0 wt %), which was due to the recycle of LSRC (light solvent-refined coal) to the dissolver stage at Wilsonville. However, starting liquefaction solvent derived from Kentucky #9 coal contained an insignificant amount of pentane-insoluble material.

Pentane-insoluble material not only complicates the treatment of liquefaction solvent, but also makes interpretation of coal liquefaction data very difficult. Therefore, this material was removed from the Illinois #6 coal derived starting liquefaction solvent by pentane extraction, and the resulting pentane-soluble product was used as the base liquefaction solvent for this program. Both the pentane solubles and insolubles recovered from the extraction were analyzed. As summarized in Table 3, the analyses revealed that pentane extraction was effective in segregating the high heteroatom-containing compounds, namely the SRC-type material present in the starting liquefaction solvent, into the raffinate. The pentane-soluble oils of the extracted product revealed a reduction in oxygen and nitrogen content of 32 and 35%, respectively.

PROCESS SOLVENT FROM SRC HYDROTREATER

Process solvent from a hydrotreater typically contains more than 8.5% hydrogen. The aromatic compounds present in the hydrotreater are predominantly paraffins and cycloparaffins, which are thought to be poor hydrogen donors. Hydrotreater process solvent, however, contains less than 1 wt % poisonous heteroatoms. Therefore, the hydrotreater solvent presented an opportunity to determine the effect of poisonous heteroatoms during both thermal and catalytic coal liquefaction reactions. It was also instrumental in determining the role of cycloparaffins in coal liquefaction.

TABLE 2

ANALYSIS OF STARTING LIQUEFACTION SOLVENTS

	wt %	
	Kentucky #9	Illinois #6
Solvent separation[a]		
Oil	98.0	87.0
SRC	1.8	12.3
Insoluble organic material (IOM)	0.2	0.7
Element		
Carbon	86.49	86.56
Hydrogen	8.64	8.06
Oxygen	3.18	3.31
Nitrogen	0.84	1.03
Sulfur	0.62	0.68

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[a] Oil - pentane solubles
SRC - pentane insolubles, methylene chloride/methanol solubles
IOM - methylene chloride/methanol insolubles

TABLE 3

PENTANE EXTRACTION OF STARTING LIQUEFACTION SOLVENT DERIVED FROM ILLINOIS #6 COAL

Element	Starting liquefaction solvent	wt %	
		Solubles	Insolubles
Carbon	86.56	88.02	80.59
Hydrogen	8.06	8.57	6.83
Oxygen	3.31	2.25 (32)[a]	6.89
Nitrogen	1.03	0.67 (35)	2.10
Sulfur	0.68	0.62	1.07

---

[a] Numbers in parentheses are weight percent reduction upon extraction.

The hydrotreater solvent used in liquefaction experiments was generated by hydrotreating a mixture of process solvent and SRC in a catalytic hydrocracker at Wilsonville. This sample contained no appreciable amount of pentane-insoluble material such as SRC. The detailed analysis of hydrotreater solvent is presented in Table 4.

SOLVENT-REFINED COAL (SRC)

Several samples of SRC were generated in various catalytic and noncatalytic liquefaction experiments in a tubing-bomb reactor using base liquefaction and modified solvents. These samples were then recycled to study their effect on catalytic and noncatalytic liquefaction. A sample of SRC generated in a noncatalytic liquefaction experiment with base liquefaction solvent was recycled only to a liquefaction run involving no catalyst and base liquefaction solvent. A similar procedure was followed with other SRC samples to prevent a mismatch of samples.

CATALYSTS

An oil-soluble molybdenum compound, molybdenum octoate, containing 8 wt % molybdenum as free metal was obtained from Shepard Chemical Company, Cincinnati, Ohio. A number of other oil-soluble metal catalysts such as nickel octoate, iron naphthenate, and zinc naphthenate were acquired from Mooney Chemicals, Columbus, Ohio, and tested in the program for their catalytic activity. Ammonium molybdate was received from Climax Molybdenum Company, Greenwich, Connecticut. Other catalysts such as iron sulfate, zinc sulfate, nickel nitrate, and cobalt nitrate were supplied by Fisher Scientific Company, Fair Lawn, New Jersey.

TABLE 4

ANALYSIS OF HYDROTREATER SOLVENT

	wt %
Pentane solubles	100.0
Element	
Carbon	89.3
Hydrogen	9.7
Oxygen	0.5
Nitrogen	0.5
Sulfur	<0.1
Distribution of oxygen compounds	
O as O	0.35
O as OH	0.15
Distribution of nitrogen compounds	
N as N	0.16
N as NH	0.05
N as NH_2	0.29

EQUIPMENT DESCRIPTION

Tubing-Bomb Reactor

A 50-mL tubing-bomb reactor was designed and assembled at Air Products for catalytic and noncatalytic coal liquefaction screening studies. The reactor assembly is shown in Figure 1. A reaction mixture containing 3 g of coal, 6 g of liquefaction solvent, and a predetermined amount of catalyst (if any) was used in most of the experiments. The reactor was pressurized with hydrogen to 850 psig at 25°C, leak-tested, and placed in a preheated fluidized sand bath. Typically, less than two minutes was required to heat the reactor to reaction temperature. The reactor was agitated at 1,000 strokes per minute with the help of a variable-speed motor. Reactor temperature was maintained for a specified time, after which the reactor was cooled by placing it in a water bath. Product gases were collected and analyzed, and the slurry was solvent-separated to determine product distribution. A summary of the solvent separation procedure is outlined in Appendix 1.

Semicontinuous Autoclave Reactor

A 300-mL semicontinuous autoclave reactor was designed, built, and operated at Air Products for scaled-up catalytic and noncatalytic coal liquefaction studies. The unit was designed for a continuous flow of hydrogen to ensure sufficient hydrogen supply for the reaction. The experimental setup is illustrated in Figure 2.

The reaction mixture for the liquefaction experiments consisted of 40 g of coal, 60 g of liquefaction solvent, and a predetermined amount of catalyst (if any). The system was leak-tested with helium to 2,500 psig pressure at room temperature. The system was depressurized and hydrogen flow was established to thoroughly purge the system. The reactor was then pressurized with hydrogen to 1,000 psig. The reactor heating was started at this point. The reactor's pressure was raised to 2,000 psig when its temperature reached 250°C. The continuous flow of hydrogen was also initiated to ensure availability of enough hydrogen for the reaction. The reactor was maintained at the desired temperature for a specific length of time, after which the

FIGURE 1
REACTOR SYSTEM USED IN LIQUEFACTION EXPERIMENTS

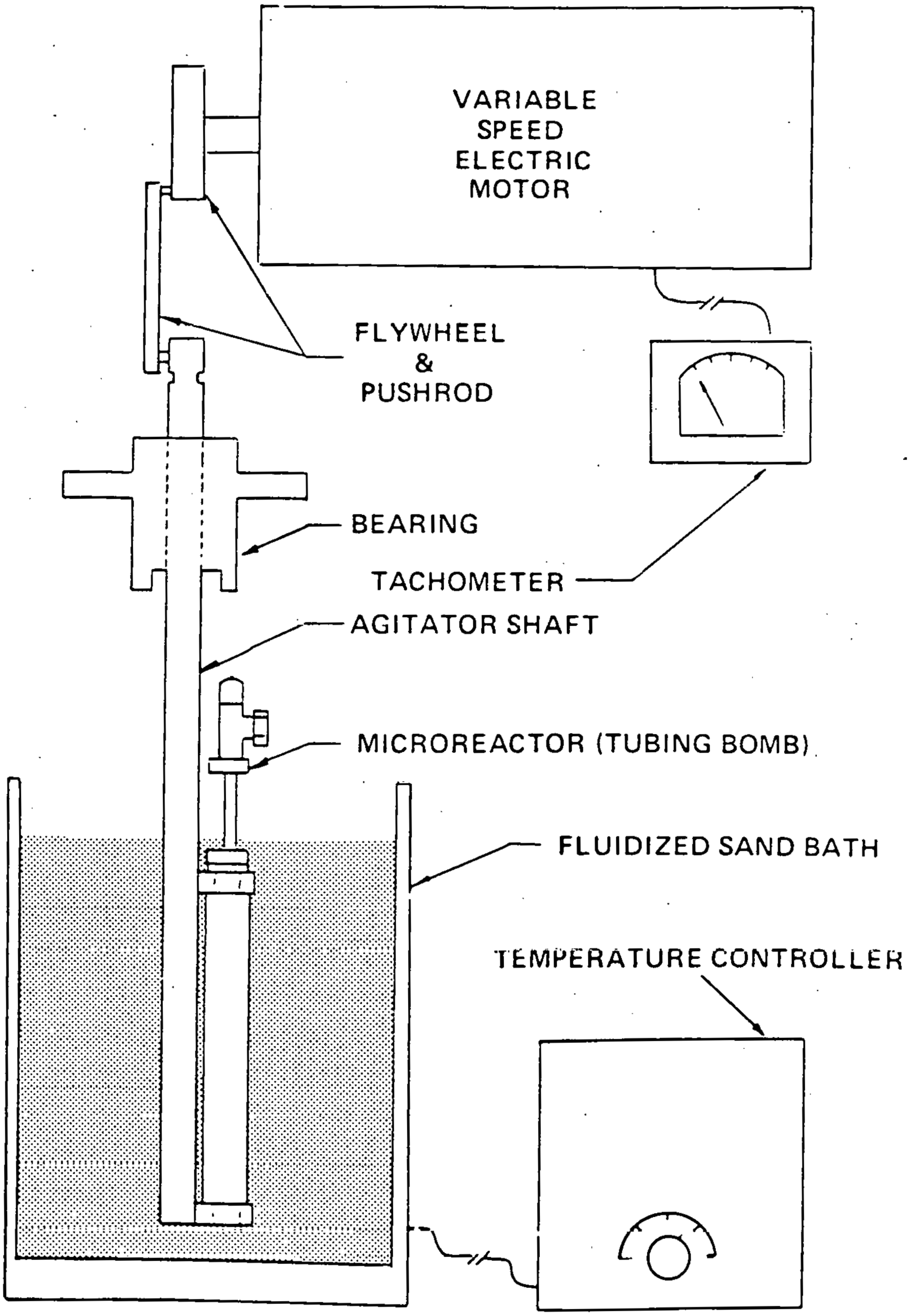
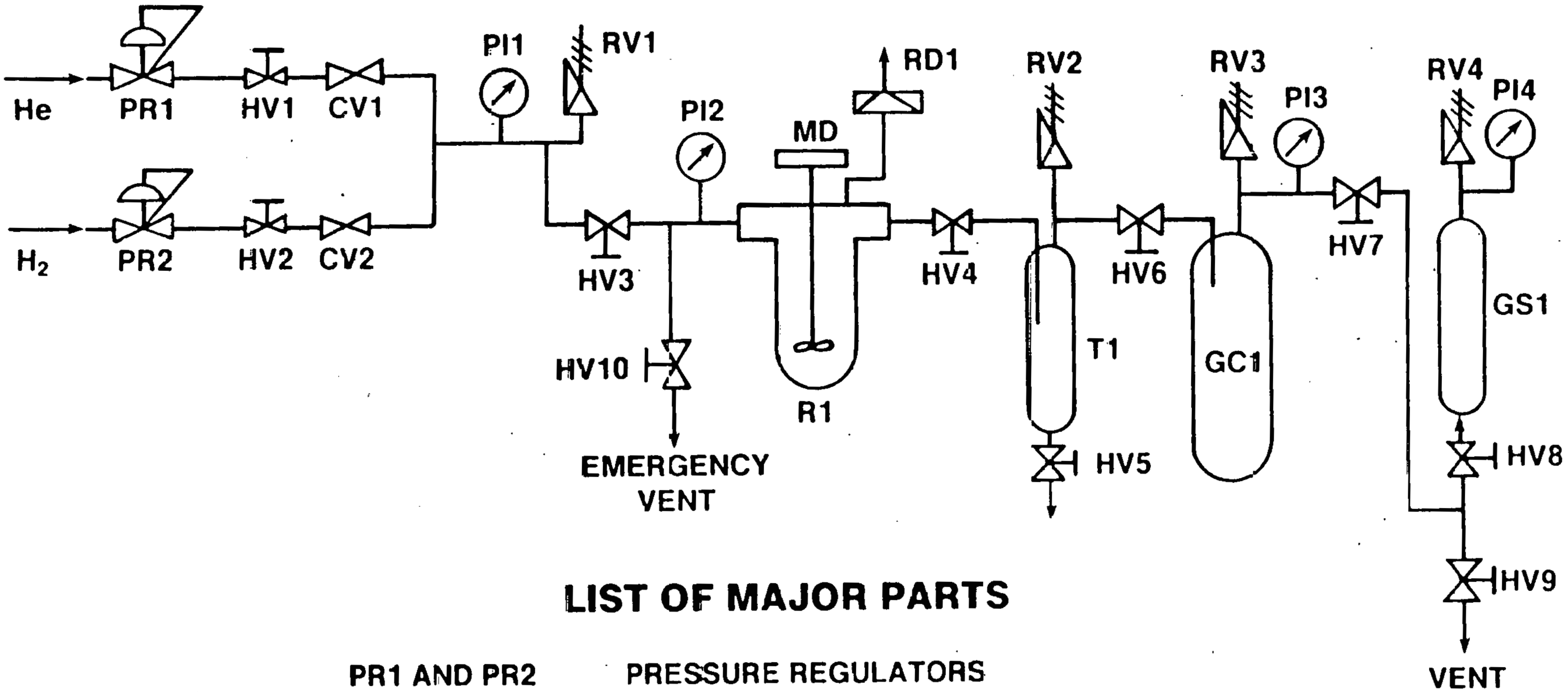


FIGURE 2
SCHEMATIC OF 300-ML AUTOCLAVE REACTOR



LIST OF MAJOR PARTS

PR1 AND PR2	PRESSURE REGULATORS
HV1 TO HV10	HIGH-PRESSURE FLOW-CONTROL VALVES
CV1 AND CV2	CHECK VALVES
PI1 TO PI4	PRESSURE INDICATORS
RV1 TO RV4	RELIEF VALVES
R1	300-ML AUTOCLAVE REACTOR
MD	MAGNE-DRIVE UNIT
RD1	RUPTURE DISC

heaters were turned off and the hydrogen flow was discontinued. The product gases were collected and analyzed, and the slurry was distilled to determine the product distribution. The detailed operating and calculation procedures for the autoclave reactor are presented in Appendix 2.

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III. SOLVENT MODIFICATION

Samples of process solvents derived from Illinois #6 and Kentucky #9 coals were treated to remove nitrogen bases or phenols or both. A sample of hydrotreater solvent was also treated to remove heteroatomic compounds. Several methods were employed to treat the process solvent derived from Illinois #6 coal, but only limited work was conducted to remove heteroatomic compounds from both the Kentucky #9 coal and hydrotreater solvents. In each case, since the process solvents were soluble in n-pentane, it was used as a diluent in experiments to remove the nitrogen bases and phenols from the process solvent.

TREATMENT OF ILLINOIS #6 COAL DERIVED LIQUEFACTION SOLVENT

Removal of Nitrogen Bases

To remove nitrogen bases, samples of the base liquefaction solvent were treated with either anhydrous hydrochloric acid, silica gel, or a mixture of 50% silica gel/50% neutral alumina. The hydrochloric acid treatment was performed by dissolving the base liquefaction solvent in pentane and bubbling dry hydrogen chloride gas through it, which precipitated the hydrogen chloride salts of the nitrogen bases from the solution. The liquid was then decanted, neutralized with ammonia gas, and filtered, and the pentane was removed by rotoevaporation.

In the other two treatments, namely, with silica gel and a mixture of 50/50 silica gel and neutral alumina, the base liquefaction solvent was dissolved in pentane and mixed with an equal weight of the solid adsorbent. The mixture was decanted, the solid adsorbent was washed with additional pentane, and all of the pentane was removed by rotoevaporation. The resulting material was then used in subsequent liquefaction experiments.

The elemental analysis and distribution of nitrogen and oxygen in the products from the solvent treatments are summarized in Table 5. From all three procedures, approximately 80% of the original material was recovered. The remaining 20% of the material either reacted with HCl or adsorbed on silica gel was not recovered. Treatment with HCl, silica gel, and silica gel/neutral

TABLE 5

SOLVENT TREATMENT TO REMOVE NITROGEN BASES FROM BASE LIQUEFACTION SOLVENT

	Base liquefaction solvent	Treated solvents		
		HCl gas	Silica gel	Silica g neutra alimin
Treated solvent (wt % of base liquefaction solvent)	--	82	80	83
Element				
Carbon	88.02	88.78	89.14	89.25
Hydrogen	8.57	9.17	8.78	8.72
Oxygen	2.25	1.68	1.31	1.67
Nitrogen	0.67	0.16	0.08	0.14
Sulfur	0.62	0.69	0.69	0.63
Distribution of nitrogen compounds				
N as N	0.28	ND[a]	ND	ND
N as NH	0.15	ND	0.02	0.08
N as NH_2	0.24	0.16	0.06	0.06
Distribution of oxygen compounds				
O as O	1.10	1.18	0.71	1.20
O as OH	1.15	0.50	0.60	0.47

---

[a] ND - not detected

76, 88, and 79% removal of total nitrogen, respectively. The near-infrared (NIR) data show complete removal of basic nitrogen compounds (nitrogen as quinoline) by HCl and silica gel treatment. The nitrogen base removal was accompanied by a corresponding removal of oxygen, namely, 25, 42, and 25%, respectively. The reason for this simultaneous removal of nitrogen and oxygen compounds is not understood. To understand why, more work is required to ascertain the true chemistry of the compounds that are removed and their interaction.

Removal of Phenols

Samples of base liquefaction solvent were also treated in various ways to remove the phenolic components. Aqueous sodium hydroxide treatment was carried out by vigorously shaking a 10% solution of sodium hydroxide with a sample of base liquefaction solvent dissolved in pentane. After standing, the organic phase was separated from the aqueous phase and washed with distilled water, after which the pentane was removed by rotoevaporation. Both basic alumina and a Y-type zeolite (see Table 6 for detailed analysis) were used to adsorb the phenols by mixing an equal weight of the adsorbent with base liquefaction solvent dissolved in pentane. A pentane wash of the solid adsorbent was added to the decanted liquid and the material rotoevaporated to remove the pentane.

The results of the phenol removal experiments are presented in Table 7. The amount of treated solvent recovered varied from 83 to 87% of the original amount, which was slightly higher than that noted in the experiments to remove nitrogen bases. Treatment with NaOH, basic alumina, and zeolite removed approximately 24-25% total oxygen from the base liquefaction solvent. There was also removal of 10% nitrogen with NaOH, 13% with basic alumina, and 39% with zeolite. The treatments did not remove basic nitrogen compounds (nitrogen as quinoline) -- only NH_2 compounds (Table 7). The NIR data summarized in Table 7 show only a negligible removal of ethereal oxygen compounds from the base liquefaction solvent. The removal of phenols was highest with NaOH (61%) and lowest with zeolite (45%).

TABLE 6

ANALYSIS OF LINDE LZ-Y82 ZEOLITE[a]

	Weight %
SiO_2	72.2
Al_2O_3	22.8
Na_2O	0.2
$(NH_4)_2O$	4.0
SiO_2/Al_2O_3, molar ratio 5.38	

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[a] Analysis provided by Union Carbide Corporation, Moorestown, N.J.

TABLE 7

SOLVENT TREATMENT TO REMOVE PHENOLS FROM BASE LIQUEFACTION SOLVENT

	Base liquefaction solvent	Treated solvents		
		NaOH	Basic alumina	Y-Zeolite
Treated solvent (wt % of base liquefaction solvent)	--	--	87	83
Element				
Carbon	88.02	88.59	88.61	88.29
Hydrogen	8.57	8.52	8.74	8.85
Oxygen	2.25	1.63	1.62	1.77
Nitrogen	0.67	0.60	0.58	0.41
Sulfur	0.62	0.66	0.61	0.60
Distribution of nitrogen compounds				
N as N	0.28	0.33	0.29	0.29
N as NH	0.15	0.17	ND[a]	0.04
N as NH_2	0.24	0.10	0.29	0.08
Distribution of oxygen compounds				
O as O	1.10	1.18	1.04	1.14
O as OH	1.15	0.45	0.58	0.63

---

[a] ND - not detected

Removal of Both Phenols and Nitrogen Bases

Two samples of base liquefaction solvent, one pretreated with HCl to remove nitrogen bases and the other pretreated with NaOH to remove phenols, were treated further to remove additional heteroatomic compounds. The sample pretreated with HCl was further treated with silica gel, and the sample pretreated with NaOH was further treated with HCl. Analyses of the base liquefaction and treated solvent samples are compared in Table 8. The amount of treated solvent recovered was approximately 63% of the original amount, and nitrogen compounds were completely removed from the base liquefaction solvent in both cases. Treatment with HCl followed by silica gel resulted in a 64% removal of oxygen, whereas treatment with NaOH followed by HCl gave 59% oxygen removal.

Additional Treatment

In addition to the treatments just discussed, several other techniques were applied to remove nitrogen bases and phenols from the pentane-extracted starting liquefaction solvent (base liquefaction solvent) derived from Illinois #6 coal.

Removal of Nitrogen Compounds. Samples of base liquefaction solvent were treated with several clays to remove nitrogen compounds. The treatment involved dissolving the solvent in pentane and mixing in an equal weight of the solid adsorbent (clays). The mixture was decanted, the solid adsorbent was washed with additional pentane, and all of the pentane was removed by rotoevaporation. The detailed analyses of the treated solvents are summarized in Table 9.

Treatment of the solvent with bentonite (natural magnesium/aluminum silicate) and kaolin (natural aluminum silicate) removed almost none of the nitrogen or oxygen compounds. Likewise, attapulgus clay (natural magnesium silicate) and syloid (natural silica) were marginally effective in removing nitrogen and oxygen compounds compared to silica gel (Table 9). Contrary to attapulgus clay, another form of natural magnesium silicate, sepiolite, was moderately active in removing nitrogen and oxygen compounds compared to silica gel.

TABLE 8

SOLVENT TREATMENT TO REMOVE BOTH PHENOLS AND NITROGEN BASES FROM BASE LIQUEFACTION SOLVENT

	Base liquefaction solvent	Treated solvents: HCl followed by silica gel	Treated solvents: NaOH followed by HCl
Treated solvent (wt % of base liquefaction solvent)	--	63	--
Element			
Carbon	88.02	89.52	89.50
Hydrogen	8.57	9.06	9.14
Oxygen	2.25	0.81	0.93
Nitrogen	0.67	<0.05	<0.05
Sulfur	0.62	0.66	0.65
Distribution of oxygen compounds			
O as O	1.10	0.60	0.67
O as OH	1.15	0.21	0.26
Distribution of nitrogen compounds			
N as N	0.28	ND[a]	ND
N as NH	0.15	ND	ND
N as NH_2	0.24	ND	ND

[a] ND - not detected

TABLE 9

SOLVENT TREATMENT TO REMOVE NITROGEN COMPOUNDS FROM BASE LIQUEFACTION SOLVENT

	Base liquefaction solvent	Treated solvents								
								HCl-treated sepiolite		
		Bentonite	Kaolin	Porocel	Attapulgus clay	Syloid	Sepiolite	Not activated	Activated	Silica gel
Treated solvent (wt % of base liquefaction solvent)	--	98.6	98.9	89.2	92.0	92.2	92.4	94.0	90.4	80.0
Element										
Carbon	88.02	87.87	87.76	88.37	ND	88.11	88.50	88.64	88.84	89.14
Hydrogen	8.57	8.47	8.43	8.48	ND	8.77	8.62	9.14	9.10	8.78
Oxygen	2.25	2.32	2.43	2.18	2.07	2.02	1.80	1.75	1.60	1.31
Nitrogen	0.67	0.73	0.77	0.75	0.62	0.59	0.50	0.42	0.39	0.08
Sulfur	0.62	ND[a]	ND	0.65	ND	ND	ND	ND	ND	0.69
Heteroatom removal (wt %)										
Nitrogen	--	0.0	0.0	0.0	7.5	11.9	25.4	37.3	41.8	88.1
Oxygen	--	0.0	0.0	3.1	8.0	10.2	20.0	22.2	28.9	41.8

---

[a] ND - not determined

Sepiolite's ability to remove nitrogen compounds increased considerably when washed with dilute hydrochloric acid before use (Table 9). Furthermore, activation of acid-washed sepiolite by heat treatment further enhanced its heteroatom removal activity.

Based on our results, silica gel appears to be the best solid adsorbent for removing both nitrogen and oxygen compounds from the base liquefaction solvent compared to several other clays and solid adsorbents tested in the program.

Removal of Oxygen Compounds. A sample of base liquefaction solvent was treated with acidic alumina to compare its ability to remove phenolic components with that of basic alumina. First, an equal weight of the adsorbent was mixed with the solvent dissolved in pentane. A pentane wash of the solid adsorbent was then added to the decanted liquid and the material rotoevaporated to remove the pentane. The amount of treated solvent recovered was 88% of the original amount, which was very similar to that noted with the use of basic alumina (Table 10).

The treatment removed approximately 17% total oxygen from the base liquefaction solvent, which was, as expected, lower than that noted with basic alumina. The treatment, however, removed mainly oxygen compounds such as phenols (O as OH) from the solvent (approximately 31%). Surprisingly, it did not remove any nitrogen compounds.

TREATMENT OF KENTUCKY #9 COAL DERIVED LIQUEFACTION SOLVENT

Samples of starting liquefaction solvent derived from Kentucky #9 coal were also treated with both silica gel and basic alumina to remove nitrogen bases and phenols. In the experiments with these materials, the adsorbed phenols and nitrogen bases were recovered by eluting them with a mixture of methylene chloride and methanol. The amounts and analyses of treated liquid product and adsorbed material are presented in Table 11.

TABLE 10

SOLVENT TREATMENT TO REMOVE OXYGEN COMPOUNDS FROM BASE LIQUEFACTION SOLVENT

	Base liquefaction solvent	Treated solvents	
		Acidic alumina	Basic alumina
Treated solvent (wt % of base liquefaction solvent)	--	88	87
Element			
Carbon	88.02	88.38	88.61
Hydrogen	8.57	8.57	8.74
Oxygen	2.25	1.86	1.62
Nitrogen	0.67	0.70	0.58
Sulfur	0.62	0.68	0.61
Distribution of nitrogen compounds			
N as N	0.28	0.28	0.29
N as NH	0.15	0.19	ND[a]
N as NH_2	0.24	0.23	0.29
Distribution of oxygen compounds			
O as O	1.10	1.07	1.04
O as OH	1.15	0.79	0.58

[a] ND - not determined

TABLE 11

ANALYSIS OF STARTING LIQUEFACTION AND MODIFIED SOLVENTS DERIVED FROM KENTUCKY #9 COAL TREATED WITH BASIC ALUMINA AND SILICA GEL

	Liquefaction solvent	Basic alumina Modified solvent	Basic alumina Adsorbed	Silica gel Modified solvent	Silica gel Adsorbed
Wt % of liquefaction solvent	--	88.8	11.2	80.2	19.8
Element					
Carbon	86.49	88.13	81.34	88.45	82.25
Hydrogen	8.64	8.19	7.54	9.24	7.61
Oxygen	3.18	1.94	8.68	1.65	6.60
Nitrogen	0.84	0.70	1.64	0.23	2.56
Sulfur	0.62	0.54	0.55	0.51	0.47
Solvent separation[a]					
Oil	98.0	100.0	--	100.0	--
SRC	1.8	0.0	--	0.0	--
Insoluble organic material (IOM)	0.2	0.0	--	0.0	--

[a] Oil - pentane solubles

SRC - pentane insolubles, methylene chloride/methanol solubles

IOM - methylene chloride/methanol insolubles

The recovery of modified liquefaction solvent from silica gel and basic alumina treatment was 80 and 89%, respectively. Treatment with basic alumina resulted in 39 and 16% removal of oxygen and nitrogen, respectively. Silica gel not only adsorbed more material compared to basic alumina, but also removed considerably more oxygen and nitrogen from the solvent, namely, 48 and 73%, respectively.

TREATMENT OF HYDROTREATER SOLVENT

A hydrotreater solvent also used in liquefaction experiments was generated by hydrotreating a mixture of process solvent and SRC in a catalytic hydrocracker at the Wilsonville Advanced Coal Liquefaction Facility. This sample contained no appreciable amount of pentane-insoluble material such as SRC, and was used to prepare modified hydrotreater solvent by removing parts of both nitrogen bases and phenols with silica gel. This modified hydrotreater solvent was also used in the liquefaction tests. The detailed analyses of hydrotreater and modified hydrotreater solvents are presented in Table 12. Notice that treatment of hydrotreater solvent with silica gel removed only 30 and 50%, respectively, of the oxygen and nitrogen compounds. The extent of oxygen and nitrogen removal from the hydrotreater solvent by silica gel was considerably lower than that noted in the cases of base liquefaction solvent (Illinois #6 coal) and liquefaction solvent (Kentucky #9 coal).

TABLE 12

ANALYSIS OF HYDROTREATER AND MODIFIED HYDROTREATER SOLVENTS

	wt %	
	Hydrotreater solvent	Modified hydrotreater solvent
Pentane solubles	100.0	100.0
Element		
Carbon	89.3	89.2
Hydrogen	9.7	10.2
Oxygen	0.5	0.35
Nitrogen	0.5	0.25
Sulfur	<0.1	<0.1
Distribution of oxygen compounds		
O as O	0.35	0.23
O as OH	0.15	0.12
Distribution of nitrogen compounds		
N as N	0.16	0.12
N as NH	0.05	<0.01
N as NH_2	0.29	0.12

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IV. EFFECT OF SOLVENT MODIFICATION ON COAL LIQUEFACTION

The liquefaction behavior of Illinois #6 and Kentucky #9 coals was studied in a 50-mL tubing-bomb reactor using base liquefaction, modified, and hydrotreater solvents in the presence and absence of catalyst. A temperature of 425°C, a time of 60 min, 850 psig cold hydrogen pressure, 3 g of coal, 6 g of liquefaction solvent, and an agitation rate of 1,000 strokes per minute were chosen as standard reaction conditions (these reaction conditions are termed as low-severity conditions in this report) for evaluating the impact of modified liquefaction solvents and/or catalyst on dissolution.

ESTABLISHING BASELINE DATA

Liquefaction of Illinois #6 Coal with Base Liquefaction Solvent

To establish baseline data, the noncatalytic liquefaction behavior of Illinois #6 coal was first studied by using the Illinois #6 coal derived base liquefaction solvent discussed earlier. Duplicate runs were made to determine the reproducibility of the data.

As summarized in Table 13, the data show an overall coal conversion of 82%, which is low compared to the 90-92% range reported in the literature for the same coal. The reason for this difference is the use of a mixture of methylene chloride and methanol in the solvent separation procedure, instead of pyridine or creosol oil, which, because they are stronger solvents, would yield higher values for overall coal conversion. The production of oils and gases was 13 and 8%, respectively. The data in Table 13 show very good reproducibility for overall coal conversion and gas production. The variation in oil production from the mean value was approximately 2 wt % absolute, which was acceptable for the tubing-bomb reactor experiments.

To establish baseline data for a catalyzed reaction, molybdenum octoate was added to a reaction mixture identical to the one used above at a concentration of 500-ppm molybdenum metal based on coal. The data in Table 13 show that overall coal conversion increased from 82 to 92% with molybdenum catalyst

TABLE 13

LOW-SEVERITY LIQUEFACTION OF ILLINOIS #6 COAL[a]

	No catalyst			500-ppm molyb
	Run 1	Run 2	Average	catalyst
Product distribution (wt % MAF coal)[b]				
Gases	7.9	8.3	8.1	8.2
Oil	14.4	10.4	12.4	25.4
SRC	60.0	64.2	62.1	58.4
IOM	17.7	17.1	17.4	8.0
Conversion	82.3	82.9	82.6	92.0

---

[a] Reaction mixture:

Coal	3 g
Solvent	6 g

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per minute

[b] Oil - pentane solubles
SRC - pentane insolubles, methylene chloride/methanol solubles
IOM - methylene chloride/methanol insolubles

addition. Furthermore, oil production increased from 12 to 25% and, as expected, SRC production decreased, from 62 to 58%. The increase in oil production was due to the increased conversion of coal as well as SRC.

These baseline data were generated at 425°C -- low-severity reaction conditions. In addition, baseline data were developed under high-severity reaction conditions -- 440°C and 1,200-psig hydrogen pressure. The effect of reaction conditions and catalyst concentration on coal liquefaction is discussed in detail in the Exploratory Studies section. Results of the baseline runs are presented in Table 14. Without catalysts, more oil and gases were produced at high-severity than at low-severity conditions (compare Tables 13 and 14). However, conversion dropped when the severity of reaction conditions increased, indicating an onset of retrograde reactions.

Addition of 250 ppm of molybdenum catalyst at high-severity conditions significantly increased the oil yield from 29 to 45% (Table 14). Coal conversion was also significantly higher.

Comparison of the data in Tables 13 and 14 indicates that, in noncatalytic liquefaction, increasing the reaction severity increased oil yield, but at the expense of coal conversion. Contrary to this, increasing the reaction severity in the presence of a catalyst increased the oil yield but without any penalty for coal conversion.

Liquefaction of Illinois #6 Coal with Hydrotreater Solvent

Baseline data were also generated with hydrotreater solvent under high-severity reaction conditions. The data summarized in Table 15 show that the use of hydrotreater solvent in the noncatalytic liquefaction of Illinois #6 coal resulted in approximately 45% oil yield and 90% coal conversion, values significantly higher than those noted with base liquefaction solvent (see Tables 13 and 15). The reasons for these higher yields could be that (1) the hydrotreater solvent contained much more hydrogen than did the base liquefaction solvent, possibly resulting in more hydrogen available for donation, as well as a higher rate of hydrogen transfer, and (2) the

TABLE 14

HIGH-SEVERITY LIQUEFACTION OF ILLINOIS #6 COAL[a]

	No catalyst	250 ppm molybdenum catalyst
Product distribution (wt % MAF coal)		
Gases	11.7	9.6
Oil	29.2	44.9
SRC	35.8	39.2
IOM	23.3	6.3
Conversion	76.7	93.7

---

[a] Reaction Mixture:

Coal	3 g
Solvent	3 g

Reaction conditions:

Temperature	440°C
H_2 Pressure	1,200 psig cold
Time	60 min
Agitation	1,000 strokes per min

TABLE 15

LIQUEFACTION OF ILLINOIS #6 COAL WITH HYDROTREATER SOLVENT[a]

	No catalyst			250-ppm molybdenum catalyst		
	I	II	Average	I	II	Average
Product distribution (wt % MAF coal)						
Gases	9.8	10.4	10.1	12.4	12.6	12.5
Oil	45.6	43.6	44.6	47.9	49.6	48.8
SRC	34.3	36.9	35.6	31.5	29.5	30.5
IOM	10.3	9.1	9.7	8.2	8.3	8.2
Conversion	89.7	90.9	90.3	91.8	91.7	91.8

[a] Reaction mixture:

Coal	3 g
Solvent	3 g

Reaction conditions:

Temperature	440°C
Pressure	1,200 psig H_2 cold
Time	60 min
Agitation	1,000 strokes per min

hydrotreater solvent contained significantly fewer heteroatomic compounds (se Table 12), resulting in higher autocatalytic activity of the mineral matter i the coal.

Experimental data obtained with 250 ppm of molybdenum catalyst in the presenc of hydrotreater solvent showed minor increases in both oil yield and coal conversion over the values obtained without catalyst. These results contrast sharply with the tremendous increases in both oil yield and coal conversion previously observed with base liquefaction and modified base liquefaction solvents during catalytic liquefaction compared to noncatalytic liquefaction. This information reveals that the properties of a liquefaction solvent are more important in controlling coal liquefaction than is the catalyst.

Liquefaction of Kentucky #9 Coal with Starting Liquefaction Solvent

The baseline data for the liquefaction of Kentucky #9 coal were generated using a starting liquefaction solvent derived from Kentucky #9 coal. Replicate runs made to determine experimental variance are summarized in Tabl 16. Noncatalytic liquefaction at 425°C resulted in overall coal conversion o 74%, and oil and gas yields of 12.7 and 6.5%, respectively. The data in Table 16 also show a maximum standard deviation of 2.5% for coal conversion, which reflects the good reproducibility of the experimental procedure.

To generate catalytic baseline data, 500 ppm of molybdenum metal based on coa was added to the reaction mixture in the form of molybdenum octoate. Reactio conditions were similar to those used for noncatalytic liquefaction. The catalyst was instrumental not only in increasing overall coal conversion from 74 to 85%, but also in increasing oil production from 13 to 17% (Table 16). However, the increase in oils was considerably lower than that observed with Illinois #6 coal. SRC production also increased from 55 to 64% with the catalyst. The increase in oil and SRC production was basically due to increased coal conversion.

TABLE 16

LIQUEFACTION OF KENTUCKY #9 FIES COAL[a]

	No catalyst	500-ppm molybdenum catalyst
Product distribution (wt % MAF coal)		
Gases	6.5 ± 1.1	5.0
Oil	12.7 ± 2.4	16.9
SRC	54.6 ± 1.9	63.5
IOM	26.2 ± 2.5	14.6
Conversion	73.8 ± 2.5	85.4

---

[a] Reaction mixture:

Solvent	6 g
Coal	3 g
Catalyst	500 ppm molybdenum based on coal

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per min

EFFECT OF SOLVENT TREATMENT ON LIQUEFACTION

Noncatalytic Liquefaction of Illinois #6 Coal

Modified Base Liquefaction Solvent. Samples of solvent prepared by treating coal-derived base liquefaction solvent by the different techniques discussed earlier were used in noncatalytic liquefaction experiments to evaluate their effect, and thereby the effect of heteroatom removal, on liquefaction. The results of these experiments are discussed below.

Samples prepared by treating the base liquefaction solvent with a mixture of silica gel and neutral alumina, or HCl followed by silica gel, were used in low-severity noncatalytic liquefaction experiments. The data are presented in Table 17. Oil production with these treated solvents increased considerably over the baseline run with base liquefaction solvent, and gas and SRC production decreased considerably. However, the overall conversion of coal, defined as methylene chloride/methanol solubles, decreased considerably with both treated solvents. This decrease in overall coal conversion could be due to the use of methylene chloride/methanol as an extracting solvent. Also, the lower dissolution power (physical solution power) of the treated solvents could have affected this value.

The data in Table 17 show that as more and more heteroatomic compounds were removed from the base liquefaction solvent, the physical dissolution power of the treated solvent decreased, as evidenced by decreasing coal conversion. However, oil production increased with increased removal of heteroatomic compounds.

The modified solvent generated by treating base liquefaction solvent with HCl followed by silica gel was also used to determine the effect of solvent treatment at high-severity reaction conditions. Once again, oil production was higher with treated solvent than with base liquefaction solvent (see Table 18). Coal conversion at these conditions was also higher with treated

TABLE 17

EFFECT OF SOLVENT TREATMENT ON LOW-SEVERITY NONCATALYTIC LIQUEFACTION OF ILLINOIS #6 COAL

	Base liquefaction solvent	Treated solvents	
		Silica gel/ neutral alumina	HCl/silica gel
Heteroatom concentration (wt %)			
N	0.67	0.14	<0.05
O	2.25	1.67	0.81
Nitrogen as nitrogen bases (N as quinoline)	0.28	ND [b]	ND
Oxygen as phenols (O as OH)	1.15	0.47	0.21
Product distribution (wt % of MAF coal)			
Gases	8.1	5.4	5.7
Oil	12.4	19.4	21.5
SRC	62.1	51.2	46.0
IOM	17.4	24.0	26.8
Conversion	82.6	76.0	73.2

[a] Reaction mixture:

Coal	3 g
Solvent	6 g

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per min

[b] ND - not detected

TABLE 18

EFFECT OF SOLVENT TREATMENT ON HIGH-SEVERITY NONCATALYTIC LIQUEFACTION OF ILLINOIS #6 COAL[a]

	Base liquefaction solvent	HCl/silica gel treated solvent
Product distribution (wt % MAF coal)		
Gases	11.7	11.9
Oil	29.2	33.3
SRC	35.8	32.2
IOM	23.3	22.6
Conversion	76.7	77.4

[a] Reaction mixture:

Coal	3 g
Solvent	3 g

Reaction conditions:

Temperature	440°C
H_2 pressure	1,200 psig H_2 cold
Time	60 min
Agitation	1,000 strokes per min

solvent, which contrasted with observations at low severity. Surprisingly, both oil yield and coal conversion with treated solvent were higher at high severity than at low severity (see Tables 17 and 18).

However, note that when base liquefaction solvent was used, oil yield increased as the reaction conditions became more severe, whereas coal conversion decreased. This indicates that base liquefaction solvent is a poor solvent for overall coal conversion. The above data clearly show the benefits of using treated solvent rather than base liquefaction solvent in noncatalytic liquefaction of coal.

Hydrotreater Solvent. Experiments were also carried out to determine the effect of removing heteroatomic compounds from hydrotreater solvent on noncatalytic liquefaction. Interestingly, removal of some of the heteroatomic compounds by silica gel from the hydrotreater solvent did not change the liquefaction behavior of Illinois #6 coal (Table 19). However, this is not surprising because detailed analysis of the modified hydrotreater solvent (Table 12) showed only marginal removal (20-25%) of both basic nitrogen (N as N) and phenolic (O as OH) compounds from the hydrotreater solvent by silica gel treatment. It would be interesting, however, to determine the effect upon liquefaction of complete removal of either nitrogen bases or phenols or both from the hydrotreater solvent.

Catalytic Liquefaction of Illinois #6 Coal

Modified Base Liquefaction Solvent. Base liquefaction solvent samples from which nitrogen bases or phenols or both were removed were used as liquefaction solvents with Illinois #6 coal in the presence of catalysts to evaluate the impact of removing heteroatomic compounds from the solvent on catalytic

TABLE 19

NONCATALYTIC LIQUEFACTION OF ILLINOIS #6 COAL WITH HYDROTREATER SOLVENT[a]

	Hydrotreater solvent			Modified hydrotreater solvent		
	I	II	Average	I	II	Avera
Product distribution (wt % MAF coal)						
Gases	9.8	10.4	10.1	10.8	12.0	11.
Oil	45.6	43.6	44.6	44.4	45.1	44.
SRC	34.3	36.9	35.6	35.5	32.9	34.
IOM	10.3	9.1	9.7	9.3	10.0	9.
Conversion	89.7	90.9	90.3	90.7	90.0	90.

[a] Reaction mixture:

Coal	3 g
Solvent	3 g

Reaction conditions:

Temperature	440°C
Pressure	1,200 psig H_2 cold
Time	60 min
Agitation	1,000 strokes per min

liquefaction. Again, molybdenum octoate was added to the reaction mixture at a concentration level of 500 ppm based on coal. Low-severity reaction conditions described earlier were used in all experiments. Results are discussed below.

Effect of Nitrogen Bases: Liquefaction solvent samples treated with anhydrous HCl or silica gel were tested to establish the effect of nitrogen bases on coal liquefaction. The experimental data summarized in Table 20 show a considerable increase in oil production, from 25 to 38%, when nitrogen bases were removed, with a corresponding decrease in SRC yield. Gas production decreased only marginally. In addition, overall coal conversion did not change with the removal of nitrogen bases, an observation that was contrary to that noted in noncatalytic coal liquefaction, in which overall coal conversion decreased with the removal of heteroatoms. Furthermore, this observation seriously questions the importance of a solvent's physical solvency power, which is due to the presence of heteroatomic compounds in the solvent, in catalytic coal liquefaction.

Of importance is the fact that removal of nitrogen bases from the coal-derived base liquefaction solvent was accompanied by removal of phenols. Therefore, any increase in oil production cannot be wholly attributed to the removal of nitrogen bases, since phenol removal might also have positively affected the reaction. However, the above experiments were unable to make this distinction. We can only conclude that nitrogen base removal does indeed enhance oil production in the catalyzed liquefaction reaction.

Effect of Phenols: Like the nitrogen base removal experiments, liquefaction solvents prepared by treating the base liquefaction solvent samples with NaOH, acidic alumina, basic alumina, or Y-zeolite were also tested to establish the effect of phenol removal. As shown in Table 21, oil production generally increased considerably with phenol removal, although the increase was only marginal for the solvents treated with NaOH and acidic alumina. Detailed analysis of the solvent treated with NaOH showed that water and other contaminants were present in the sample, which could have been responsible for the marginal increase.

TABLE 20

EFFECT OF BASIC NITROGEN REMOVAL ON CATALYTIC COAL LIQUEFACTION[a]

	Base liquefaction solvent	Treated solvents	
		HCl	Silica gel
Heteroatom concentration (wt %)			
N	0.67	0.16	0.08
O	2.25	1.68	1.31
Nitrogen as nitrogen bases	0.28	ND[b]	ND
Oxygen as phenols	1.15	0.50	0.60
Product distribution (wt % MAF coal)			
Gases	8.2	6.9	7.6
Oil	25.4	37.8	38.8
SRC	58.4	46.9	47.8
IOM	8.0	8.4	5.8
Conversion	92.0	91.6	94.2

[a] Reaction mixture:

Coal	3 g
Solvent	6 g
Catalyst	500 ppm molybdenum based on coal

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per min

[b] ND - not detected

TABLE 21

EFFECT OF PHENOL REMOVAL ON CATALYTIC COAL LIQUEFACTION[a]

	Base liquefaction solvent	Treated solvents NaOH	Acidic alumina	Basic alumina	Zeolite
Heteroatom concentration (wt %)					
N	0.67	0.60	0.70	0.58	0.44
O	2.25	1.63	1.86	1.62	1.77
Nitrogen as nitrogen bases	0.28	0.33	0.28	0.29	0.29
Oxygen as phenols	1.15	0.45	0.79	0.58	0.63
Product distribution (wt % MAF coal)					
Gases	8.2	7.6	7.2	7.6	7.4
Oil	25.4	28.3	27.4	34.2	33.9
SRC	58.4	55.4	58.0	49.6	49.6
IOM	8.0	8.7	7.4	8.6	9.1
Conversion	92.0	91.3	92.6	91.4	90.9

[a] Reaction mixture:

Coal	3 g
Solvent	6 g
Catalyst	500 ppm molybdenum based on coal

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per min

Gas production decreased marginally in all cases, but SRC production decreased considerably. Once again, overall coal conversion did not change upon phenol removal. As noted in the nitrogen base removal experiments, phenol removal did not appear to alter the physical solvency power of the solvent.

Removing phenol from the base liquefaction solvent also decreased the overall nitrogen content of the treated solvents somewhat. Near-infrared analysis, which was used to determine the nature of nitrogen compounds, clearly showed no removal of nitrogen bases, but some NH- and NH_2-type compounds were removed from the treated solvents in a few cases. Since no basic nitrogen compounds were removed from the solvent, the above data show that solvents from which the phenols have been removed do enhance oil production in catalyzed liquefaction.

Effect of Removing Both Nitrogen Bases and Phenols: Solvent samples were also prepared by treating base liquefaction solvent with HCl followed by silica gel and with NaOH followed by HCl, to remove both nitrogen bases and phenols. The sample treated with HCl/silica gel was tested in the catalytic liquefaction of coal, at both low- and high-severity reaction conditions.

At low-severity reaction conditions using 500 ppm of molybdenum catalyst, the oil yield increased significantly from 25 to 45% (Table 22) and SRC production decreased considerably. In fact, most of the increase in oil yield came from increased conversion of SRC. Although overall coal conversion was unaffected by solvent modification, gas production was decreased slightly.

At high-severity conditions using 250 ppm of molybdenum catalyst, modified solvent again increased the oil yield (Table 22), although not as much as noted at low severity. Again, SRC production was lower with modified solvent, and overall coal conversion was not greatly changed.

The above data clearly show the advantages of removing both nitrogen bases and phenols from the liquefaction solvent.

TABLE 22

EFFECT OF COMBINED REMOVAL OF NITROGEN BASES AND PHENOLS ON CATALYTIC COAL LIQUEFACTION

	Base liquefaction solvent	HCl/silica gel
Heteroatom concentration (wt %)		
N	0.67	<0.05
O	2.25	0.81
Nitrogen as nitrogen bases	0.28	ND[a]
Oxygen as phenols	1.15	0.21

	Low[b] Severity	High[c] Severity	Low Severity	High Severity
Product distribution (wt % MAF coal)				
Gases	8.2	9.6	6.7	10.9
Oil	25.4	44.9	45.4	50.9
SRC	58.4	39.2	40.1	31.6
IOM	8.0	6.3	7.8	6.6
Conversion	92.0	93.7	92.2	93.4

---

[a] ND - not detected

[b] Catalyst concentration - 500 ppm molybdenum based on coal

[c] Catalyst concentration - 250 ppm molybdenum based on coal

Hydrotreater Solvent. Experiments were also conducted to determine the effect of modified hydrotreater solvent on catalytic liquefaction. A sample treated with silica gel to remove part of the heteroatomic compounds was used in liquefaction testing with 250 ppm of molybdenum catalyst at high-severity reaction conditions.

Results summarized in Table 23 show that removing heteroatomic compounds enhanced the oil yield and slightly improved overall coal conversion. However, the magnitude of improvements was small, possibly because only small amounts of heteroatomic compounds were removed. The improvements in both oil yield and coal conversion with catalyst are somewhat surprising, because these did not improve at all during noncatalytic liquefaction with the treated solvent (Table 23).

Catalytic Liquefaction of Kentucky #9 Coal

Heteroatoms were removed from Kentucky #9 coal derived starting liquefaction solvent by treatment with silica gel or basic alumina. The treated solvent samples were then used in experiments to evaluate the effect of heteroatom removal.

Oil production increased considerably: from 17 to 31% with the solvent prepared with basic alumina and from 17 to 39% with the solvent prepared with silica gel. The increase in oil production was obtained at the expense of increased SRC conversion, since the gas yield was within the limits of experimental error. Overall coal conversion also increased slightly with heteroatom removal, as shown in Table 24.

The data in Table 24 show that more heteroatoms were removed by silica gel than by basic alumina. The additional removal did not improve coal conversion, but it significantly increased oil production. Similar results were noted in the liquefaction experiments with Illinois #6 coal.

Clearly, removing heteroatoms from a liquefaction solvent increases the activity of a slurry-phase catalyst in terms of oil production. Furthermore, the catalyst's activity is strongly dependent on the extent of heteroatom removal.

	Noncatalytic liquefaction				Catalytic liquefaction			
	Hydrotreater solvent		Modified hydrotreater solvent		Hydrotreater solvent		Modified hydrotreater solvent	
	I	II	I	II	I	II	I	II
Product distribution (wt % MAF coal)								
Gases	9.8	10.4	10.8	12.0	12.4	12.6	10.5	11.2
Oil	45.6	43.6	44.4	45.1	47.9	49.6	53.5	53.0
SRC	34.3	36.9	35.5	32.9	31.5	29.5	29.6	29.2
IOM	10.3	9.1	9.3	10.0	8.2	8.3	6.4	6.6
Conversion	89.7	90.9	90.7	90.0	91.8	91.7	93.6	93.4

[a] Reaction mixture:

Coal	3 g
Solvent	3 g
Catalyst	250 ppm molybdenum based on coal

Reaction conditions:

Temperature	440°C
Pressure	1,200 psig H_2 cold
Time	60 min
Agitation	1,000 strokes per min

TABLE 24

EFFECT OF HETEROATOMS REMOVAL ON CATALYTIC LIQUEFACTION OF KENTUCKY #9 COAL[a]

	Starting liquefaction solvent	Treated solvents	
		Basic alumina	Silica gel
Heteroatom concentration (wt %)			
N	0.84	0.70	0.23
O	3.18	1.94	1.65
Product distribution (wt % MAF coal)			
Gases	5.0	6.1	5.1
Oil	16.9	30.7	39.0
SRC	63.5	52.4	43.0
IOM	14.6	10.8	12.9
Conversion	85.4	89.2	87.1

---

[a] Reaction mixture:

Coal	3 g
Solvent	6 g
Catalyst	500 ppm molybdenum based on coal

Reaction conditions:

Temperature	425°C
Pressure	850 psig H_2 cold
Time	60 min
Agitation	1,000 strokes per min

FUNDAMENTAL STUDIES RELATED TO SOLVENT MODIFICATION

Role of Heteroatomic Compounds in Liquefaction

The experimental results just discussed clearly show the benefits of removing heteroatomic compounds from process solvents before using them in coal liquefaction. Data also show that the solvents' effectiveness improves as more and more heteroatomic compounds are removed.

To better understand the role of heteroatomic compounds in catalytic coal liquefaction and to provide support for our unique findings, Auburn University was subcontracted in October 1982 to conduct several fundamental experiments. A number of model nitrogen and oxygen compounds were added to a modified solvent to increase its heteroatomic compound concentration; this was then used as a liquefaction solvent to determine the effect of heteroatoms on catalytic coal liquefaction. In addition, the heteroatomic compounds removed from base liquefaction solvent to yield modified solvent were added back to the modified solvent. The reconstituted solvent was also used in catalytic coal liquefaction experiments.

The effect of the heteroatomic compounds on coal liquefaction was measured in terms of oil production. However, the reaction conditions and the reactor design used at Auburn University differed considerably from those at Air Products, which made comparison of Auburn's and Air Products' data very difficult. Therefore, no attempt is made here to provide a one-to-one comparison.

Baseline Data. First, Auburn University used base liquefaction solvent and modified solvent (base liquefaction solvent treated with anhydrous HCl followed by silica gel) in catalytic experiments to establish the effect of solvent modification. As expected, oil yields were higher with modified than with base liquefaction solvent. Overall coal conversion was marginally higher with modified solvent, and gas production was slightly lower.

Effect of Adding Model Nitrogen Compounds. Several model basic nitrogen compounds such as quinoline were added to modified solvent to increase its total nitrogen concentration. This reconstituted solvent was then tested in catalytic coal liquefaction experiments to determine the effect of nitrogen compounds upon liquefaction.

Effect of Adding Quinoline: A sufficient amount of quinoline (5.9 wt %) was added to modified solvent to increase its nitrogen concentration from 0.08% to that of the base liquefaction solvent (0.67%). When this reconstituted solvent was used for liquefaction, the oil yield dropped considerably compared to that with modified solvent (Table 25). However, the oil yield with the reconstituted solvent was slightly higher than that with base liquefaction solvent, possibly because the concentration of oxygen compounds in the reconstituted solvent was lower than in base liquefaction solvent. These results confirm our earlier finding that heteroatomic compounds will reduce oil yield.

Effect of Adding Phenanthridine: Since quinoline's molecular weight is relatively lower than many of the nitrogen-containing compounds generally identified in coal-derived solvents, we decided to add a higher molecular weight nitrogen-containing compound that might be more representative of the heteroatomic compounds present in coal-derived liquid. For this reason, phenanthridine (3,4-benzoquinoline) was added to modified solvent and tested for its effect upon liquefaction.

A carefully calculated amount of phenanthridine (7.7 wt %) was added to modified solvent to increase its nitrogen concentration from 0.08 to 0.67%. When this reconstituted mixture was used as solvent in coal liquefaction, the oil yield was found to be even lower than that noted with base liquefaction solvent (Table 26), confirming the negative effect of nitrogen compounds on oil production. Overall coal conversion and gas yield were not greatly affected.

In another experiment, 30.5 wt % phenanthridine was added to modified solvent, raising its nitrogen concentration from 0.08 to 2.42%. When this solvent was used in coal liquefaction, the oil yield was considerably lower than that

TABLE 25

EFFECT OF ADDING QUINOLINE TO MODIFIED SOLVENT[a]

	Base liquefaction solvent	Modified solvent[b]	Modified solvent with quinoline added (5.9 wt %)
Product distribution (wt % MAF coal)			
HC gases	11.8	9.7	11.9
Oils	28.9	34.5	30.1
SRC	51.9	49.2	51.6
IOM	7.4	6.6	6.4
Conversion	92.6	93.4	93.6

[a] Reaction conditions:

Temperature	425°C
Initial H_2 pressure	1,250 psig cold
Time	60 min
Agitation rate	860 rpm
Reactor	Tubing bomb (46.7 mL volume)

Reaction mixture:

Solvent	6 g
Coal	3 g (Illinois #6)
Catalyst	500 ppm molybdenum added as molybdenum octoate

[b] Modified solvent is generated by treating base liquefaction solvent with anhydrous HCl gas followed by silica gel.

TABLE 26

EFFECT OF ADDING PHENANTHRIDINE TO MODIFIED SOLVENT[a]

	Base liquefaction solvent	Modified solvent[b]	Modified solvent with phenanthridine added (7.7 wt %)	Modified solvent w phenanthr added (30.5 wt
Product distribution (wt % MAF coal)				
HC Gases	11.8	9.7	9.6	8.9
Oils	28.9	34.5	26.4	19.6
SRC	51.9	49.2	56.5	65.8
IOM	7.4	6.6	7.5	5.7
Conversion	92.6	93.4	92.5	94.3

[a] Reaction conditions:

Temperature	425°C
Initial H_2 pressure	1,250 psig cold
Time	60 min
Agitation rate	860 rpm
Reactor	Tubing bomb (46.7 mL volume)

Reaction mixture:

Solvent	6 g
Coal	3 g (Illinois #6)
Catalyst	500 ppm molybdenum added as molybdenum octoate based on coal

[b] Modified solvent is generated by treating base liquefaction solvent with anhydrous HCl gas followed by silica gel.

noted with base liquefaction solvent (Table 26). This observation further shows the detrimental effect of nitrogen compounds on oil production.

Effect of Adding Acridine: Like phenanthridine, 7.7% acridine was added to modified solvent, increasing the nitrogen concentration from 0.08 to 0.67%. The use of this reconstituted solvent in catalytic coal liquefaction also yielded less oil than that noted with modified solvent (Table 27). The oil production with the reconstituted solvent was also slightly lower than with base liquefaction solvent, showing the detrimental effect of nitrogen compounds on oil production.

Summary: Figure 3 summarizes how adding different model nitrogen compounds to modified solvent inhibited oil production in coal liquefaction. Furthermore, oil production decreased with an increase in the total nitrogen content of the solvent used for liquefaction. Finally, we can conclude that the addition of nitrogen-containing compounds to liquefaction solvent is detrimental to oil production. In other words, removing nitrogen compounds from the process solvent before using it for coal liquefaction will undoubtedly improve oil production.

Effect of Adding Model Oxygen Compound. Approximately 13.3 wt % ß-naphthol was added as a representative oxygen compound to modified solvent to increase its oxygen concentration from 0.81% to that of the base liquefaction solvent (2.25%). When this reconstituted solvent was used in catalytic coal liquefaction, oil production (Table 28) was unchanged. This observation indicates that adding phenol would also not affect coal liquefaction, but more work is required to determine specifically the effect of high-molecular-weight phenols on coal liquefaction.

Effect of Adding Indigenous Heteroatomic Compounds. As mentioned earlier, modified solvent was prepared by treating the base liquefaction solvent with HCl followed by silica gel. The polar-compound-rich stream extracted from the base liquefaction solvent was added back to modified solvent to raise its oxygen and nitrogen concentration to the same level as that of base liquefaction solvent. This reconstituted solvent was then used in catalytic

TABLE 27

EFFECT OF ADDING ACRIDINE TO MODIFIED SOLVENT[a]

	Base liquefaction solvent	Modified solvent[b]	Modified solvent with acridine added (7.7 wt %)
Product distribution (wt % MAF coal)			
HC gases	11.8	9.7	9.9
Oils	28.9	34.5	28.0
SRC	51.9	49.2	53.8
IOM	7.4	6.6	8.3
Conversion	92.6	93.4	91.7

[a] Reaction conditions:

Temperature	425°C
Initial H_2 pressure	1,250 psig cold
Time	60 min
Agitation rate	860 rpm
Reactor	Tubing bomb (46.7 mL volume)

Reaction mixture:

Solvent	6 g
Coal	3 g (Illinois #6)
Catalyst	500 ppm molybdenum added based on coal

[b] Modified solvent is generated by treating base liquefaction solvent with anhydrous HCl gas followed by silica gel.

FIGURE 3
EFFECT OF ADDING VARIOUS NITROGEN-CONTAINING COMPOUNDS TO MODIFIED SOLVENT

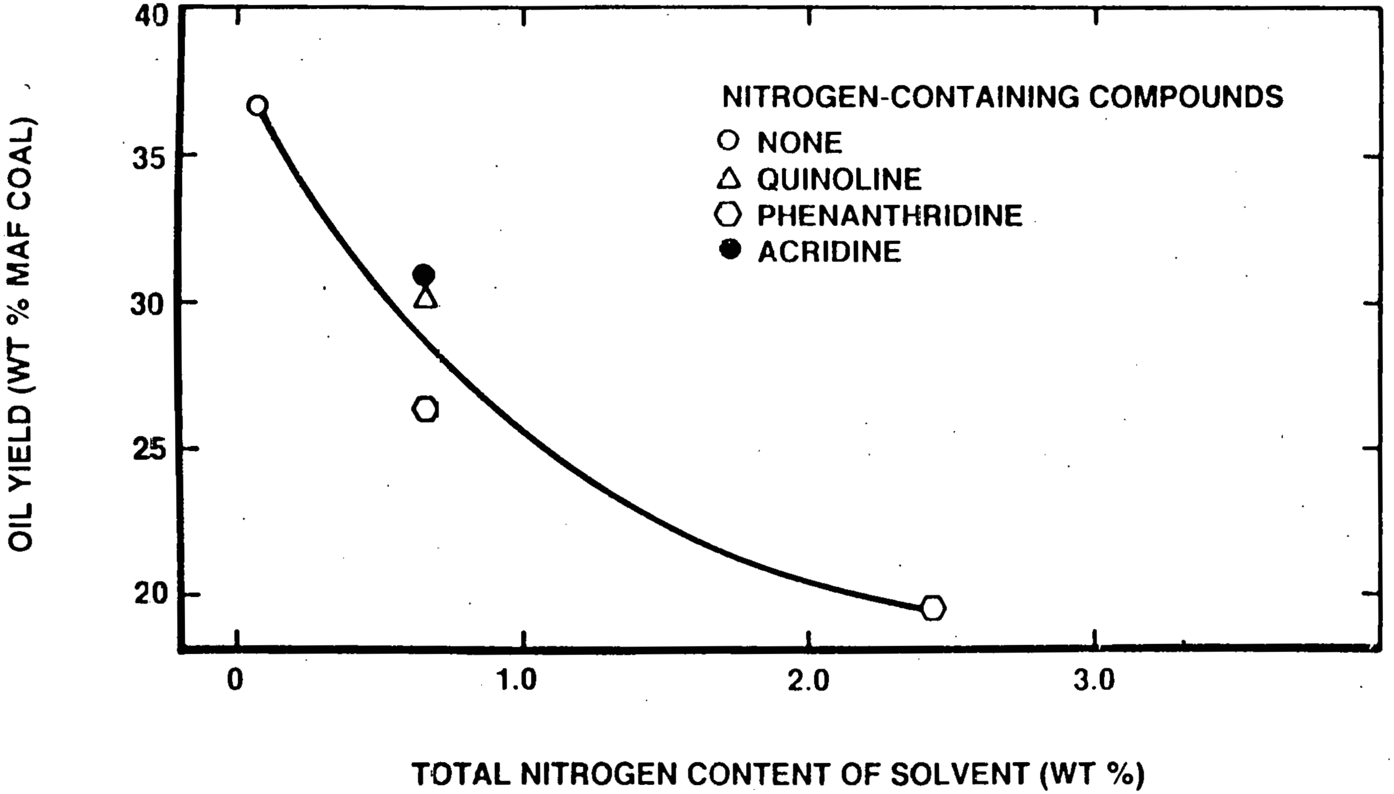


TABLE 28

EFFECT OF ADDING β-NAPHTHOL TO MODIFIED SOLVENT[a]

	Base liquefaction solvent	Modified solvent[b]	Modified solvent with β-naphthol adde (13.3 wt %)
Product distribution (wt % MAF coal)			
HC gases	11.8	9.7	9.5
Oils	28.9	34.5	34.6
SRC	51.9	49.2	48.4
IOM	7.4	6.6	7.6
Conversion	92.6	93.4	92.4

[a] Reaction conditions:

Temperature	425°C
Initial H_2 pressure	1,250 psig cold
Time	60 min
Agitation rate	860 rpm
Reactor	Tubing bomb (46.7 mL volume)

Reaction mixture:

Solvent	6 g
Coal	3 g (Illinois #6)
Catalyst	500 ppm molybdenum added based on coal

[b] Modified solvent is generated by treating base liquefaction solvent with anhydrous HCl gas followed by silica gel.

coal liquefaction experiments, and the results showed lower oil production than with both base liquefaction and modified solvents. These data clearly show the detrimental effect of adding a stream of polar compounds to solvent during coal liquefaction (Table 29).

Explanation of the Role of Heteroatomic Compounds in Liquefaction

The detrimental effect of heteroatomic compounds on coal liquefaction has been demonstrated by modifying the base liquefaction solvent and also by adding model compounds to modified solvent. However, the role of heteroatomic compounds in coal liquefaction is not clearly understood because of the complex nature of the solvents and the number of variables involved in coal liquefaction. It is generally accepted that hydrogenation or liquefaction of coal involves transfer of hydrogen from gas phase to solvent (solvent hydrogenation) and from solvent to coal free radicals formed by thermal reaction. If hydrogen transfer from any one of these steps is limited by any mechanism, free radicals from the coal will be hydrogen-starved and will condense to form coke. In addition, hydrogen starvation conditions will severely limit the formation of oil, which is basically a hydrogenated coal product. Therefore, hydrogen transfer plays an important role in controlling the coal liquefaction reaction.

To provide a simple explanation for the role of heteroatomic compounds in coal liquefaction, a simple model-compound hydrogenation reaction system was studied. It was thought that if the coal liquefaction reaction was limited by heteroatomic compounds, these compounds should also limit the model compound hydrogenation reaction. Phenanthrene was selected as the model compound and molybdenum octoate, once again, was used as a catalyst.

In the absence of any model nitrogen compound, the hydrogenation of phenanthrene in the presence of hexadecane used as carrier showed conversions of 66 and 81% at 380 and 425°C, respectively (see detailed reaction conditions in Figure 4). The addition of model nitrogen compounds such as quinoline and phenanthridine to the reaction mixture severely limited the hydrogenation of phenanthrene, as also shown in Figure 4. However, the addition of a model

TABLE 29

EFFECT OF ADDING POLAR-COMPOUND-RICH STREAM TO MODIFIED SOLVENT[a]

	Base liquefaction solvent	Modified solvent[b]	Modified solven with addition o polar compound-rich stream
Product distribution (wt % MAF coal)			
HC gases	11.8	9.7	10.5
Oils	28.9	34.5	25.4
SRC	51.9	49.2	57.9
IOM	7.4	6.6	6.2
Conversion	92.6	93.4	93.8

[a] Reaction conditions:

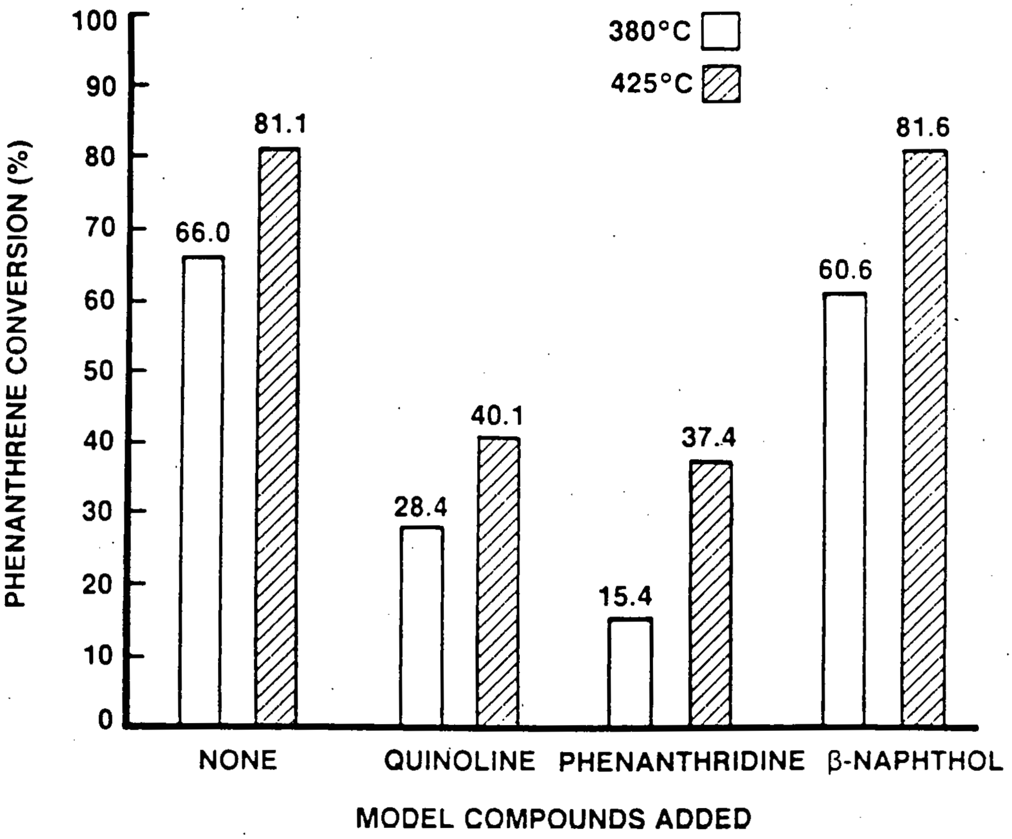
Temperature	425°C
Initial H_2 pressure	1,250 psig cold
Time	60 min
Agitation rate	860 rpm
Reactor	Tubing bomb (46.7 mL volume)

Reaction mixture:

Solvent	6 g
Coal	3 g (Illinois #6)
Catalyst	500 ppm molybdenum based on coal

[b] Modified solvent is generated by treating base liquefaction solvent with anhydrous HCl gas followed by silica gel.

FIGURE 4
HYDROGENATION OF PHENANTHRENE



REACTION MIXTURE:	5.0 g OF 2 WT % PHENANTHRENE IN HEXADECANE 0.01 g OF MODEL COMPOUND 1000 PPM OF IN SITU SULFIDED Mo CATALYST	
REACTION CONDITIONS:	INITIAL H_2 PRESSURE	1250 PSIG AT 25°C
	TIME	20 MINUTES
	AGITATION RATE	860 RPM
	REACTOR	TUBING BOMB

oxygen compound, ß-naphthol, had a marginal effect on phenanthrene hydrogenation. These observations tend to indicate that the presence of heteroatomic compounds, especially nitrogen-containing compounds, severely limits the solvent hydrogenation or transfer of hydrogen from gas phase to liquid phase, resulting in a hydrogen-starved condition. This hydrogen starvation condition is probably the prime reason why nitrogen-containing compounds negatively affect coal liquefaction.

V. CATALYST SELECTION

BACKGROUND

Most of the experimental work discussed earlier was performed using dispersed molybdenum catalyst. Although we did not know whether molybdenum was optimal, in order to save time we opted to use it for the solvent modification runs while simultaneously conducting catalyst selection experiments. Most of the work was subcontracted to Auburn University, which evaluated the activities of various water-soluble catalysts both individually and in combination.

Catalyst selection for a coal liquefaction process is very important. Although a number of metals can be used, some may actually inhibit the coal liquefaction reaction rather than catalyzing it. Furthermore, metal catalysts can be used in bulk, impregnated, or dispersed forms. Depending on the type of metal used, the activity of its different forms may differ.

Eight metals were tested for their catalytic activity in coal liquefaction. Since their activity in bulk form is limited, often necessitating large amounts, no attempts were made to test them in bulk form. Furthermore, since the cost of the catalyst depends on the amount used and determines the economics of the coal liquefaction process, bulk application of the catalyst was ruled out as impractical.

However, the economics can be improved by effectively dispersing the metal catalysts in the reaction mixture. Effective dispersion can be achieved either by impregnating the initial catalysts on coal or dispersing the metal catalysts in solvent. Auburn impregnated the catalysts on coal in its catalytic selection experiments and tests of the synergism between metal catalysts. The form of metal catalyst application was then decided at Air Products by testing the activities of both impregnated and dispersed metal catalysts.

IMPREGNATION OF METAL CATALYSTS

Individual Metals

The activity of various water-soluble catalysts was evaluated at Auburn University by dissolving them in water and impregnating them on coal. The metal concentrations used were based on the cost of the metal: molybdenum and nickel, being very expensive, were used in very small amounts (250 ppm based on coal), whereas cheap metals such as iron, zinc, and copper were used in large amounts (up to 1 wt % based on coal). The catalytic activity was determined on the basis of oil production during coal liquefaction. The standard reaction conditions listed in Table 30 were used in all the experiments, as was base liquefaction solvent. Results are described below.

Impregnating coal with 250 ppm of molybdenum as ammonium molybdate or 250 ppm of nickel nitrate increased overall coal conversion from 87 to 90% (Table 31). Oil production increased from 18 to 21% with nickel and from 18 to 24% with molybdenum, indicating that molybdenum was more active than nickel. The changes in yields of both gases and SRC were insignificant with both metals.

Although impregnation of coal with 250 ppm of cobalt increased overall coal conversion from 87 to 91% (Table 31), oil production decreased from 18 to 14%. Impregnation with either 0.5 or 1.0% iron increased coal conversion and oil production. In fact, both were slightly higher with 0.5% iron than with 1.0% iron, clearly indicating the benefit of using a lower concentration of iron. On the contrary, reducing the concentration of zinc from 1.0 to 0.5% significantly reduced oil production. Furthermore, the application of zinc at both 0.5 and 1.0% levels was detrimental to coal liquefaction, as was use of copper at the same levels. Finally, the use of either 1.0% manganese or lead was also extremely detrimental to oil production.

The data summarized in Table 31 clearly show that cobalt, zinc, copper, manganese, and lead are not good catalysts, but that molybdenum, nickel, and iron seem to catalyze the coal liquefaction reaction.

TABLE 30

STANDARD CONDITIONS FOR METAL-IMPREGNATED COAL LIQUEFACTION EXPERIMENTS

Reaction Conditions:	
Temperature	425°C
Initial H_2 pressure	1,250 psig cold
Time	60 minutes
Agitation rate	860 rpm
Reactor	Tubing bomb (46.7 mL)
Reaction Mixtures:	
Solvent	6 g (base liquefaction solvent)
Coal	3 g (Illinois #6)
CS_2 [a]	0.08 g

[a] CS_2 was added to the reaction mixture to ensure complete sulfiding of the catalyst.

TABLE 31

LIQUEFACTION OF ILLINOIS #6 COAL USING METAL CATALYSIS[a]

					Iron		Zinc		Copper		Manganese	Lead
	None	250-ppm molybdenum	250-ppm nickel	250-ppm cobalt	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	1.0%	1.0%
Product distribution (wt % MAF coal)												
Gases	12.0 ± 1.9	10.2	12.5 ± 1.2	12.6	10.0	8.2	12.2	10.5	10.6	11.4	11.5	11.5
Oil	17.6 ± 2.5	23.9	20.5 ± 0.2	13.6	21.8	21.0	8.5	15.4	15.2	14.8	16.8	12.2
SRC	57.3 ± 2.0	56.7	57.5 ± 2.0	65.0	60.4	59.5	65.6	58.8	59.5	56.8	55.8	65.4
IOM	13.1 ± 2.0	9.2	9.5 ± 0.9	8.8	7.8	11.3	13.7	15.3	14.7	17.0	15.9	10.9
Conversion	86.9 ± 2.0	90.8	90.5 ± 0.9	91.2	92.2	88.7	86.3	84.7	85.3	83.0	84.1	89.1

[a] Reaction mixture:

Coal	3 g (Illinois #6)
Base liquefaction solvent	6 g

Reaction conditions:

Temperature	425°C
Initial H_2 pressure	1,250 psig cold
Time	60 min
Agitation rate	860 strokes per min

Auburn also noted that molybdenum was more active than nickel at a very low concentration -- 250-ppm metal based on coal. Furthermore, 250-ppm molybdenum was more active than iron at a very high concentration (1 wt %).

Since molybdenum and iron displayed good catalytic activity in coal liquefaction with base liquefaction solvent, the catalytic activity of these two metals impregnated on coal was evaluated at Air Products in the presence of modified solvent, which was generated by treating base liquefaction solvent with anhydrous hydrochloric acid followed by silica gel. Two different concentrations of iron (0.3 and 1.0 wt % based on coal) and 500 ppm of molybdenum were used for the liquefaction test. The experimental work was limited to iron and molybdenum catalysts because of the lack of time and resources.

As shown in Table 32, both oil production and coal conversion increased considerably with 0.3%-iron-impregnated coal compared to a run without catalyst. Increasing the iron concentration from 0.3 to 1.0% further increased oil production from 29 to 44%, in sharp contrast to the lack of a change in yield in the presence of base liquefaction solvent when the iron concentration was increased from 0.5 to 1.0% (Table 31). This observation clearly indicated that the catalytic activity of iron was severely hindered by the presence of heteroatoms in the solvent. Overall coal conversion, however, increased marginally from 84 to 87% with an increase in iron concentration from 0.3 to 1.0%.

Impregnating coal with 500-ppm molybdenum increased oil yield to 28%, which was slightly higher than that noted with base liquefaction solvent (see Tables 31 and 32). Overall coal conversion was somehow considerably lower in the presence of modified solvent than base liquefaction solvent. When the activity of 1% impregnated iron was compared to that of 500-ppm impregnated molybdenum, it was surprisingly noted that both oil production and coal conversion obtained with 1% iron were higher than noted with 500-ppm molybdenum. This information reveals that when catalyst is impregnated on coal, an inexpensive catalyst like iron can be used to replace an expensive catalyst like molybdenum in coal liquefaction without incurring any loss in oil yield.

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Metal Catalyst Combinations

As just discussed, addition of iron, zinc, copper, lead, cobalt, nickel, and molybdenum during coal liquefaction did not always increase oil production over the noncatalytic baseline yields. This was in part due to cost factors; because nickel and molybdenum are expensive, their concentrations had to be kept low in order to make their use economically feasible. In contrast, iron, copper, and zinc were much cheaper, and therefore could be used at much higher concentrations. However, as shown, adding more iron did not have any significant beneficial effect with base liquefaction solvent.

These results led to several exploratory experiments to determine whether combining a weak or detrimental catalyst like iron or zinc with a strong catalyst like molybdenum would be beneficial. The results in Table 33 show that the combination of metals in all cases yielded higher overall conversion and significantly more oil than the individual metals. Oil production was highest using the combination of zinc and molybdenum. These results indicate that combining a cheap metal like iron, zinc, or copper and an expensive metal like molybdenum shows great promise for improving liquefaction.

DISPERSED CATALYST

As stated earlier, metal catalysts can be used in bulk, impregnated, and dispersed forms. In addition to those just described, experiments were performed to test the activity of metal catalysts dispersed well in the reaction mixture. The activities of well-dispersed and impregnated metal catalysts were compared to determine the most efficient way of using catalytic activity.

To accomplish this task, coal liquefaction experiments were carried out by Air Products using molybdenum catalyst in both impregnated and dispersed forms (molybdenum dispersion was achieved by using an oil-soluble molybdenum compound like molybdenum octoate) in the presence of modified solvent. In both cases, a concentration level of 500-ppm molybdenum based on coal was used.

TABLE 33

COAL LIQUEFACTION WITH A COMBINATION OF METALS[a]

	250-ppm Mo	250-ppm Ni	1.0% Fe	1.0% Cu	1.0% Zn	250-ppm Mo and 1% Fe	250-ppm Ni and 1% Fe	250-ppm Mo and 1% Cu	250-ppm Mo and 1% Zn
Product distribution (wt % MAF coal)									
Gases	10.2	12.5	8.2	11.4	10.5	8.5	8.8	10.1	7.8
Oil	23.9	20.5	21.0	14.8	15.4	28.2	28.9	27.1	32.1
SRC	56.7	57.5	59.5	56.8	58.8	57.3	55.8	55.6	52.7
IOM	9.2	9.5	11.3	17.0	15.3	6.0	6.5	7.2	7.4
Conversion	90.8	90.5	88.7	83.0	84.7	94.0	93.5	92.8	92.6

[a] Reaction conditions: see Table 31

Liquefaction of molybdenum-impregnated Illinois #6 coal at 425°C resulted in an overall coal conversion of 83% (Table 34). Oil and gas production were 28 and 7.2%, respectively. Interestingly, oil production increased from 28 to 44% by molecularly dispersing molydenum instead of impregnating it into the coal. Overall coal conversion also increased to 92% when molybdenum was molecularly dispersed in the reaction mixture as molybdenum octoate.

These results clearly indicate that the way the catalyst is applied is very important in coal liquefaction. Molybdenum when dispersed in the reaction mixture as oil-soluble molybdenum octoate was much more active than when impregnated into the coal. Similar behavior could be expected with other metal catalysts such as iron and zinc. If this is true, the amount of an inexpensive catalyst like iron required to catalyze coal liquefaction could be reduced considerably by molecular dispersion in the reaction mixture. However, the relative cost of the water-soluble form of the metal catalyst and of the oil-soluble compound should be considered before final selection for actual plant design and operation.

TABLE 34

APPLICATION OF MOLYBDENUM CATALYST[a]

	Molybdenum impregnation	Molybdenum dispersion		
		I	II	Average
Product distribution (wt % MAF coal)				
Gases	7.2	6.7	5.1	(5.9)
Oil	28.0	45.4	42.5	(44.0)
SRC	47.5	40.1	43.7	(41.9)
Residue	17.3	7.8	8.7	(8.2)
Conversion	82.7	92.2	91.3	(91.0)

[a] Reaction mixture:

Coal	3 g (Illinois #6)
Solvent	6 g (modified solvent)

Reaction conditions:

Temperature	425°C
Pressure	850 psig H_2 cold
Time	60 min
Agitation	1,000 strokes per min

VI. EFFECT OF COAL PRETREATMENT AND BENEFICIATION ON LIQUEFACTION

In an attempt to find ways of improving the oil production from coal liquefaction, we also examined several coal pretreatment techniques, including solvent extraction, oxidation, cation exchange, pulverization, and beneficiation. The following sections briefly describe each of these pretreatment methods and the results of liquefying samples of the pretreated coals under both low- and high-severity reaction conditions.

SOLVENT EXTRACTION OF COAL

The efficiency of coal liquefaction depends on the mass transfer of hydrogen from the hydrogen-donor solvent to the active sites that form upon thermal reaction of the coal. When the active sites are quenched with donatable hydrogen from the solvent, desirable low-molecular-weight products are formed. If, on the other hand, hydrogen is not readily available, the active sites will react to form undesirable products of high molecular weight. When a coal is extracted with certain solvents at temperatures appreciably below the liquefaction temperatures, various proportions of small molecules (such as waxes, resins, bitumens, and simple aromatics) are removed from the microporous network. The amount of extract will typically vary between 5 and 25% by weight depending on the nature of the solvent system and the type and rank of coal. By opening up the structure and increasing access to the micropores, solvent extraction should render the internal molecular structure of the coal more readily accessible to the "preferred" hydrogen-donor solvent, thereby enhancing the liquefaction efficiency.

In addition, removal of the smaller molecules also should benefit the liquefaction process because of the reduction in mobile heteroatom constituents. If not removed, mobile constituents can easily participate in undesirable condensation reactions or in other side reactions requiring unnecessary consumption of molecular hydrogen.

To determine whether solvent extraction of coal before liquefaction would enhance the yield of desirable products from subsequent thermal or catalytic liquefaction, a series of experiments was conducted with Illinois #6 coal. Samples were treated with benzene and ethanol alone and with mixtures of the two. Also, Illinois #6 coal was first soaked in a process middle distillate and then extracted with either methylene chloride or benzene/ethanol. In another experiment, the coal was extracted with citric acid. Representative solvent-extracted samples were then liquefied in a tubing-bomb reactor under both high- and low-severity reaction conditions. Individual experiments are described below.

Solvent Extraction with Benzene and Ethanol

Benzene-Extracted Illinois #6 Coal. Fifty grams of Illinois #6 coal pulverized to -200 mesh was placed in a Soxhlet extractor to which 600 mL of benzene was added. The coal was extracted for 3 days, after which the extract was collected by evaporating the solvent and then weighed. The extracted coal was dried under vacuum at 70°C to remove residual solvent and also weighed. The yield of extract on a MAF coal basis was 2.7%.

A sample of the extracted coal was then liquefied with base liquefaction solvent at 425°C for 1 hr in a 50-cm^3 tubing-bomb reactor. The results in Table 35 show that the oil yield has decreased somewhat compared to the liquefaction of original coal, and conversion decreased significantly.

Ethanol-Extracted Illinois #6 Coal. Another sample of freshly ground -200 mesh Illinois #6 coal was Soxhlet extracted with absolute ethanol exhaustively for 7 days. The ethanol-extracted residue was dried and subjected to liquefaction using base liquefaction solvent. The results, reported in Table 35, are compared to liquefaction of the original Illinois #6 coal. Notice that ethanol pretreatment also reduces oil yield. The conversion also decreased dramatically.

TABLE 35

LIQUEFACTION OF BENZENE- AND ETHANOL-EXTRACTED ILLINOIS #6 COAL USING BASE LIQUEFACTION SOLVENT[a]

	Original coal				
	Run 14-48	Run 18-53	Ave.	Benzene-extracted coal	Ethanol-extracted coal
Product distribution (wt % MAF coal)					
Gases	7.8	8.2	8.0	8.5	8.7
Oils	14.5	10.5	12.5	9.8	9.8
SRC	60.0	64.3	62.1	54.8	51.5
IOM	17.7	17.0	17.4	26.9	30.0
Conversion	82.3	83.0	82.6	73.1	70.0

[a] Pretreatment:

50 g of coal (-200 mesh); Soxhlet extraction in 600 mL of ethanol or benzene

Reaction mixture:

Solvent	6 g
Coal	3 g

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per minute

Benzene/Ethanol-Extracted Illinois #6 Coal. Illinois #6 coal was Soxhlet extracted for 2 days using an azeotropic mixture of 67.6 wt % benzene and 32. wt % ethanol. The yield of extract based on recovered weights averaged 8.6% (dry basis), as shown in Table 36. Table 36 also compares the elemental composition of the extract with that of the raw coal.

The samples extracted with benzene/ethanol were subjected to both thermal and catalytic liquefaction using base liquefaction and modified (HCl/silica gel treated) solvents. The liquefaction conditions and results are summarized in Tables 37 and 38, including comparison with the baseline runs. The data in each table for the extracted coal are reported on both an extracted-coal and whole-coal basis. The data based on the whole coal conservatively assume a conversion of approximately 70% of the extracted material to oils. On the basis of previous experience with materials of similar composition, one can reasonably assume that the extracted material can be readily converted to distillate products by catalytic hydrotreating.

The data in Table 37 show a significantly higher oil yield for the extracted coal, even when the contribution by the extracted material is ignored. When the contribution by the extracted material is included in the product distribution (as can be seen in the right-hand column of Table 37), the oil yield increased almost twofold.

Table 38 shows the results of the liquefaction of the extracted Illinois #6 coal in the presence of a modified liquefaction solvent plus a molybdenum catalyst. Although the magnitude of the differences is less due to the higher conversion yields, a significant increase in the oil yield can again be seen when the data are reported on either an extracted-coal or whole-coal basis.

TABLE 36

SOLVENT EXTRACTION OF ILLINOIS #6 COAL WITH BENZENE AND ETHANOL

	Extraction yield	
Run number:	7514-3-1	7514-3-2
Extract (wt %):		
MF basis	8.98	8.27
MAF basis	10.07	9.27
Mass recovery (wt % MF)	100.98	100.88

	wt % (MAF) elemental composition	
Element	Raw coal	Extract
C	78.6	81.4
H	5.7	6.4
O	(10.3)[a]	(8.5)[b]
N	1.6	1.2
S	3.7	2.2

[a] Determined by difference.

[b] Direct determination on Coulometrics oxygen analyzer.

TABLE 37

LIQUEFACTION OF BENZENE/ETHANOL-EXTRACTED ILLINOIS #6 COAL WITH BASE LIQUEFACTION SOLVENT[a]

	Raw Illinois #6		Benzene/ ethanol extracted coal basis	Extra co who coal
Run no.	14-48	18-53	31-53	31
Liquefaction product distribution (wt % MAF coal)				
Gases	7.8	8.2	6.8	6
Oil	14.5	10.5	17.5	22
SRC	60.0	64.3	53.7	51
IOM	17.7	17.0	22.0	19
Conversion	82.3	83.0	78.0	80
Mass recovery (wt %)	97.5	93.2	93.2	

[a] Reaction mixture:

Solvent	6 g
Coal	3 g

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per minute

[b] Conversion data were calculated on a whole-coal basis using the average extract yield of 9.6% (MAF). Extract is conservatively assumed to contribute 70% to the oil fraction and 30% to the SRC fraction.

TABLE 38

LIQUEFACTION OF BENZENE/ETHANOL-EXTRACTED ILLINOIS #6 COAL WITH MODIFIED LIQUEFACTION SOLVENT AND SOLUBLE MOLYBDENUM CATALYST[a]

	Raw Illinois #6	Benzene/ ethanol extracted coal basis	Extracted coal, whole-coal basis
Run no.	17-45	33-54	33-54
Liquefaction product distribution (wt % MAF coal)			
Gases	6.7	7.6	6.9
Oils	45.4	48.3	50.4
SRC	40.1	35.1	34.6
IOM	7.8	9.0	8.1
Conversion	92.2	91.0	91.9
Mass recovery (wt %)	94.3	91.8	

[a] Reaction mixture:

Solvent	6 g
Coal	3 g
Catalyst	500 ppm molybdenum based on coal

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per minute

Summary. Although simple aromatic hydrocarbon solvents such as benzene, toluene, and m-xylene are suitable solvents for dissolving the types of small molecules that are present in coal, our benzene extraction experiment showed that these solvents alone apparently do not adequately penetrate the microporous structure and improve the liquefaction distribution. Likewise, simple alcohols, such as methanol or ethanol, are suitable polar solvents, since they are especially effective in swelling coal to increase the accessibility to the microporous structure. However, our ethanol extraction experiment showed that alcohols alone are poor extracting solvents for coal and therefore have little or no influence on coal liquefaction.

In contrast, a binary mixture of the two solvent types does seem to uniquely possess the ability to carry out both desired functions, that is, to increase access to the microporous structure and to simultaneously extract the desired amount of small molecules from the coal. When the coal was extracted with a mixture of benzene and ethanol at temperatures below liquefaction, the hydrogen-donor solvent had maximal access to the internal structure with the result that liquefaction (oil yield) was improved.

The true mechanism of improvement in oil yield is unknown, but several theories can be offered. One can reasonably assume that removal of the occluded material (which may act as a diluent during liquefaction) and replacement with hydrogen-donor solvent improves coal liquefaction. The hydrogen-donor solvent is better dispersed within the coal making hydrogen readily available for donation at the critical onset of liquefaction.

Another possibility is that replacement of moisture at the surface by alcohol or benzene has altered the coal's reactivity. For example, a small amount of ethanol bound on the surface after the extraction could impart a donor-solvent effect in the liquefaction reaction. If appreciable ethanol remained in the coal, a net increase in the oil yield would also result; however, our calculations show that 1-5% residual ethanol left on the extracted coal would increase the oil yield by only 0.2-1.0%, which is negligible compared to the observed increase in the oil yield. The mass balances from the extraction (Table 36) clearly indicate that the residual ethanol could not have surpassed

5%. The increase in the oil yield by solvent extraction was further substantiated by the results obtained by extracting coal with middle distillate, as discussed in the following section.

Pretreatment with Middle Distillate Followed by Solvent Extraction

In this set of experiments, Illinois #6 coal was pretreated with a coal-derived middle distillate solvent at various temperatures and then solvent-extracted to investigate the effect of the middle distillate on both the solvent extraction and subsequent liquefaction. Treatment with middle distillate, which contains appreciable amounts of phenols, was expected to enhance swelling of the coal and hence the separation of small molecules.

Table 39 lists the boiling-point distribution of the middle distillate used in these experiments; most of the solvent distilled between 350 and 650°F. Pretreatment consisted of mixing equal amounts of coal and middle distillate at various temperatures between ambient and 250°C. The coal/solvent slurry was then subjected to Soxhlet extraction using either methylene chloride or benzene/ethanol (70:30). The extraction yields were determined on the basis of recovered coal, because it was impractical to determine the weight of extract due to the presence of the middle distillate. The results of the extractions are summarized in Table 40, including an analysis of the oxygen and nitrogen in the extracted coals.

The mass recoveries were excellent for the methylene chloride experiments, but were erratic when the benzene/ethanol mixture was used for extraction. These extraction solvents were very difficult to remove from the middle distillate during rotoevaporating.

The data in Table 40 show that a marked increase in methylene chloride solubility occurred upon treatment of the coal at an elevated temperature. Although the oxygen data of the extracted coal samples were inconclusive, the modest increase in nitrogen might indicate that adduction of the middle distillate was taking place to some extent.

TABLE 39

BOILING-POINT DISTRIBUTION OF MIDDLE DISTILLATE

Temperature (°F)	wt % off
<350	0.7
350-450	23.3
450-550	44.8
550-650	19.4
650-750	5.7
750-850	6.2
>850	0.0

TABLE 40

PRETREATMENT OF ILLINOIS #6 COAL WITH COAL-DERIVED MIDDLE DISTILLATE FOLLOWED BY SOLVENT EXTRACTION

	Feed coal	Run No.				
		7514-18	7514-20	7514-22	7414-30	7514-34[a]
Pretreatment temp. (°C)	--	22	70	150	70	250
Extraction solvent	--	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	Bz/EtOH	Bz/EtOH
Mass recovery (wt %)	--	99.7	98.7	97.8	106.7	101.7
Extract (wt %[b])	--	1.1	1.6	6.1	9.5	15.8
Extracted coal (% MAF)						
Ash	10.99	10.42	11.74	10.79	11.20	12.43
N	1.44	1.59	1.58	1.81	1.68	1.58
O[c]	13.06	11.09	10.58	12.19	11.10	11.83

---

[a] Run in autoclave at 1,000 psig helium.

[b] Extract yield based on weight of recovered coal.

[c] Direct determination on Coulometrics oxygen analyzer.

In a special experiment (sample number 7514-34), the coal was pretreated with the middle distillate at 250°C in an autoclave reactor pressurized under 1,000 psig of helium. The yield of benzene/ethanol-soluble material was nearly double that obtained upon extraction of coal treated at 70°C.

Although the oxygen data are difficult to interpret, several observations are noteworthy. The oxygen data reported in Table 40 are based on direct determination of oxygen using a Coulometrics, Inc. oxygen analyzer. The test theoretically detects all organic oxygen and any oxygen formed upon pyrolysis of minerals such as carbonates, sulfates, and clays. In these analyses, the coal samples were run "as received," and the moisture content, determined by the ASTM method, was used to correct the oxygen analysis to the dry basis. The direct oxygen determined for the raw coal was several percent higher than for the extracted coals. This result was unexpected, as one would assume the oxygen content would increase as the result of the adduction of oxygen compounds from the solvent. After scrutinizing these data, including the carbon and hydrogen analyses, we concluded that the difference might represent an amount of moisture not reported by the ASTM test, but determined in the direct oxygen analysis. Also, during solvent extraction, this moisture, which is presumably tightly bound to the coal surface, is displaced by the solvent.

Three of the coal samples treated with middle distillate (Table 40) were subjected to liquefaction in the presence of base liquefaction solvent. The results of these runs are shown in Table 41.

Coal that had been pretreated with middle distillate at 150°C and then extracted with methylene chloride yielded the same amount of oils as raw coal upon liquefaction in base liquefaction solvent. However, there was a significant decrease in total conversion, as evidenced by the 10% increase in the IOM yield alone. This result substantiates the argument that a chemical interaction of the middle distillate with the coal has taken place that is not reversible with methylene chloride extraction. Whatever this effect is, it is clearly detrimental to liquefaction.

TABLE 41

LIQUEFACTION OF ILLINOIS #6 COAL TREATED WITH MIDDLE DISTILLATE[a]

		Middle distillate treated coal		
Treatment temperature		70°C	150°C	250°C, 1,000-psi He
Extraction solvent		Benzene/ethanol	CH_2Cl_2	Benzene/ethanol
Sample number	Baseline[b]	(7514-30)	(7514-22)	(7514-34)
Product distribution (wt % MAF coal)				
Gases	8.0	7.5	7.1	6.4
Oils	12.5	19.2	13.9	-10.0
SRC	62.1	54.2	52.0	66.0
IOM	17.4	19.1	27.0	37.6
Conversion	82.6	80.9	73.0	62.4
Mass recovery (wt %)	95.3	95.9	95.8	92.7

[a] Reaction mixture:

Base liquefaction solvent	6 g
Coal	3 g

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per minute

[b] Baseline data averaged from runs 14-48 and 18-53 in Table 35.

The coal sample pretreated with middle distillate at 70°C and then extracted with benzene/ethanol gave an extract yield comparable to that for raw coal extracted with benzene/ethanol, as shown in Tables 36 and 40. Both coals also gave comparable liquefaction yields (see Tables 37 and 41). This further confirms the beneficial effect of solvent extraction on oil yield. In this case, the solvency power of the benzene/ethanol mixture was sufficient to reverse any solvent adduction effect that might have resulted during the middle distillate treatment.

In the final run reported in Table 41, in which the coal was pretreated with middle distillate at 250°C at 1,000-psig helium pressure followed by benzene/ethanol extraction, overall conversion decreased substantially. The negative oil yield indicates that constituents in the process solvent strongly interacted with the treated/extracted coal at high temperature and pressure. It is quite clear from these data that simple pretreatment of coal with a coal-derived middle distillate at elevated temperature will detrimentally affect coal conversion.

Citric Acid Extracted Illinois #6 Coal

As part of the solvent extraction studies, coal was extracted with a mild acid to leach cations out of the clay components and to remove exchangeable sodium and calcium metals. Most of the relevant work in the literature reported the use of mineral acids to pretreat coal and obtain partial demineralization. In the current experiment, an organic acid (a concentrated solution of citric acid, pH ~0.5) was used instead of a mineral acid to avoid possible side effects in the liquefaction reaction due to the halogens. By virtue of its adjacent carboxylic groups, citric acid tends to act as an efficient complexing agent for many metals, and thereby serves to efficiently clean up the coal surface and extract soluble minerals from the pores. Treatment of Illinois #6 coal with citric acid solution followed by exhaustive water extraction succeeded in reducing the ash content by 20-30%.

The extracted samples were liquefied with base liquefaction and modified solvents to determine the effect of this pretreatment on liquefaction. The results, summarized in Table 42, show no marked differences between the product distribution obtained by liquefying both original and citric acid washed coal samples under thermal and catalytic conditions.

TABLE 42

LIQUEFACTION OF CITRIC ACID EXTRACTED ILLINOIS #6 COAL[a]

	Base liquefaction solvent		Modified solvent and 500 ppm Mo catalyst	
Run number	31-050	Baseline[b]	33-037	Baseline[c]
Pretreatment	Citric acid extracted	Raw Ill. #6	Citric acid extracted	Raw Ill. #6
Product distribution (wt % MAF coal)				
Gases	7.6	8.0	6.4	6.7
Oil	12.4	12.5	45.3	45.4
SRC	60.6	62.1	38.7	40.1
IOM	19.4	17.4	9.6	7.8
Conversion	80.6	82.6	90.4	92.2
Mass recovery (wt %)	90.6	95.3	96.1	94.3

[a] Reaction mixture:

Coal	3 g
Solvent	6 g
Catalyst	500-ppm molybdenum based on coal (if any)

Reaction conditions:

Temperature	425°C
H_2 pressure	850 psig cold
Time	60 min
Agitation	1,000 strokes per min

[b] Average of run numbers 14-48 and 18-53.

[c] Run numbers 17-45.

OXIDATION OF COAL

Oxidized coals are generally not suitable for liquefaction because they are known to produce a considerable debit in overall conversion compared to the liquefaction of "fresh" or unoxidized coal (3, 4). Oxygen incorporations of several percent or more from oxidation in air at temperatures below 200°C are known to cause extensive decreases in coal conversion yields. Consequently, coal liquefaction process development groups have been concerned with the problem and have made a substantial investment in ways to minimize or eliminate the oxidation of coal during routine mining, transportation, preparation, and handling prior to its liquefaction. Naturally weathered coals (e.g., from stockpiling) can be oxidized to such an extent that they are typically excluded as candidates for coal liquefaction processing.

On the other hand, bituminous coals that have been severely weathered or oxidized do contain beneficial carboxyl groups and other ion-exchange sites that are not found naturally. These ion-exchange sites are beneficial because they can complex metals, thus allowing catalysts to be dispersed throughout the coal. By molecularly dispersing a catalyst throughout the coal structure by ion exchange prior to liquefaction, catalytic effect and subsequent liquefaction yields should be improved considerably.

Because we were interested in performing cation-exchange experiments with oxidized coal, we first designed a series of experiments to determine how mil oxidation would affect liquefaction under our conditions. Hence, Illinois #6 Burning Star coal was subjected to the following pretreatments:

- Coal was oxidized in a fluidized bed reactor with dry air at controlled temperatures of 70 and 170°C for 1, 2, and 5 hr and with wet air at 170°C for 5 hr.

- Coal was oxidized in a 50:50 (by volume) solution of dilute sulfuri acid (0.1 N) and methanol containing 5% hydrogen peroxide as an oxidizing agent.

- Coal was oxidized in 0.1 N H_2SO_4 with 5% H_2O_2.
- Coal was oxidized with 72% sulfuric acid at a mild condition of 1 hr at 0°C and at more severe conditions of 1 and 18 hr at 50°C.

To determine the extent of oxygen incorporation, the oxidized coals were analyzed using a direct oxygen analyzer (Coulometrics, Inc.). Thermogravimetric analysis was also used to determine the relative rate of oxidation of the Illinois #6 coal at different temperatures prior to setting the conditions in the fluidized-bed oxidizer. The oxygen analyses of the treated coals are summarized in Table 43.

As shown by the data in Table 43 and the thermograms in Figure 5, temperature definitely affected the rate of air oxidation; it proceeded much more rapidly at 170°C than at 70°C. Hence, those samples oxidized at 170°C were selected for the liquefaction studies. Also, the initial peroxide treatment (5% H_2O_2 in 50/50 methanol/H_2SO_4) was very effective in adding oxygen, so these samples were liquefied, as were those oxidized in 72% H_2SO_4 for 1 and 18 hr.

Because we had learned from our coal grinding experiments (to be discussed below) that oxidation was extremely detrimental to oil production when original (base liquefaction) solvent was used, all the liquefaction experiments in this series were run with modified solvent (5).

The results, compared to the original coal, are summarized in Table 44. The most significant finding was that the oil yields from liquefaction of the air-oxidized coal were unaffected, even though the oxidized coals gained 2.4 and 3.0% oxygen. Both Neavel (4) and Chang et al. (3) indirectly imply that oxygen incorporation beyond about 2% will significantly reduce the conversion yield. This is apparently not the case for oil generation when a modified solvent is used. Moreover, these results lead to the conclusion that oxidized coal can be successfully liquefied without creating a debit in either oils or conversion by using modified rather than base liquefaction solvent.

TABLE 43

OXIDATION OF ILLINOIS #6 BURNING STAR COAL BY VARIOUS METHODS

Treatment condition	% oxygen[a] Dry basis	% oxygen[a] DAF basis	% ash (dry)	% sulfur (dry)
None (original coal)	11.65	13.06	10.78	3.92
Fluidized dry air				
At 70°C for 1 hr	11.61	13.00	10.55	
for 2 hr	12.63	14.14	10.71	
for 5 hr	12.48	13.97	10.67	
At 170°C for 1 hr	14.12	15.78	10.49	
for 2 hr	14.68	16.38	10.42	
for 5 hr	16.42	18.30	10.37	
Fluidized wet air at 170°C for 5 hr	20.23	--	NA[b]	
5% H_2O_2 in 50:50 methanol/ 0.1 N H_2SO_4	17.19	18.70	8.07	
5% H_2O_2 in 0.1 N H_2SO_4	14.25	--	NA	
72% H_2SO_4 at 0°C for 1 hr	11.83	--	NA	
At 50°C for 1 hr	11.88	13.03	8.79	4.79
At 50°C for 18 hr	14.06	15.34	8.35	6.11

---

[a] Direct determination of oxygen using modified Coulometrics, Inc. oxygen analyzer.

[b] NA, not available.

FIGURE 5
EFFECT OF TEMPERATURE ON THE RATE OF AIR OXIDATION OF ILLINOIS #6 COAL AS DETERMINED BY THERMOGRAVIMETRIC ANALYSIS

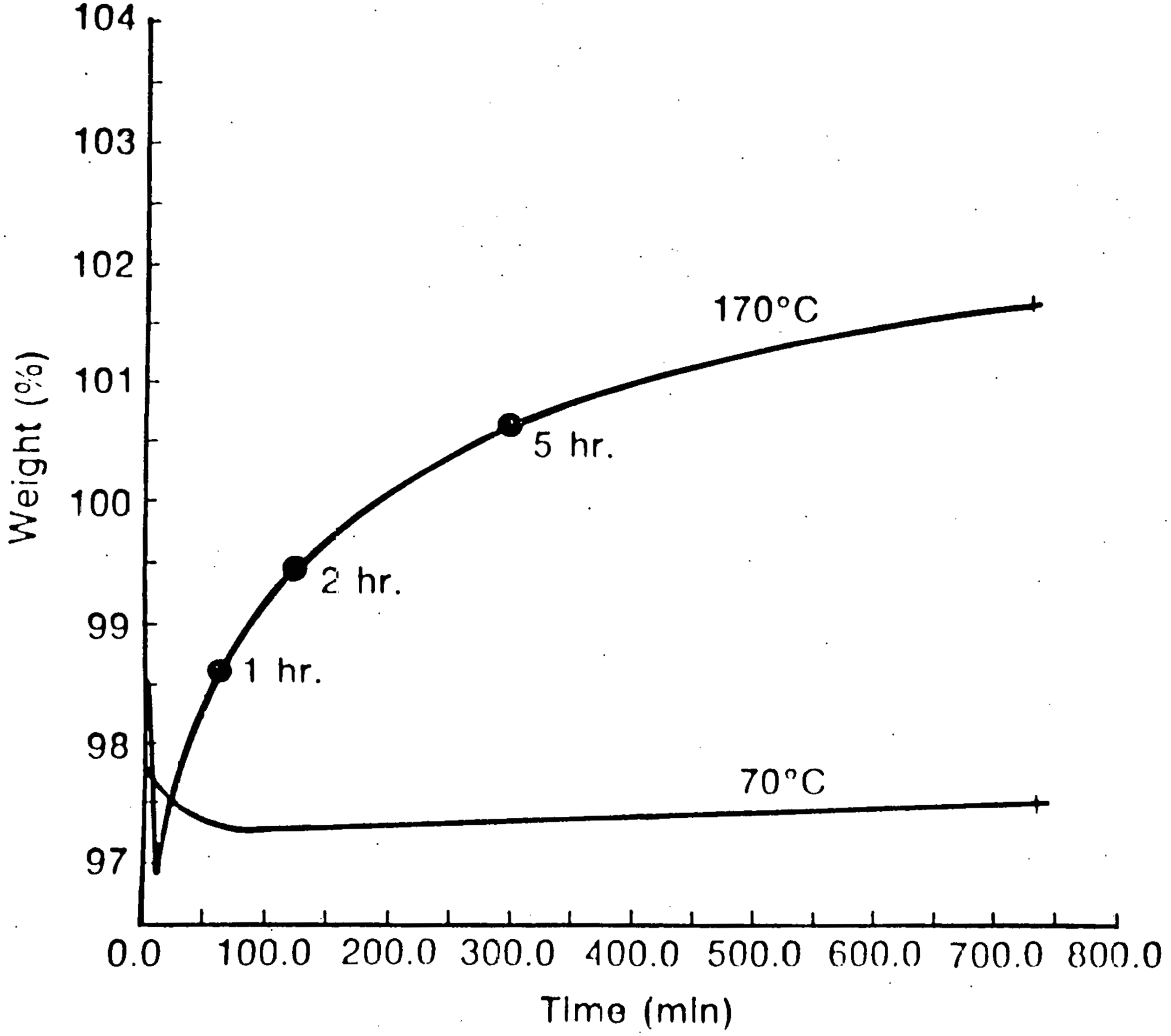

TABLE 44

MODIFIED SOLVENT LIQUEFACTION OF ILLINOIS #6 COAL PREOXIDIZED UNDER VARIOUS CONDITIONS (LIQUEFACTION CONDITIONS: 425°C; 1 HR; 850-PSIG H_2 COLD CHARGE)

	Original coal	Air-oxidized coal, 170°C		72% H_2SO_4-oxidized coal		H_2O oxidi coa
		1 hr	2 hr	1 hr; 0°C	18 hr; 50°C	
Run no.	16-51	1 59	62-56	62-48	60-70	60-
Oxygen incorporation (%)	--	2.4	3.0	0.1	2.4	5.
Product distribution (wt % MAF coal)						
Gases	5.7	9.1	10.6	9.8	11.8	10.
Oils	21.4	20.5	22.8	19.9	4.1	4.
SRC	46.0	44.2	42.7	46.5	42.9	43.
IOM	26.9	26.2	23.9	23.8	41.2	42.
Conversion	73.1	73.8	76.1	76.2	58.8	57.
Mass recovery (wt %)	92.3	92.6	89.4	92.5	91.2	92.

A plausible interpretation of this unexpected phenomenon centers around the nature of the heteroatom interactions between the coal and solvent. When coal is oxidized in air at conditions below its normal ignition temperature (ambient to <200°C), the incorporation of oxygen proceeds with the ultimate formation of relatively stable carbonyl and hydroxyl groups. During liquefaction, these oxygenated groups compete for the donatable hydrogen during the critical thermal reaction period. They also interact with other constituents in the solvent and those formed from thermal reaction of the coal, resulting in undesirable side reactions leading to high molecular weight products rather than oils. Consequently, the lower oil yield observed when oxidized coal is liquefied with an original coal-derived solvent can be attributed to these interactions occurring between the oxygenated sites in the coal and the heteroatom constituents of the process solvent. Furthermore, the higher the heteroatom content of the solvent or the larger the extent of oxidation of the coal, the greater will be their effect upon decreasing the conversion yields.

The use of modified solvent (treated by adsorption on a substrate such as silica gel or by reaction with acid gases such as HCl) was shown earlier to significantly enhance oil production. We have attributed this phenomenon to increases in the inherent catalytic activity due to removal of catalyst poisons and to the reduction of solvent/coal adduct formation. Because of oxidation effects, we did <u>not</u> predict comparable oil yields from modified solvent and oxidized coal, and unexpectedly found that liquefaction did produce <u>optimal</u> yields. This suggests that the heteroatom constituents in the solvent are the "key" agents that cause the negative effects when oxidized coal is liquefied. When the heteroatoms are removed from the solvent, the oil conversion yields are restored.

In contrast, coal that was mildly oxidized with hydrogen peroxide (5.5% oxygen added) yielded drastically lower amounts of oil, and overall conversion was reduced by almost 20%, even in the presence of modified solvent. This result is indeed consistent with that observed by others (5, 6) using original solvent, but is somewhat surprising because the oxygen uptake for the peroxide-oxidized coal is only several percent greater than the air-oxidized coal. Hence, one might assume that the oxidation mechanism when hydrogen peroxide is used is quite different from that of air oxidation at elevated temperature, and so the type of solvent makes little difference.

Oil production was also destroyed when 72% H_2SO_4 was used to preoxidize the coal at 50°C for 18 hr, and conversion dropped by 20%. This is also a contradiction, since less oxygen was incorporated (only 2.4%) than in the case of the air-oxidized coal, which showed no change in oil yield. Other coal samples were preoxidized with 72% H_2SO_4 at less severe conditions of only 1 hr at 0°C. At these conditions, very little oxygen was incorporated and relatively no change in the oil yield or conversion was observed upon liquefaction compared to yields with air-oxidized coal.

In all cases, the gas yields from liquefaction of oxidized coals were considerably higher than that from liquefaction of the original coal. Part of the increase can be attributed to an increase in the carbon oxide gases; however, there was also an equivalent increase in the C_2 through C_4 hydrocarbon gases. The reasons for the increase in CO_x are obvious, but the source of the increase in light hydrocarbon gases is unknown.

Since the air-oxidized Illinois #6 coals exhibited relatively unchanged liquefaction behavior, they were selected for most of the ion-exchange tests described in the next section.

CATION EXCHANGE OF PREOXIDIZED COAL

Earlier work (7) has shown that effectively dispersing a catalyst in the coal liquefaction reaction mixture markedly improves oil production. For example, addition of iron by impregnation using aqueous ferrous sulfate, as opposed to dry-mixing pyrite or powdered $FeSO_4$ with the coal, significantly increases the oil yield. Conceivably, therefore, the catalytic activity could be improved even further by molecularly dispersing a catalyst in the coal structure by ion exchange prior to liquefaction.

Dispersion of a metal by ion exchange from aqueous solution is possible with certain coals that contain the appropriate functional groups. For example, low-rank coals that typically contain 1-4 mequiv/g carboxyl groups are readily amenable to ion exchange (6). However, bituminous coals naturally contain relatively few carboxyl groups or other ion-exchange sites that can readily ionize at intermediate acidities, unless the coals have been severely weathered. Hence, in order to use ion exchange as a method for dispersing catalysts on bituminous coal, one must first chemically alter the coal in order to produce the functional groups that are capable of complexing metals. This was accomplished by oxidizing Illinois #6 coal, as described in the preceding section.

Selected coals from the preoxidation experiments were slurried with dilute salt solutions to effect ion exchange of various cations (Ca^{2+}, Na^{+}, Fe^{2+}, Fe^{3+}). The ion-exchange procedure consisted of slurrying a sample of preoxidized coal in a dilute solution of the desired salt (i.e., ferrous sulfate, ferric chloride, calcium acetate, sodium acetate, or sodium hydroxide). This was followed by filtration and exhaustive water extraction to remove excess or nonadsorbed salts. The amount of specific cation adsorbed onto the coal was then measured by following a "back-exchange" procedure similar to the hydrochloric acid digestion step of the ASTM D-2492 (8) procedure used to determine pyrite. In the back-exchange, the cation-exchanged coal was first treated with 0.1 N HCl at similar conditions to that of the ion exchange. Then the HCl extract was collected and analyzed for the presence of desired cations removed by the acid.

The results of exchange experiments for Illinois #6 coal are summarized in Table 45 for Ca^{2+} and Na^{+} exchange at pH 7, for Na^{+} exchange at pH 12, and for Fe^{2+} and Fe^{3+} exchange at pH 3 to 5. An additional exchange experiment with peroxide-treated coal was also conducted using ferrous sulfate in which the pH of the exchange medium was varied between 2 and 6 using a standard phthalate buffer. However, no appreciable difference in the extent of ion exchange was detected except that appreciable iron precipitated upon addition of the coal to the pH 6 solution.

TABLE 45

CATION EXCHANGE OF PREOXIDIZED ILLINOIS #6 BURNING STAR COAL

Exchange salt:	$Ca(C_2H_3O_2)_2$	$Na(C_2H_3O_2)$	NaOH	$FeCl_3$	F
Initial pH:	7	7.1	12.6	3 to 5	
	% Ca^{2+}	% Na^+	% Na^+	% Fe^{3+}	%
FSM-116: original	0.19	0.05	0.06	0.30	0
Back exchange of original	--[a]	--	--	0.05	0
Air oxidation: 5 hr 70°C	0.26	0.04	--	--	-
1 hr 170°C	--	--	--	--	-
2 hr 170°C	0.17	0.12	--	--	-
5 hr 170°C	0.17	0.22	0.41	--	0.
5% H_2O_2 in CH_3OH/dilute H_2SO_4	0.12	0.16	0.26	0.27	-
72% H_2SO_4 at 50°C, 1 hr	0.04	0.13	0.14	--	-
18 hr	0.18	0.46	--	0.24	-

[a] --: Not determined.

The Ca-exchange data presented in Table 45 are complicated by the fact that back-exchange with dilute HCl dissolved a portion of the calcite ($CaCO_3$) present in Illinois #6 coal, giving rise to the observed 0.19% Ca. But as the oxidized coals did not show any appreciable increase over the original coal, we can infer that relatively little or no Ca exchange has taken place.

Na-exchange data present a somewhat different picture. Very little Na^+ was found after back-exchange of the coals treated with sodium acetate and sodium hydroxide, indicating that relatively few functional groups were available for monovalent ion exchange. On the other hand, the Na adsorption capacity of one oxidized coal increased significantly, from 0.07 to 0.41% sodium adsorbed on coal. However, in terms of the actual ion exchange capacity (IEC), 0.40% Na is equivalent to only 0.17 mequiv/g, which is quite low for an ion-exchange substrate. For comparison, lignite or subbituminous coals typically yield IECs of 1-4 mequiv/g. Although there is a modest correlation between the extent of sodium adsorption and the amount of oxygen incorporation, the amount of sodium adsorption represents only a very small fraction of the amount of oxygen incorporated. Hence, we can assume that most of the incorporated oxygen was present in functional groups that were otherwise <u>not</u> suitable for ion exchange.

As with calcium, exchange of either ferrous or ferric cations onto oxidized coals, via $FeSO_4$ and $FeCl_3$ treatment, respectively, was not any better than exchange onto original (nonoxidized) coal.

It is especially important, however, to point out that appreciable iron was absorbed onto the original Illinois #6 coal under the conditions of the experiment, compared to the amount of sodium absorbed. Note that back-exchange of the original coal with dilute acid removed only 0.05% acid-soluble Fe, while back-exchange of the $FeSO_4$-treated coal removed 0.30% Fe. Whether or not the net difference (0.25% Fe) represents an actual ion exchange of Fe is uncertain, although the modest drop in pH from 5.2 to 4.6 during the experiments lends credibility to an ion-exchange type of adsorption. Regardless, pretreatment by oxidation should produce optimal dispersion of iron or other metals compared to other methods of adding iron at the same loading capacity.

Liquefaction tests were conducted on air-oxidized Illinois #6 coals that had been treated with $FeSO_4$. Modified solvent was used exclusively for liquefaction, because original solvent showed relatively poor behavior with oxidized coals. The results of the liquefaction tests are summarized in Table 46.

The addition of only 0.25% Fe to the original (unoxidized) coal by the exchange procedure appeared to produce a fairly significant increase in both conversion (+11.4%) and oil production (+7.9%) (see Table 46). When the coal was preoxidized at 170°C for 1 hr, no appreciable change was observed in the liquefaction product distribution compared to liquefaction of original coal. However, $FeSO_4$ treatment of the oxidized coal produced a significant increase of nearly 13% in the oil yield compared to liquefaction of the oxidized coal. Nonetheless, this increase represented only a marginal improvement over that seen when the original coal was treated with $FeSO_4$ without preoxidation. When the coal was preoxidized for a longer period (i.e., 5 hr at 170°C, corresponding to an oxygen uptake of about 5%), the extent of Fe adsorption was increased only slightly relative to the original coal, while the liquefaction conversion and oil yields were reduced to the original coal level.

These results clearly show that mild air oxidation of Illinois #6 coal produces only a minor fraction of metal adsorption sites relative to the large amount of oxygen incorporated. Hence, ion-exchange treatment of oxidized coal with $FeSO_4$ does not produce a significant increase in oil yield over that found with $FeSO_4$ treatment of original coal. Nevertheless, the exchange of Fe onto original Illinois #6 coal does indeed produce a substantial increase in the yield of oils at a relatively low loading capacity (0.2 to 0.3% on coal) when liquefaction is conducted in the presence of modified solvent.

TABLE 46

MODIFIED SOLVENT LIQUEFACTION OF AIR-OXIDIZED ILLINOIS #6 COAL EXCHANGED WITH FERROUS SULFATE (LIQUEFACTION CONDITIONS: 425°C; 1 HR; 850-PSIG H_2 COLD CHARGE)

	Original coal		Preoxidized coal (170°C)		
			1 hr		5 hr
Catalyst exchange:	None	$FeSO_4$	None	$FeSO_4$	$FeSO_4$
% HCl-soluble Fe determined by back exchange	0.05	0.30	0.05	0.33	0.38
Liquefaction run no.	16-51	52-58	1-59	3-48	3-61
Product distribution (wt % MAF coal)					
Gases	5.7	6.8	9.1	7.5	10.3
Oils	21.4	29.3	20.5	33.3	22.3 (22.8)[a]
SRC	46.0	48.3	44.2	40.4	43.6 (44.9)[a]
IOM	26.9	15.6	26.2	18.8	23.6 (23.8)[a]
Conversion	73.0	84.4	73.8	81.1	76.4 (75.3)[a]
Mass recovery (wt %)	92.3	96.3	92.6	92.8	97.8

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[a] Duplicate values.

PULVERIZATION OF COAL

The liquefaction performance of Illinois #6 Burning Star coal pulverized under various conditions, including in the presence of modified solvent, was also investigated. When coal is comminuted, the decrease in particle size appreciably increases the amount of fresh surface area containing many highly active sites. It would follow that comminution is probably accompanied by reaction of the newly generated surface sites with specific molecules either contained in or constituting the medium used in the pulverization process. These interactions could, in turn, significantly influence the liquefaction performance of the pulverized coal. In particular, if coal were pulverized in the presence of a hydrogen-donor solvent, there would be a higher propensity for the newly generated surface sites to interact with the solvent molecules. This situation could influence the subsequent thermal liquefaction reaction by improving the transfer of hydrogen from the solvent to the coal. Furthermore, such detrimental side effects as surface oxidation leading to poor conversion would be appreciably reduced by pulverizing coal in the presence of solvent or under inert conditions.

To date, little information has been published on the effects of solvent grinding on subsequent liquefaction, as discussed in literature reviews published in one of our Quarterly Reports for this program (2). Only Chang et al. (9) demonstrated in batch tubing-bomb experiments that grinding of coal by hand in the presence of tetralin, as opposed to dry grinding in air, appreciably improved coal conversion. However, the improvement, ranging from 10 to 20%, was based on total conversion to creosol solubles, which provided absolutely no information about effect upon distillate oil yields.

Therefore, a series of experiments aimed at testing the propensity for Illinois #6 Burning Star coal to be converted to distillate oils after having been pulverized under various conditions was performed. The pulverization conditions are listed below:

- Inert gas (helium at 0°C)
- Air under slightly elevated temperature and pressure (82°C/120 psi)

- Alcohol with and without the presence of soluble molybdenum octoate as catalyst
- Base liquefaction solvent at low temperature
- Modified solvent at low temperature
- Modified solvent at elevated temperature
  - Under helium pressure with and without molybdenum hexacarbonyl
  - Under hydrogen pressure and $Mo(CO)_6$ with and without H_2S and added Fe compounds
- Ethanol, with base liquefaction and modified solvents, with and without molybdenum octoate as catalyst
- Toluene containing $Mo(CO)_6$ at elevated temperature

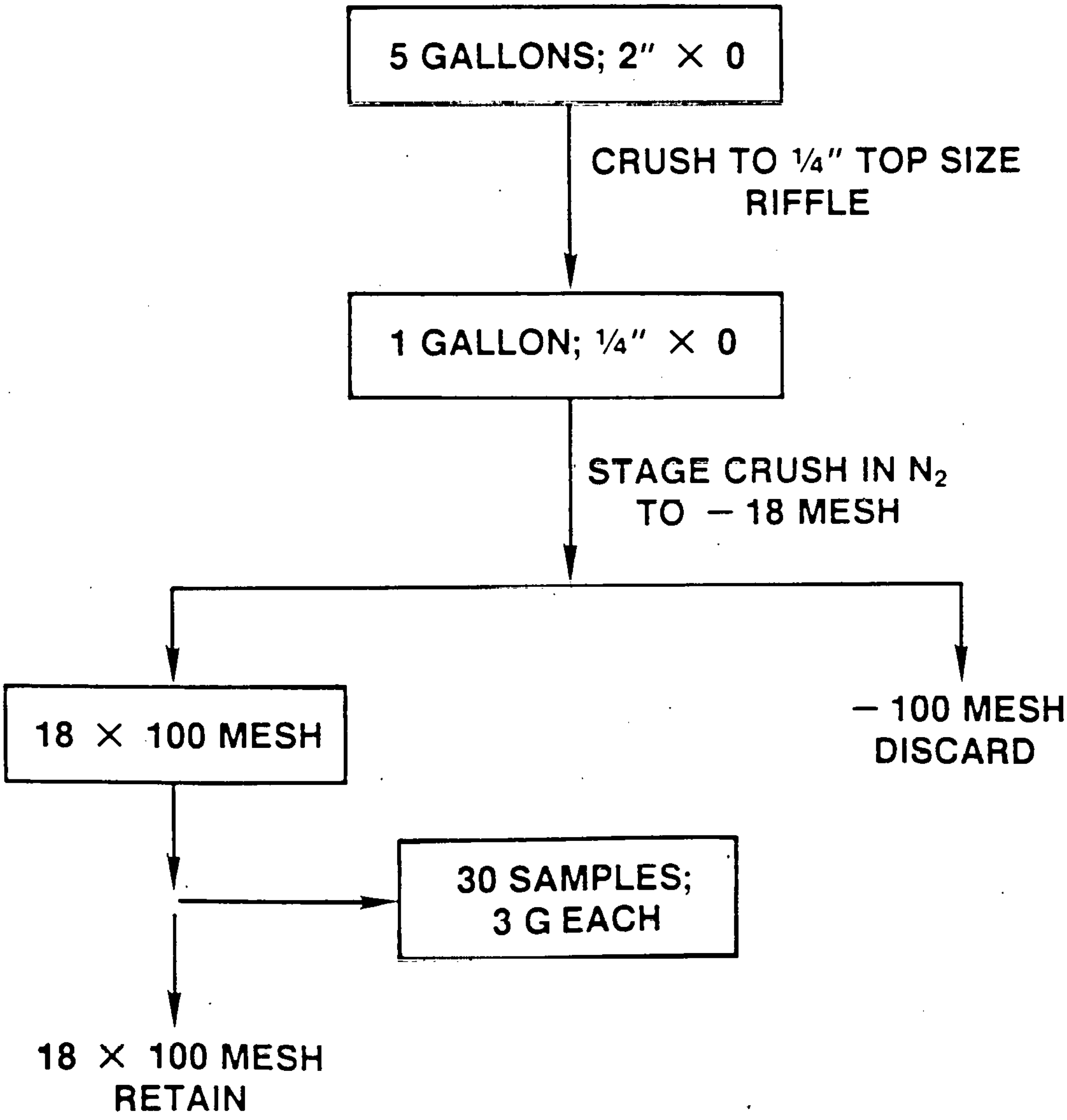
Feedstock Preparation

A fresh sample of Illinois #6 coal was obtained directly from the Burning Star #2 mine by Air Products. The as-received cleaned coal (2 in. x 0) was subjected to milling to generate a 1/4 in. x 0 sample from which 1 gallon was recovered for further processing, as outlined in Figure 6. The 1/4 in. x 0 coal was carefully stage crushed in a general purpose mill contained in a nitrogen-filled glove box to obtain a size fraction of 18 x 100 mesh (or 1 mm x 150 μm), which represented 79.8% of the original coal. Since the specific objective of this part of the program was to study the effects of grinding the coal, the fines (-100 mesh material) were not included in the study. The 18 x 100 mesh fraction was then subdivided by representative splitting to obtain multiple samples containing about 3 g each to be used for the liquefaction experiments.

Grinding Experiments

To simplify the grinding method, coal or coal plus the solvent was charged into a 50-cm^3 tubing-bomb reactor normally used for liquefaction. The weights of the coal and solvent were conveniently chosen to be 3 and 6 g, respectively, since this was the usual charge for the liquefaction test, which could be run immediately following the grinding step without the need to make sample transfers.

FIGURE 6
PREPARATION OF ILLINOIS #6 COAL FOR GRINDING EXPERIMENTS



In order to grind the coal, a small steel rod was placed inside the tubing-bomb reactor, which was agitated at 1,000 strokes per minute using the microautoclave shaker assembly. During the grinding period, which was varied between 5, 10, and 30 min, the reactor temperature was maintained at 0°C by immersing it in an ice bath.

Table 47 lists the particle-size distribution obtained upon sieve analysis of the coal pulverized with one steel rod in the presence of both air (dry) and process solvent. When process solvent was used during grinding, a n-pentane wash was used to remove the solvent from the coal prior to the analysis. The data in Table 47 clearly indicate that only 10 min was needed to reduce the particle size to the desired level (<200 mesh) when air was used as the pulverization medium. However, as can be seen from Figure 7, which compares the rate of pulverization in the presence of air and process solvent, the conditions were not severe enough to achieve the desired particle-size reduction when solvent was used.

Hence, additional experiments were conducted to find the optimum conditions for pulverizing coal in the presence of process solvent. Runs were made at similar conditions as above, except that two steel balls were placed within the reactor and grinding was allowed to proceed for 60 min. The particle-size data are presented in Table 48 and the results of the solvent grinding are plotted in Figure 8. The rate of pulverization was improved significantly by using two steel balls rather than one steel rod, and the goal of reducing >90% of the material to below 200 mesh was achieved. Hence, all the grinding experiments were run under these conditions (two steel balls and 1-hr grinding time). The actual particle-size distributions for both helium-ground coal and process solvent ground coal, graphically depicted in Figure 9, compare favorably.

In addition to the above runs, several exploratory runs were made to test the pulverization rate in the presence of alcohol (at the same weight ratio used for process solvent, i.e., 6 g of solvent/3 g of coal). However, the grinding efficiency in alcohol was markedly lower than noted with process solvent.

TABLE 47

PRELIMINARY GRINDING EXPERIMENTS OF ILLINOIS #6 COAL USING ONE STEEL ROD[a]

Particle sizes (wt %)	Air			Process solvent (6 g)		
	5 min	10 min	30 min	5 min	10 min	30 min
20 x 100 mesh	50.0	1.6	1.6	74.4	48.7	28.7
100 x 170 mesh	24.4	6.2	4.8	14.3	24.7	29.0
170 x 325 mesh	2.1	21.7	2.8	3.4	11.8	4.7
-325 mesh	23.5	71.0	90.8	8.0	14.8	37.4

[a] Grinding conditions:

3 g (20 x 100 mesh) Illinois #6 coal
0°C bath temperature
50-cm^3 tubing-bomb reactor with one steel rod (3/16 in. D x 1 in. L)
1,000 strokes/min agitation

FIGURE 7
EFFECT OF MEDIUM ON RATE OF GRINDING OF ILLINOIS #6 COAL
(3 g OF 20 × 100 MESH COAL; ONE STEEL ROD)

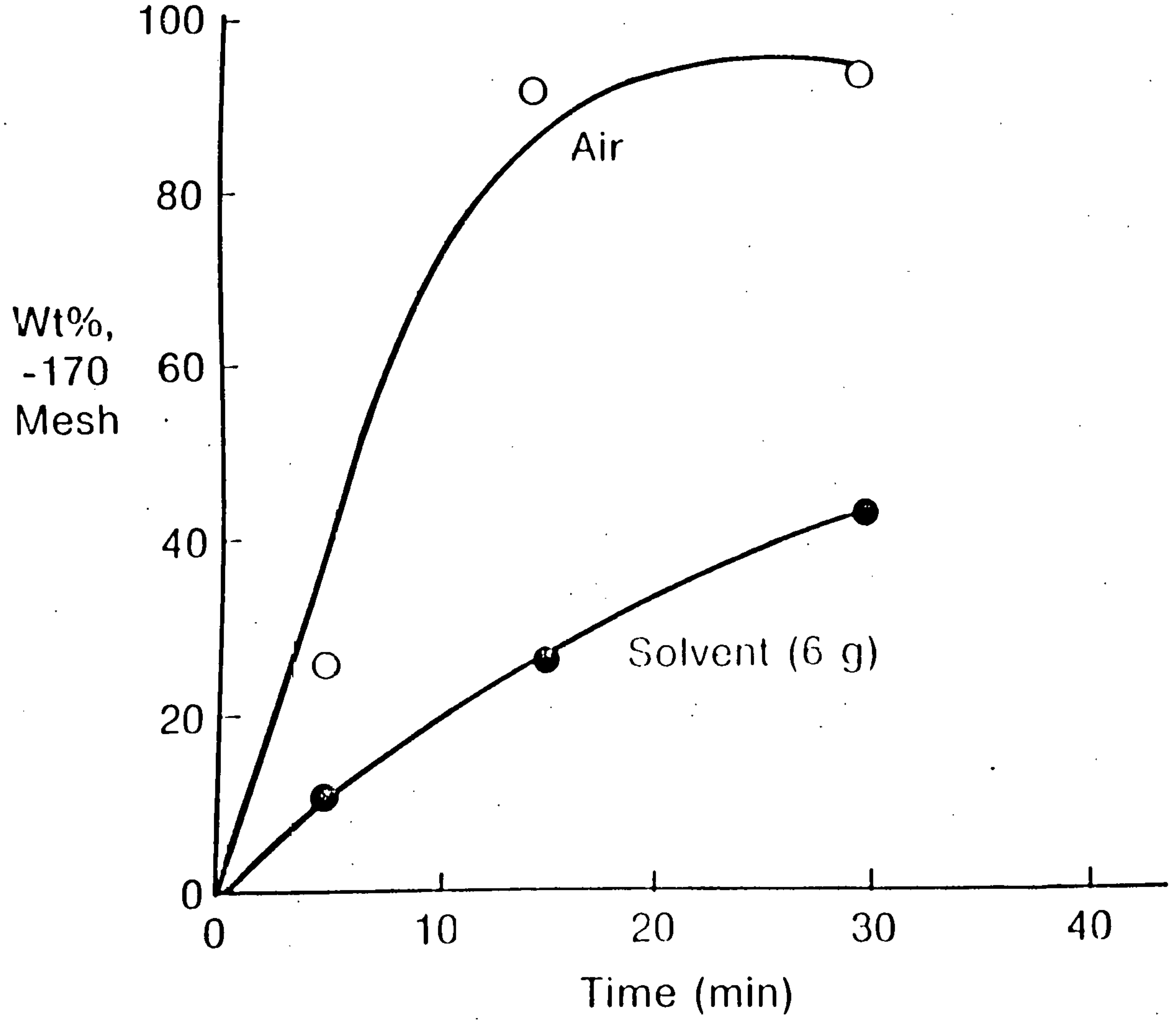


TABLE 48

PRELIMINARY GRINDING EXPERIMENTS OF ILLINOIS #6 COAL USING TWO STEEL BALLS[a]

Particle sizes (wt %)	Air, 5 min	Helium, 60 min	Process solvent			Ethanol, 90 min
			30 min	60 min	60 min	
20 x 100 mesh	4.1	0.3	5.4	1.7	1.9	6.0
100 x 170 mesh	10.0	3.2	15.1	8.9	7.1	8.4
170 x 325 mesh	2.7	17.9	4.7	9.9	6.7	0.6
325 x 400 mesh	48.0	18.7	50.2	30.1	37.5	14.1
-400 mesh	35.3	59.9	24.6	49.4	46.8	70.8

[a] Grinding conditions:

3 g (20 x 100 mesh) Illinois #6 coal
0°C bath temperature
50-cm^3 tubing-bomb reactor
1,000 strokes/min agitation

[b] Ethanol grinding was done in the presence of three steel balls and 4 g of ethanol to 3 g of coal.

FIGURE 8
GRINDING OF ILLINOIS #6 COAL IN THE PRESENCE OF PROCESS SOLVENT
(3 g OF 20 × 100 MESH COAL; 6 g OF SOLVENT)

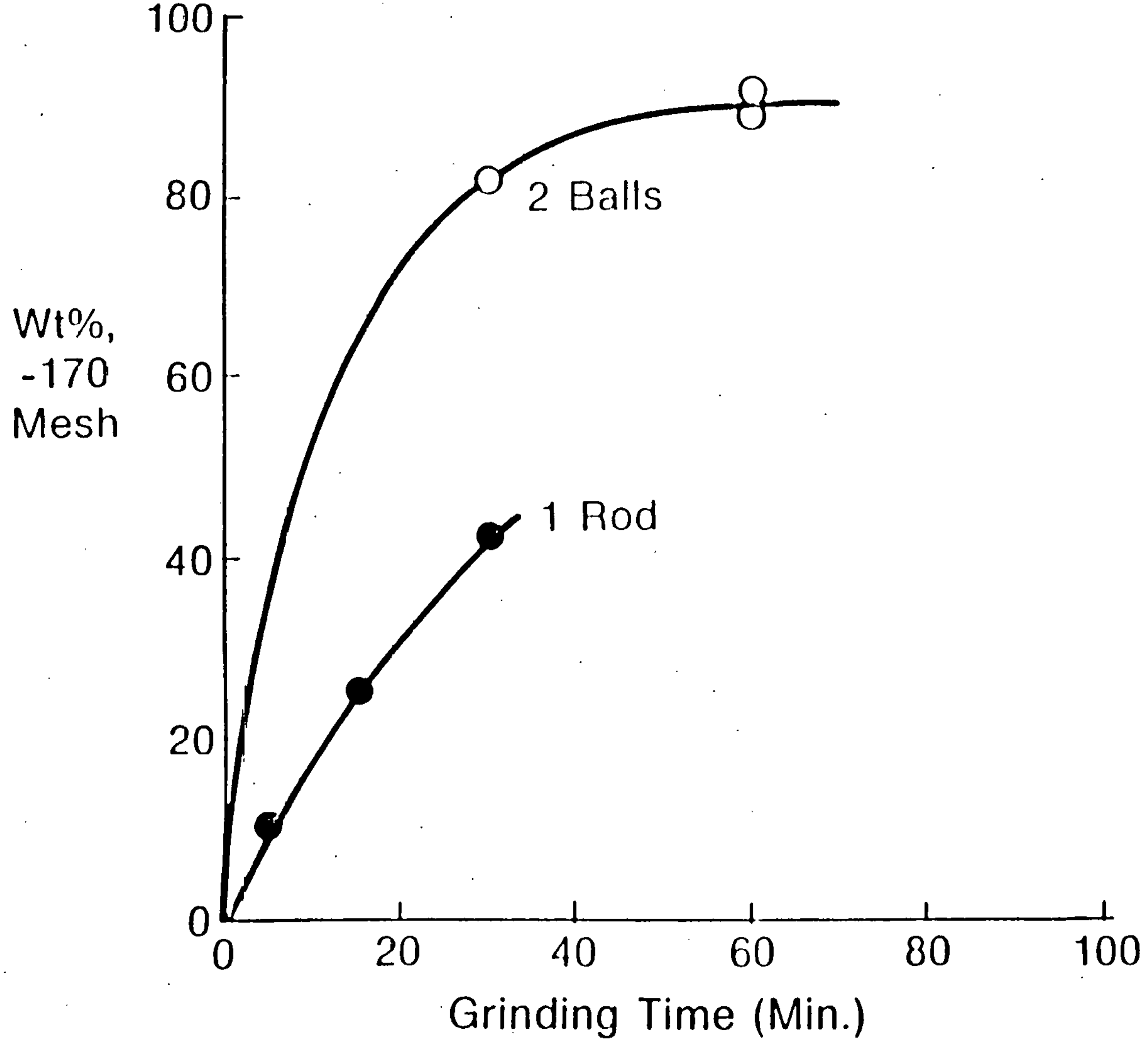
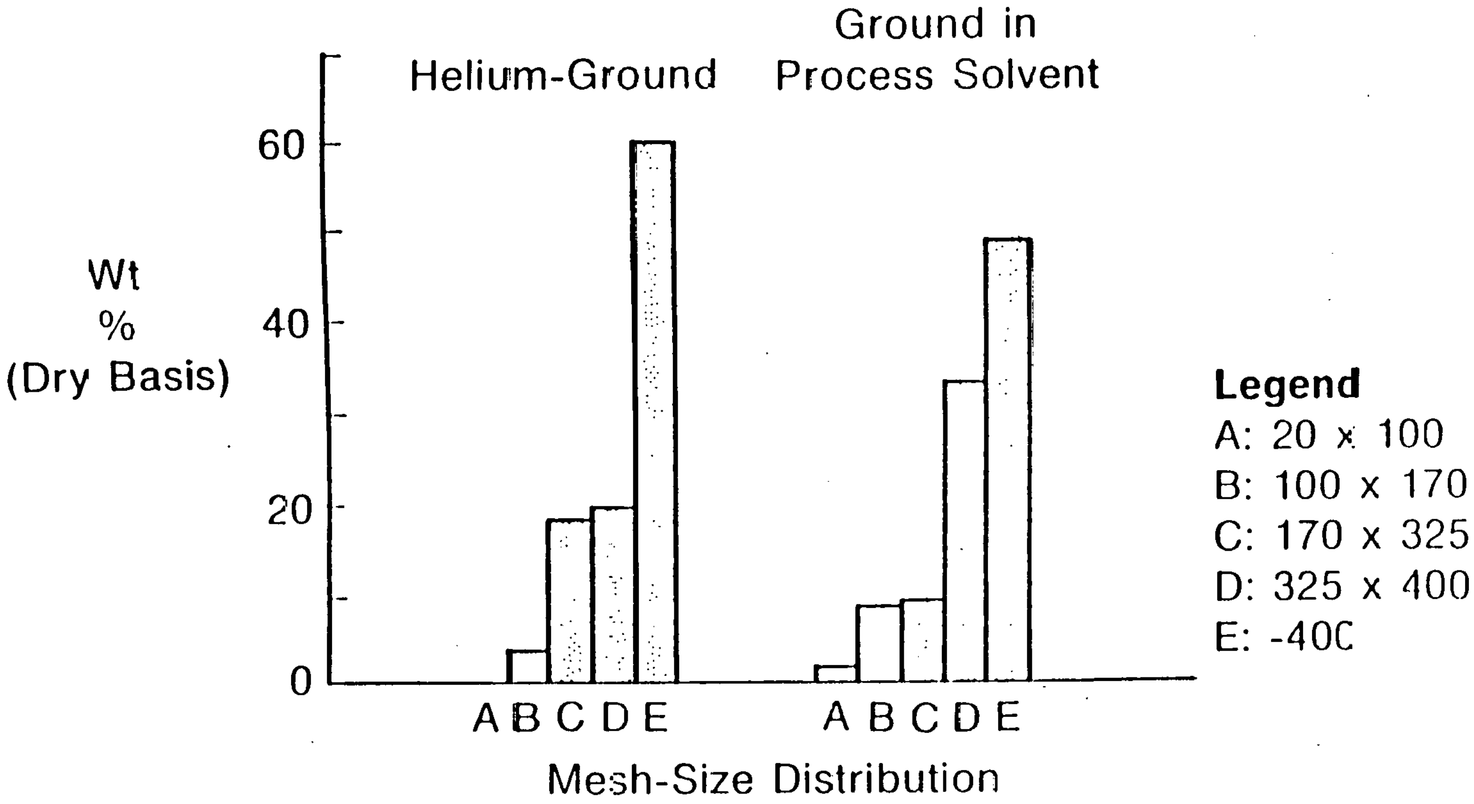


FIGURE 9

COMPARISON OF PARTICLE-SIZE DISTRIBUTION OF ILLINOIS #6 COAL GROUND IN HELIUM AND PROCESS SOLVENT (3 g OF 20 × 100 MESH COAL; 60 MIN; TWO STEEL BALLS)



herefore, it was necessary to go to 90-min grinding time with three steel balls and only 4 g of alcohol/3 g of coal to achieve a comparable particle-size distribution. The particle-size distribution obtained is also listed in Table 48.

Liquefaction Experiments

The pulverized coals were subjected to liquefaction in a tubing-bomb reactor to establish the effect of pulverization upon liquefaction. When the coal was pulverized in either air or helium, the tubing bombs were charged with 3 g of the freshly pulverized coal and 6 g of solvent and pressurized with H_2 to 850 psig.

Liquefaction runs in all cases were made at 425°C for 1 hr. The product gases were collected and analyzed by gas chromatography, while the total product liquid was separated by a solvent workup procedure to obtain an oil fraction (n-pentane soluble), an SRC fraction (methylene chloride/methanol soluble, pentane insoluble), and a residue.

Illinois #6 Coal Ground in Helium (Baseline Runs). Illinois #6 coal was ground in helium and then liquefied according to the conditions shown in Table 49 using base liquefaction solvent, modified solvent, and modified solvent containing 500 ppm of molybdenum as molybdenum octoate. Solvent modification significantly improved the oil yield, and the addition of catalyst produced an even larger increase in the oil yield from the coal (see Table 49).

Illinois #6 Coal Ground in Air. The grinding of Illinois #6 coal was examined in an air environment. The grinding tubing bomb was pressurized to 120 psig with air and then heated to a slightly elevated temperature of 82°C (which happens to be similar to that used in a typical commercial gas-swept mill). After 10-, 40-, and 60-min grinding intervals, an air sample was taken and analyzed by gas chromatography to measure the change in oxygen concentration. The results from this experiment are shown in Figure 10 where the measured loss of oxygen has been used to calculate the oxygen incorporation on the coal and plotted against time. The linearity of the

TABLE 49

LIQUEFACTION OF ILLINOIS #6 COAL PULVERIZED UNDER INERT CONDITIONS[a]

	Base liquefaction solvent	Modified solvent	
		No catalyst	500-ppm Mo
Run no.	47-63	47-61	57-56
Product distribution (wt % MAF coal)			
Gases	6.8 (8.1)[b]	6.2 (5.7)[b]	9.2 (6.7)[b]
Oil	13.3 (12.4)	24.1 (21.3)	37.6 (45.4)
SRC	58.1 (62.1)	41.4 (46.0)	46.4 (40.1)
IOM	21.7 (17.4)	28.3 (27.0)	6.8 (7.8)
Conversion	78.3 (82.6)	71.7 (73.0)	93.2 (92.2)
Mass recovery (wt %)	94.4	96.7	

[a] Pretreatment:

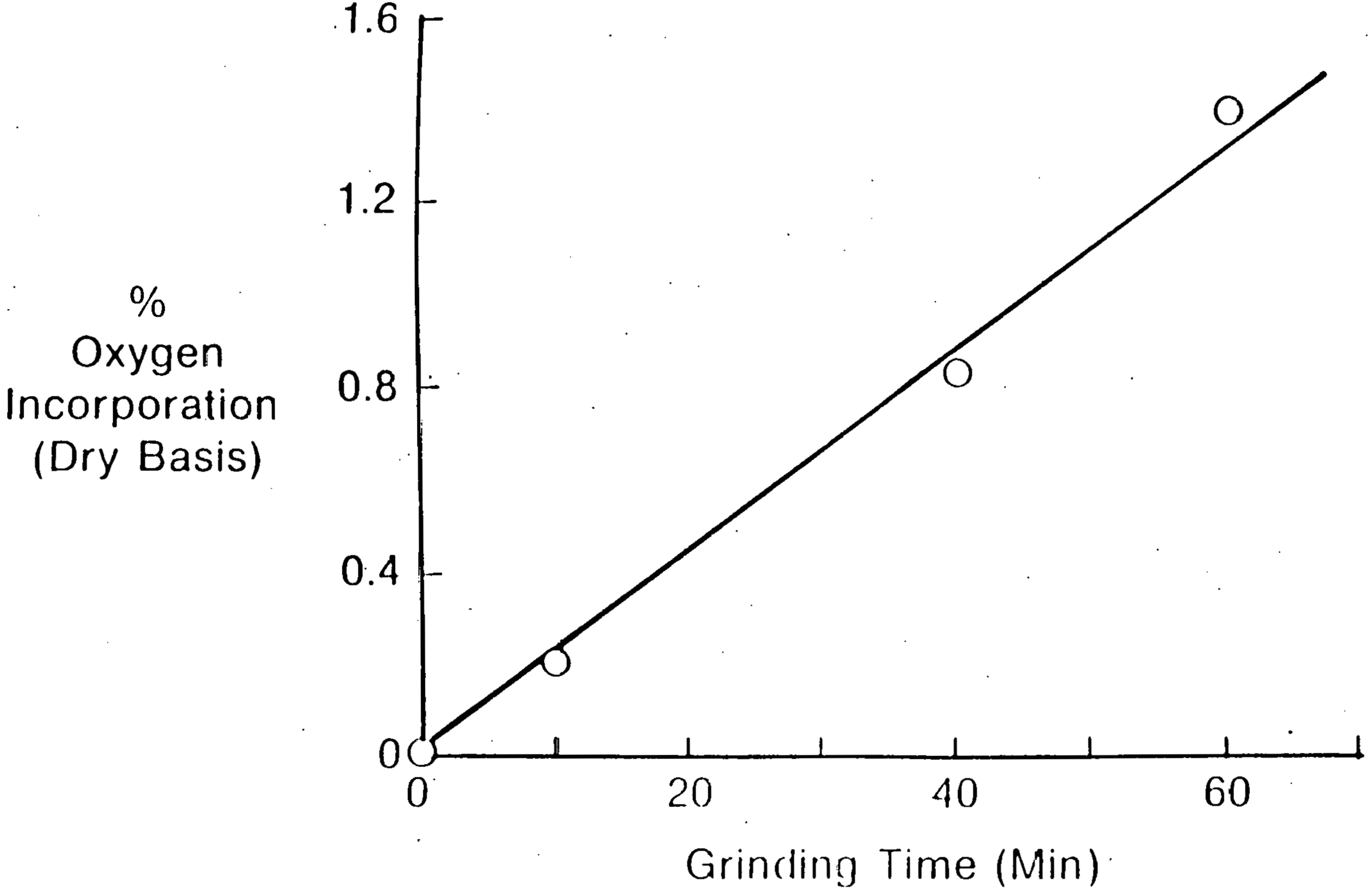
3 g of coal (20 x 100 mesh); 1 hr; 2 steel balls; 2 psig helium; 0°C

Liquefaction:

425°C; 1 hr; 3 g of coal; 6 g of solvent; 850 psig H_2 cold; 1,000 strokes per minute agitation

[b] Data in parentheses represent previous liquefaction run made with a representative sample of -200 mesh Illinois #6 coal.

FIGURE 10
GRINDING OF ILLINOIS #6 COAL IN THE PRESENCE OF AIR UNDER SLIGHTLY ELEVATED CONDITIONS
(3 g OF 20 × 100 MESH COAL; 120 PSIG AIR; 180°F; TWO STEEL BALLS)



relationship is indeed surprising, but is probably attributed to the increase reactive surface area as the material is being ground finer with time. Figure also shows that Illinois #6 coal has gained 1.4% oxygen after grinding for 1 h and it is this condition that was used to generate the sample for the liquefac tests.

The results of liquefaction testing are compared in Table 50 with results from helium baseline runs (Table 49). The most striking feature of the data is the negative impact that air-grinding has on both conversion and oil yields, especially when base liquefaction solvent is used. In fact, the negative oil yield (-3.9%) with base liquefaction solvent indicates not only that the oil y has declined dramatically, but more importantly that process solvent has been incorporated into heavier products from the liquefaction, as discussed previously.

When modified solvent and catalyst were used to liquefy the air-ground coal, conversion and, in particular, the oil yield increased significantly, although grinding still showed a negative effect compared to the baseline helium runs. Because our intention was to maximize the oil yield, additional runs of the air-ground coal with modified solvent but without catalyst were not conducted. Nevertheless, the conversion <u>debit</u> due to oxidation in air is improved by 6-7% when modified solvent and catalyst are used in liquefaction.

One can certainly postulate from these data that interaction of the "oxygenated species" generated during air-grinding of the coal and the heteroatom constitue contained in the base liquefaction solvent leads to retrograde reactions during liquefaction. Hence, if the heteroatom constituents and/or the oxidation effec were removed from the system, there would be a significant increase in oil yiel We have observed that the use of a modified solvent somewhat restores the conversion and significantly decreases the oil debit due to the oxidation effects.

Furthermore, concerns about oxidation of coal that have arisen in liquefaction processes using recycle solvents may be alleviated by using modified solvent. using modified solvent in liquefaction, N_2 blanketing and other costly handling procedures to avoid oxidation could be eliminated.

TABLE 50

LIQUEFACTION OF ILLINOIS #6 COAL PULVERIZED IN HOT AIR[a]

	Base liquefaction solvent		Modified solvent + 500 ppm Mo octoate	
	Air	Helium[b] baseline	Air	Helium[b] baseline
Run no.	52-48	47-63	52-37	57-56
Product distribution (wt % MAF coal)				
Gases	7.4	6.8	6.5	9.2
Oil	-3.9	13.4	26.9	37.6
SRC	63.0	58.1	52.8	46.4
IOM	33.5	21.7	13.8	6.8
Conversion	66.5	78.3	86.2	93.2
Mass recovery (wt %)	104.5	94.4	98.1	96.7

[a] Pretreatment:

3 g of coal (20 x 100 mesh); 1 hr; 2 steel balls; 1 hr; 82°C; 120 psi air

Liquefaction:

425°C; 1 hr; 3 g of coal; 6 g of solvent; 850 psig H_2 cold; 1,000 strokes per minute agitation

[b] Helium baseline runs from Table 49.

Illinois #6 Coal Ground in Coal-Derived Solvent. It was suggested in the literature that pulverization of coal in the presence of solvent prior to liquefaction would potentially improve the conversion, and indeed Chang's data showed some positive indications in this regard (9). But what is the effect upon oil yield? And, how does modification of the solvent affect the yields? To answer these questions, the liquefaction of Illinois #6 coal ground in coal-derived solvents was studied; results are discussed below.

Grinding at Low Temperature. Table 51 shows the results of liquefaction tests on coal ground in base liquefaction and modified solvents. These data are compared to the helium baseline runs from Table 49, where the coal was simply ground in helium and then liquefied with the respective solvents. Table 51 readily shows that grinding in the base liquefaction solvent has significantly reduced oil yield, while the use of modified solvent resulted in similar if not marginally improved oil yields.

The effect on conversion was somewhat different. When coal was preground in helium, conversion with modified solvent was appreciably less than that with base liquefaction solvent. This is presumably because of the poor solvency power of the modified solvent due to the absence of the N-bases and phenols. On the other hand, when coal was ground in the presence of solvents prior to liquefaction, conversion with modified solvent now becomes comparable to that of base liquefaction solvent. The substantial lowering of conversion due to the poor solvency power of the modified solvent is eliminated by allowing sufficient time for the solvent to penetrate the coal during the grinding stage.

Illinois #6 coal was also pulverized in the presence of a modified solvent containing 500-ppm molybdenum based on coal added as molybdenum octoate. Comparison of the liquefaction data from this run with that when the coal was first ground in helium and then liquefied with modified solvent and catalyst shows no appreciable difference in oil yield, although the yield in both cases is 10-12% higher than without catalyst. In this case, the effects due to the grinding are relatively insignificant in the presence of the highly active molybdenum catalyst.

TABLE 51

LIQUEFACTION OF ILLINOIS #6 COAL PULVERIZED IN PROCESS SOLVENTS AT 0°C[a]

	Base liquefaction solvent		Modified solvent			Modified solvent + 500 ppm Mo octoate	
		Helium[b] baseline			Helium[b] baseline		Helium[b] baseline
Run no.	49-60	47-63	49-59	57-59	47-61	49-35	57-56
Product distribution (wt % MAF coal)							
Gases	6.2	6.8	6.4	8.0	6.2	7.1	9.2
Oil	8.2	13.3	27.6	24.9	24.1	34.4	37.6
SRC	66.9	58.1	46.3	49.6	41.4	45.7	46.4
IOM	18.7	21.7	19.7	17.5	28.3	12.8	6.8
Conversion	81.3	78.3	80.3	82.5	71.7	87.2	93.2
Mass recovery (wt %)	96.2	94.4	95.6	97.7	96.7	96.3	-

[a] Pretreatment:

3 g of coal (20 x 100 mesh); 1 hr; 2 steel balls; 6 g of solvent; 0°C

Liquefaction:

425°C; 1 hr; 3 g of coal; 6 g of solvent; 850 psig H_2 cold; 1,000 strokes per minute agitation

[b] Helium baseline runs from Table 49

Grinding at Elevated Temperature. Several experiments were conducted to determine whether increasing the temperature during solvent grinding of coal would more strongly influence liquefaction, especially in the presence of a catalyst. Accordingly, Illinois #6 coal was pulverized at 170-250°C in the presence of modified solvent under either helium or hydrogen pressures of 800-850 psig. Some of the runs were made with 500-ppm molybdenum catalyst based on coal added as $Mo(CO_6)$. This form of Mo was used because it would decompose at elevated temperature and deposit Mo metal throughout the coal during the grinding, thus serving as an effective way to distribute the metal catalyst.

The results of the various runs are reported in Table 52. Coal ground in modified solvent at 170°C under a helium pressure of 800 psig did not appear to produce a significant difference in either oil yield or conversion compared to that ground in modified solvent at 0°C under only a few pounds per square inch of helium (compare Tables 51 and 52). Elevated temperatures, as shown in Table 52, resulted in 27.7% oil yields; low-temperature-treated coal yielded 24.9 and 27.6% oil in duplicate runs. Therefore, temperature of the pretreatment does not appear to be important if the treated coal undergoes thermal liquefaction.

When catalyst [500 ppm $Mo(CO)_6$] was added to the grinding medium (modified solvent at 170°C), the oil and conversion yields (Table 52) increased to the same degree as when coal was ground first in modified solvent and molybdenum octoate at 0°C (Table 51). Hence, the effect of temperature in the solvent grinding step up to at least 170°C does not appear to influence conversion even in the catalytic case.

Another grinding experiment was run using modified solvent and 500-ppm $Mo(CO)_6$, but in this case hydrogen replaced helium and the temperature was increased to 250°C during grinding. In this run (62-35), the oil yield upon liquefaction increased to 40.0%, representing a 6% improvement over the previous run made with helium (#63-41). Contrary to the increase in oil yield, coal conversion decreased by 5%.

TABLE 52

LIQUEFACTION OF ILLINOIS #6 COAL PULVERIZED AT ELEVATED TEMPERATURES IN THE PRESENCE OF MODIFIED SOLVENT AND MOLYBDENUM CATALYST[a]

				1% H_2S in H_2 at 170°C (82 psi)		
	Helium 170°C	Helium 170°C	H_2 250°C	No iron added	0.5% oil-sol. Fe	1.0% Fe as pyrite
ppm Mo as $Mo(CO)_6$	0	500	500	500	500	500
Run no.	63-71	63-41	62-35	2-42	2-57	2-62
Product distribution (wt % MAF coal)						
Gases	8.2	7.0	8.4	5.1	6.0	5.6
Oils	27.7	34.2	40.0	44.4	45.7	44.6
SRC	44.7	47.6	35.4	42.2	41.6	42.5
IOM	19.4	11.2	16.2	8.3	5.7	5.6
Conversion	80.6	88.8	83.8	91.7	94.3	94.4
Mass recovery (wt %)	95.4	96.8	92.9	94.0	93.4	94.4

[a] Pretreatment:
3 g of coal (20 x 100 mesh); 6 g of modified solvent; three steel balls; 2 hr; 170-250°C; 800 psi except where noted

Liquefaction:
425°C, 1 hr; 850 psig H_2 cold; 1,000 strokes per minute agitation

Finally, three runs were conducted under slightly different conditions, that is, grinding was done in modified solvent at 170°C under 82-psig H_2 containing 1% H_2S. In one run, 500 ppm of molybdenum catalyst was added as $Mo(CO)_6$. In the second run, the catalyst was 500 ppm of Mo added as $Mo(CO)_6$ and 0.5 wt % Fe based on coal added as an oil-soluble compound (available as Fe Chem-Al from Mooney Chemical Co., Toledo, Ohio). The third run was made with 500-ppm Mo added as $Mo(CO)_6$ plus 1% Fe added as finely ground (-325 mesh) pyrite. The liquefaction results for these runs in Table 52 show that the oil yields increased another 4-5% to around 45%, the highest yet observed in the grinding experiments. It is interesting to note also that the extra addition of Fe in the latter two cases produced about the same oil yield as that observed when only H_2S and $Mo(CO)_6$ were added to the grinding step.

<u>Illinois #6 Coal Pulverized in Ethanol</u>. Several liquefaction runs were made to test the effect of grinding coal in ethanol. Although methanol is a preferable alcohol for swelling the coal, ethanol was chosen for these tests because of its ability to easily dissolve the oil-soluble molybdenum catalyst, which was not readily soluble in methanol.

The experimental conditions and results are reported in Table 53. In the first case, Illinois #6 coal was pulverized in the presence of ethanol, after which base liquefaction solvent was added and the ethanol removed by evaporative displacement. The alcohol-ground coal containing base liquefaction solvent was then liquefied. The results in Table 53 show that grinding in ethanol under these conditions was clearly detrimental to oil production; the oil yield was 7-8% lower than noted in a comparable run with helium ground coal.

In a second experiment. Illinois #6 coal was pulverized in ethanol as above, but was liquefied in the presence of modified solvent that contained 500 ppm (on a dry coal basis) of molybdenum as molybdenum octoate. Again, the liquefaction results shown in Table 53 indicate that, even in the presence of a catalyst, ethanol pretreatment was clearly detrimental to oil yield. In yet another experiment, catalyst was added to the ethanol prior to grinding, but the results of the liquefaction were the same as adding the catalyst to the process solvent.

TABLE 53

LIQUEFACTION OF ILLINOIS #6 COAL PULVERIZED IN ALCOHOL[d]

	Base liquefaction solvent		Modified solvent		
		Helium[a] baseline	250-ppm Mo[b] added to ethanol	500-ppm Mo[b] added to solvent	500-ppm Mo[b] helium[a] baseline
Run no.	53-53	47-63	53-62	53-44	57-56
Product distribution (wt % MAF coal)					
Gases	7.3[c]	6.8	8.3[c]	8.3[c]	9.2
Oil	5.8	13.3	21.0	24.5	37.6
SRC	62.1	58.1	60.1	51.5	46.4
IOM	24.8	21.7	10.5	15.7	6.8
Conversion	75.2	78.3	89.5	84.3	93.2
Mass recovery (wt %)	102.6	94.4	91.6	88.3	-

[a] Helium baseline runs from Table 50

[b] As octoate

[c] Corrected for excess ethane due to residual ethanol in coals

[d] Pretreatment:

(a) 3 g of coal (20 x 100 mesh); 4 g of ethanol; 1-1/2 hr, three steel balls

(b) Evaporate ethanol to dryness in presence of coal solvent

Liquefaction:

425°C; 1 hr; 6 g of solvent; 3 g of coal; 850 psig H_2 cold; 1,000 strokes per minute agitation

Illinois #6 Coal Pulverized in Toluene at Elevated Temperature. Experiments were conducted using toluene as a grinding vehicle in an attempt to obtain a uniform dispersion of the molybdenum catalyst and to investigate the use of an aromatic hydrocarbon solvent other than process solvent for dispersing the catalyst. Toluene was chosen specifically for its suitability as both a nonpolar aromatic hydrocarbon solvent and as a solvent for the molybdenum catalyst added as $Mo(CO)_6$.

Grinding was effected by adding 3 g of toluene, containing the dissolved catalyst, to the grinding reactor and pressurizing with helium to 850 psig. The mixture was ground for 2 hr at 170°C; toluene was then evaporated from the bomb, modified solvent was added, and the sample was liquefied under standard conditions.

The results of these liquefaction runs are compared in Table 54 with the previous experiment, in which modified solvent and catalyst were used as the grinding vehicle. Note that toluene grinding has enhanced the oil yield by almost 10% over that where only modified solvent was used. Even when catalyst concentration was reduced by one-half, the oil yield improved. The results are certainly in contrast to the detrimental effect that ethanol grinding had on liquefaction, and one might speculate that the polar group (-OH) on the alcohol was responsible.

COAL BENEFICIATION

Coals contain a variety of mineral species that have different effects on liquefaction. The role of some species such as silicates, is poorly understood. Quartz, feldspars, and micas appear to be nearly inert; they neither promote nor retard the liquefaction reactions. Clay minerals derived from coals, predominantly Illite and mixed-layer clays, also show little ability to promote coal liquefaction. However, pure kaolinite and montmorillonite have been shown to marginally increase oil yields in coal liquefaction.

TABLE 54

LIQUEFACTION OF ILLINOIS #6 COAL PULVERIZED IN TOLUENE AT ELEVATED TEMPERATURE (170°C)[a]

	Toluene grinding/ 250-ppm $Mo(CO)_6$	Toluene grinding/ 500-ppm $Mo(CO)_6$	Modified solvent grinding/ 500-ppm $Mo(CO)_6$
Run no.	6-59	6-54	63-41
Product distribution (wt % MAF coal)			
Gases	8.2	8.9	7.0
Oils	36.9	42.2	34.2
SRC	42.1	40.2	47.6
IOM	12.8	8.7	11.2
Conversion	87.2	91.3	88.8
Mass recovery (wt %)	94.2	93.4	96.8

[a] Pretreatment:

(a) 3 g of coal (20 x 100 mesh); 3 g of toluene; 250-500-ppm $Mo(CO)_6$; three steel balls; 2 hr; 170°C; 850 psig He

(b) Evaporate toluene to dryness

Liquefaction:

425°C; 1 hr; 850-psig H_2 cold; 6 g of modified solvent; 1,000 strokes per minute agitation

On the other hand, some inorganic components of coal are actually detrimental to the liquefaction reaction. These include organometallic alkaline species such as calcium and sodium, and alkaline oxides such as lime. The presence of these inorganics may lead to operating problems such as precipitate formation and decreased coal conversion and distillate yield.

In contrast, several iron-bearing minerals, particularly pyrite, have been reported to promote coal liquefaction reactions. Hence, their removal by physical (float/sink) or chemical methods would be expected to result in poor liquefaction yields.

Therefore, the particular type, distribution, and amount of mineral present in a coal will have differing effects on coal liquefaction. Based upon the preceding discussion, minerals can be grouped into at least three categories depending on their effect on liquefaction:

A. Mineral matter that promotes coal conversion and distillate yields (i.e., metal species, particularly iron).

B. Mineral matter that is inert or has little effect on coal liquefaction (i.e., quartz, carbonates, and clays).

C. Mineral matter that is detrimental to coal liquefaction (i.e., calcium oxides, organically associated alkaline species).

The goal of this part of the experimental program was to manipulate the proportion of these mineral classes in coal and determine their effect on liquefaction. The ideal situation would be to eliminate type C mineral matter, lower type B as much as possible, and retain or concentrate type A.

To achieve this goal, Pennsylvania State University was subcontracted to use beneficiation technology to treat coal in order to manipulate its mineral content. The effect of the beneficiation was then evaluated at Air Products by studying the noncatalytic and catalytic liquefaction behavior of the treated samples.

Beneficiation Experiments

Illinois #6 Burning Star coal was supplied by the Wilsonville Advanced Coal Liquefaction Facility for most of the liquefaction tests discussed earlier, involving generation of baseline data and evaluation of the effect of solvent modification on coal liquefaction (see the section on Effect of Solvent Modification on Liquefaction). However, this sample of coal was preground to -150 mesh at Wilsonville, and thus could not be used for the coal beneficiation experiments. Therefore, another sample of Illinois #6 coal was freshly obtained from the Burning Star #2 mine by Air Products and used for the beneficiation experiments.

This sample was first reduced in size to -2 in. by crushing it in a jaw crusher at Pennsylvania State University. The -2-in. material was then screened at 10 mesh, producing a 2 in. by 10 mesh fraction and a -10 mesh fraction. The 2 in. by 10 mesh material was fractionated further into several specific gravity fractions by sequentially placing the entire sample into a series of containers, each containing a heavier specific gravity medium than the previous one (e.g., 1.20, 1.25, 1.30, 1.35, 1.60, 1.80, 1.90, and 2.0). The samples were then thoroughly rinsed with n-pentane to ensure complete removal of various specific gravity solvents used for fractionation. These specific gravity fractions were collected and analyzed and found to contain ash varying from 3 to 75% by weight (see Table 55). The fractions containing less than 20% ash were analyzed in detail and tested for their liquefaction behavior.

The -10 mesh fraction was screened further using a 28 mesh screen to produce a 10 mesh by 28 mesh fraction and a -28 mesh fraction. The 10 mesh by 28 mesh fraction was fractionated further into various fractions containing different amounts of indigenous mineral matter using a Deister Table at Pennsylvania State University. These samples were analyzed and found to contain varying amounts of ash. The fractions containing less than 20% ash were analyzed in detail and used in the liquefaction tests.

TABLE 55

ANALYSIS OF VARIOUS BENEFICIATED COAL SAMPLES

	Coal sample						
	Sink and float treated[a]			Deister Table treated			
	1	2	3	4	5	6	Origina
Ash (wt %)	3.10	4.56	8.22	8.90	9.95	12.89	10.46
Pyritic sulfur (wt %)	0.36	0.38	0.49	0.40	0.46	0.68	1.09
Iron (wt %)	0.43	0.62	0.90	0.84	0.95	1.21	1.11
H/C ratio	0.78	0.83	0.80	0.84	0.79	0.84	0.88

[a] Sample 1 is 1.20 x 1.25 specific gravity fraction of coal.
Sample 2 is 1.25 x 1.30 specific gravity fraction of coal.
Sample 3 is 1.30 x 1.35 specific gravity fraction of coal.

Detailed analyses of the original coal sample and of all the samples generated using the specific gravity technique and the Deister Table are summarized in Table 55. These samples contained differing amounts of ash, pyrite, and total iron, but their ratios of hydrogen to carbon were very similar, indicating that they have similar organic compositions.

All the beneficated coal samples selected for liquefaction tests using both base liquefaction and modified solvents were ground and sieved to -150 mesh.

Liquefaction of Beneficiated Coal

Several experiments were carried out to determine the effect of indigenous mineral matter on liquefaction by comparing the yields from beneficiated and nonbeneficiated coal feedstocks. Runs were conducted with and without catalyst and with both base liquefaction and modified solvents.

Noncatalytic Liquefaction. Experimental data in Table 56 show that both oil production and coal conversion decreased considerably in noncatalytic liquefaction upon removing the mineral matter, particularly iron-bearing species like pyrite, from the coal. These observations were true with both base liquefaction solvent and modified solvent, generated by treating base liquefaction solvent with anhydrous HCl followed by silica gel. However, both oil production and coal conversion were higher for the beneficiated coal sample containing more ash and iron than the original coal sample. This observation, once again, shows the importance of mineral matter in coal liquefaction. The production of both gases and SRC, however, was not greatly affected by removing the minerals.

Overall, the results indicate that the removal of mineral matter, particularly iron-bearing species, is extremely detrimental to liquefaction in the absence of a catalyst.

Catalytic Liquefaction. Experimental results summarized in Table 57 show that removal of mineral matter did not change either oil yield or coal conversion significantly during slurry-phase catalytic liquefaction of coal in the presence of base liquefaction and modified solvents. Additionally, neither

TABLE 56

NONCATALYTIC LIQUEFACTION OF ORIGINAL AND BENEFICIATED COAL SAMPLES[a]

	Original	Beneficiated coal sample no.					
		1	2	3	4	5	6
Ash (wt %)	10.46	3.10	4.56	8.22	8.90	9.95	12.89
Pyritic sulfur (wt %)	1.09	0.36	0.38	0.49	0.40	0.46	0.68
Iron (wt %)	1.11	0.43	0.62	0.90	0.84	0.95	1.21
Liquefaction product distribution (wt % MAF coal)							
Base liquefaction solvent							
Gases	11.7	8.6	8.1	8.9	8.5	8.6	10.5
Oil	29.2	15.2	21.3	20.2	25.3	27.2	30.6
SRC	35.8	32.2	32.8	38.0	38.2	40.3	39.0
IOM	23.3	44.0	37.8	33.9	28.0	23.9	19.9
Conversion	76.7	56.0	62.2	66.1	72.0	76.1	80.1
Modified solvent[b]							
Gases	10.8	6.8	7.4	9.4	10.2	8.8	--
Oil	33.8	16.8	16.2	19.8	22.8	29.6	--
SRC	33.3	33.3	35.2	29.9	35.7	35.1	--
IOM	22.1	43.1	41.2	40.9	31.3	26.5	--
Conversion	77.9	56.9	58.8	59.1	68.7	73.5	--

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[a] Reaction mixture:

Coal	3 g
Solvent	3 g

Reaction conditions:

Temperature	440°C
Pressure	1,200-psig H_2 cold
Time	60 min
Agitation	1,000 strokes per min

[b] Solvent generated by treating base liquefaction solvent with HCl followed by silica gel.

TABLE 57

CATALYTIC LIQUEFACTION OF ORIGINAL AND BENEFICIATED COAL SAMPLES[c]

		Beneficiated coal sample no.					
	Original	1	2	3	4	5	6
Ash (wt %)	10.46	3.10	4.56	8.22	8.90	9.95	12.89
Pyritic sulfur (wt %)	1.09	0.36	0.38	0.49	0.40	0.46	0.68
Iron (wt %)	1.11	0.43	0.62	0.90	0.84	0.95	1.21
Liquefaction product distribution (wt % MAF coal)							
Base liquefaction solvent							
Gases	9.6	9.9	9.0	--	--	8.5	11.7
Oil	44.9	45.8	45.6	--	--	43.3	44.5
SRC	39.2	36.6	38.4	--	--	37.9	35.2
IOM	6.3	7.7	7.0	--	--	10.3	8.6
Conversion	93.7	92.3	93.0	--	--	89.7	91.4
Modified solvent #1[a]							
Gases	8.8	10.0	9.8	7.2	9.7	9.7	10.3
Oil	49.6	44.1	43.0	44.0	50.2	47.5	47.0
SRC	33.8	37.3	38.6	41.1	34.8	36.2	33.2
IOM	7.8	8.6	8.6	7.7	5.3	6.6	9.5
Conversion	92.2	91.4	91.4	92.3	94.7	93.4	90.5
Modified solvent #2[b]							
Gases	10.9	8.5	9.5	9.4	11.2	10.6	11.3
Oil	50.9	53.3	50.9	49.0	49.6	49.1	48.2
SRC	31.6	30.8	30.3	29.4	32.1	33.3	29.9
IOM	6.6	7.4	9.3	12.2	7.1	7.0	10.6
Conversion	93.4	92.6	90.7	87.8	92.9	93.0	89.4

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[a] Solvent generated by treating base liquefaction solvent with silica gel.

[b] Solvent generated by treating base liquefaction solvent with HCl followed by silica gel.

[c] Reaction mixture:

Coal	3 g
Solvent	3 g
Catalyst	250 ppm of molybdenum based on coal

Reaction conditions:

Temperature	440°C
Pressure	1,200-psig H_2 cold
Time	60 min
Agitation	1,000 strokes per min

VII. SCALE-UP STUDIES

The experimental results discussed thus far in this report have indicated that solvent modification improved oil production in both noncatalytic and catalytic coal liquefaction. However, these experiments were carried out on a small scale using a tubing bomb reactor, which may cause some experts in coal liquefaction to question the validity of the results.

Therefore, an extensive experimental program was undertaken to eliminate any doubts and answer any questions about the utility of solvent modification in coal liquefaction. The program included design and fabrication of a new 300-mL semicontinuous reactor system. This unit enabled us to scale up the reaction system and obtain more reliable, meaningful data. Predetermined amounts of solvent and coal were mixed and charged to the reactor system in a batch mode. However, a continuous flow of hydrogen was maintained through the reactor to ensure proper supply and availability of hydrogen for the reaction. A detailed description of the reactor system is found in Appendix 2.

In addition, to determine both true conversion and distillate oil production, liquefaction products from these runs were recovered and analyzed by vacuum distillation rather than the sequential solvent separation used previously. The workup procedure used is detailed in Appendix 2.

PRELIMINARY EXPERIMENTS

Earlier in the program we showed that runs at 440°C with a 1:1 solvent-to-coal ratio (termed high-severity reaction conditions in this report) yielded more oil than runs at 425°C with a 2:1 solvent-to-coal ratio (low-severity reaction conditions). However, these experiments were carried out in a tubing-bomb reactor in which there were no mixing and heating problems. Unfortunately, when autoclave runs were conducted at the high-severity conditions (1:1 solvent-to-coal ratio, 440°C) significant coking occurred, presumably due to either poor mixing or the high wall temperature of the reactor. To improve mixing, the solvent-to-coal ratio was increased from 1:1 to 1.5:1. Once again, coking was significant and the overall coal conversion with base liquefaction solvent (original solvent) was only 49% at 440°C (see Table 58). The poor conversion at this point was attributed to the wall temperature of the reactor, which had to be maintained above 440°C in order to attain and maintain the 440°C reaction temperature.

To resolve this problem, the reaction temperature was lowered to 425°C; other conditions were kept the same. Coal conversion increased to approximately 80% (see Table 58), which was very similar to that noted in the tubing-bomb reactor at the same temperature. Since the coal conversion data matched well with the tubing-bomb conversion data, 425°C was selected as the standard reaction temperature for the autoclave. The liquefaction behavior of raw Illinois #6 coal was then determined in the autoclave reactor system with and without a catalyst and with both base liquefaction (original) and modified solvents. The results of these experiments are discussed below.

NONCATALYTIC LIQUEFACTION OF ILLINOIS #6 COAL WITH ORIGINAL AND MODIFIED SOLVEN

The noncatalytic liquefaction behavior of Illinois #6 coal was evaluated in the semicontinuous autoclave system using a 1.5:1 solvent-to-coal ratio, 425°C temperature, 2,000 psig total pressure, and 60-min reaction time. Both original (base liquefaction solvent) and modified solvents were used in the tests.

Experimental results summarized in Table 58 show that the use of modified solvent resulted in slightly higher overall conversion than that noted with original solvent. Oil yield was also marginally higher. Distillate oil yield with modified solvent was very similar to that noted in the tubing-bomb reactor, whereas with original solvent it was considerably higher in the autoclave reactor (compare Tables 58 and 17). This difference could be attributed to the use of a different workup procedure for the products obtained from the two reactors.

The production of C_1-C_5 gases, heteroatomic gases, and water was very similar with both original and modified solvents.

TABLE 58

NONCATALYTIC LIQUEFACTION IN SEMICONTINUOUS AUTOCLAVE REACTOR

Run no.	GAR-2	GAR-5	GAR-7
Solvent	Original[b]	Original[b]	Modified[a]
Solvent/coal[c]	1.5/1	1.5/1	1.5/1
Temp (°C)	440	425	425
Pressure (psig)	2,000	2,000	2,000
Time (min)	60	60	60
Product distribution (wt % MAF coal)			
C_1-C_5	21.9	6.6	8.4
H_2S, CO, CO_2	6.3	4.4	4.5
Water	3.0	3.9	2.9
Distillate oil	(16.7)	21.5	22.7
SRC	34.5	48.2	47.4
IOM	51.0	15.4	14.1
Conversion (wt)	49.0%	84.6	85.9
Recovery (wt %)	95.6	98.5	99.2

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[a] Solvent treated by anhydrous hydrochloric acid followed by silica gel.

[b] Base liquefaction solvent.

[c] Illinois #6 coal.

These results show that use of modified solvent in noncatalytic liquefaction is marginally better than using original solvent. This is contrary to the significant increase in the oil yield noted with the use of modified solvent compared to base liquefaction solvent in the tubing bomb reactor (see Table 17). The reason for this difference is presently unknown.

CATALYTIC LIQUEFACTION OF ILLINOIS #6 COAL WITH ORIGINAL AND MODIFIED SOLVENTS

The catalytic liquefaction behavior of Illinois #6 coal was evaluated using 500 ppm of dispersed molybdenum catalyst in the form of molybdenum octoate. Reaction conditions were similar to those in the noncatalytic liquefaction experiments and, again, both original and modified solvents were used for liquefaction.

With original solvent, adding catalyst to the reaction mixture increased the overall conversion from ≈83 to ≈94%. Oil production also increased from ≈21 to ≈25% (compare Tables 58 and 59), and hydrocarbon gases increased substantially. In fact, most of the increase in coal conversion ended up in increased oil and gases production. SRC production increased only marginally with catalyst.

In the case of modified solvent, adding catalyst also increased overall conversion, from ≈86 to ≈93%. However, the increase in oil yield was significantly higher than that noted with original solvent (see Tables 58 and 59), due to increased conversion of coal and SRC to oil. Catalyst addition with original solvent increased both oil and SRC yield, whereas addition of catalyst with modified solvent increased both overall conversion and SRC conversion, resulting in much higher oil production (see Table 59). The production of gases in the presence of modified solvent was very similar to that noted with original solvent.

Comparison of the data in Tables 22 and 59 shows that oil production and coal conversion with base liquefaction solvent were very similar in both the tubing-bomb and autoclave reactors. However, SRC production was lower in the autoclave reactor than the tubing-bomb reactor, and gas production was higher in the autoclave.

TABLE 59

CATALYTIC LIQUEFACTION IN SEMICONTINUOUS AUTOCLAVE REACTOR

Run no.	GAR-14	GAR-17	GAR-15
Solvent	Original		Modified[a]
Solvent/coal	1.5/1.0		1.5/1.0
Mo catalyst (ppm based on coal)	500		500
Temp. (°C)	425		425
Pressure (psig)	2,000		2,000
Time (min)	60		60
Product distribution (wt % MAF coal)			
C_1-C_5	10.2	9.1	10.3
H_2S, CO, CO_2	4.5	5.0	4.6
Water	3.9	4.4	5.4
Distillate oil	25.4	23.4	32.7
SRC	50.0	52.5	40.3
IOM	6.0	5.6	6.7
Conversion (wt %)	94.0	94.4	93.3
Recovery (wt %)	100.8	100.9	94.8

[a] Solvent treated by anhydrous hydrochloric acid followed by silica gel.

With modified solvent (Tables 22 and 59), overall conversion and SRC production were very similar in both reactors. However, oil production was considerably lower in the autoclave, due to higher production of gases -- yields increased by more than a factor of two in the autoclave. Besides the discrepancies in the magnitude of oil and gas production, other variables were very consistent in both reactors.

These discrepancies could be due to two factors. First, in the tubing-bomb reactor, water produced is accounted for in the oil yield (see Appendix 1 for further information), whereas water is accounted for separately in the autoclave reactor. Secondly, a higher wall temperature (>425°C) was used in the autoclave to maintain the 425°C reaction temperature. The heat enhances cracking reactions in the vicinity of the wall, resulting in higher gas yield. However, the true reasons for the discrepancies are currently unknown, and more work is required to resolve the differences.

In summary, the above data clearly show the benefits of using modified solvent in catalytic coal liquefaction. Similar benefits were noted in the tubing-bomb experiments, as discussed earlier. Both tubing-bomb and autoclave results establish beyond any doubts the benefits of using modified solvent in catalytic coal liquefaction experiments.

LIQUEFACTION OF DEEP-CLEANED OR BENEFICIATED COAL

Earlier, we discussed tubing-bomb reactor experiments which indicated that beneficiation or removal of mineral matter was extremely detrimental to noncatalytic coal liquefaction. In contrast, catalytic liquefaction experiments showed no major differences between the behavior of raw and beneficiated coal samples. However, in terms of plant operation, several advantages of using beneficiated coal were mentioned.

To further evaluate the effects of beneficiation, a sample of beneficiated Illinois #6 coal containing ~3% ash was chosen for detailed evaluation in a semicontinuous autoclave reactor. Runs were conducted with and without catalyst and with both original and modified solvents.

Noncatalytic Liquefaction

Noncatalytic liquefaction of beneficiated coal with original (base liquefaction) solvent showed considerably lower coal conversion than liquefaction of raw coal: 57% vs. 82% (see Tables 58 and 60). In addition to lower conversion, beneficiated coal resulted in a net loss in oil yield. Both lower conversion and negative oil yield show the detrimental effect of coal beneficiation in noncatalytic liquefaction. Similar results were reported earlier in the evaluation of beneficiated coal samples in the tubing-bomb reactor (see Table 56).

Runs with modified solvent showed almost the same conversion noted with original solvent. However, use of modified solvent resulted in a net production of oil, compared to net loss noted with original solvent (Table 60). The production of hydrocarbon gases was also higher with modified solvent than original solvent. Most interestingly, the production of SRC was considerably lower with modified solvent. This observation indicates that the use of modified solvent enhances the conversion of SRC, thereby increasing the production of hydrocarbon gases and distillate oil.

Catalytic Liquefaction

In the presence of original solvent, addition of 500 ppm of molybdenum catalyst based on coal increased the overall conversion of beneficiated coal from 57 to 93% (see Tables 60 and 61). Oil yield also increased, from a net loss of ≈5% to a net production of ≈25%. The production of hydrocarbon gases and water also increased with the addition of molybdenum, although SRC production did not change. In fact, most of the increase in coal conversion ended up in the form of increased oil yield.

Liquefaction of beneficiated coal in the presence of both modified solvent and molybdenum catalyst showed slightly higher coal conversion than that noted with original solvent, and oil production was significantly higher. Similar results were reported earlier in the tubing-bomb experiments (see Table 57). Hydrocarbon gases and SRC production were slightly lower than those noted with original solvent.

TABLE 60

NONCATALYTIC LIQUEFACTION OF DEEP-CLEANED COAL

Run no.	GAR-8	GAR-9
Solvent	Original	Modified[a]
Solvent/coal	1.5/1	1.5/1
Temp (°C)	425	425
Pressure (psig)	2,000	2,000
Time (min)	60	60
Product distribution (wt % MAF coal)		
C_1-C_5	5.6	7.8
H_2S, CO, CO_2	3.2	3.4
Water	3.9	4.7
Distillate oil	(4.8)	3.6
SRC	49.3	38.4
IOM	42.8	42.1
Conversion (wt %)	57.2	57.9
Recovery (wt %)	97.5	99.3

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[a] Solvent treated with anhydrous hydrochloric acid followed by silica gel.

TABLE 61

CATALYTIC LIQUEFACTION OF DEEP-CLEANED COAL

Run no.	GAR-13	GAR-12
Solvent	Original	Modified[a]
Solvent/coal	1.5/1	1.5/1
Mo catalyst (ppm based on coal)	500	500
Temp (°C)	425	425
Pressure (psig)	2,000	2,000
Time (min)	60	60
Product distribution (wt % MAF coal)		
C_1-C_5	8.1	7.2
H_2S, CO, CO_2	3.6	4.6
Water	7.9	6.5
Distillate oil	24.9	31.1
SRC	48.5	45.1
IOM	7.0	5.5
Conversion (wt %)	93.0	94.5
Recovery (wt %)	104.6	98.4

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[a] Solvent treated with anhydrous hydrochloric acid followed by silica gel.

In summary, using modified solvent for the liquefaction of beneficiated coal results in higher oil yield and coal conversion than original solvent. Howeve the oil yield and coal conversion noted with beneficiated coal are very simila to those noted with raw coal, indicating no clear advantages of coal beneficiation for liquefaction.

The advantages of coal beneficiation, however, are obvious when compared on a same weight basis, as shown in Table 62. Beneficiated coal yields more oil an net products than raw coal. In addition, coal beneficiation reduces the overa solids (liquefaction residue) loading to the solid/liquid separator and thereb improves its efficiency. Reduction in solids loading helps to reduce the loss of SRC with solids, and therefore further increases the product recovery. It also increases the plant throughput because the feed being processed contains more organics. All these features indicate the benefits of liquefying beneficiated coal over raw coal.

TABLE 62

EFFECT OF COAL BENEFICIATION ON CATALYTIC LIQUEFACTION

Basis of Comparison: 100 g of dry coal

Sample	Raw coal	Beneficiated coal
Ash (g)	10.46	3.10
Organic material (g)	89.54	96.90
Products (g)		
HC gases	7.3	6.9
Oil	22.3	30.1
SRC	43.4	43.7
Net products[a]	65.7	73.8
Residue[b]	16.7	8.4

[a] Net products consist of oil and SRC.

[b] Residue consists of ash and unconverted coal.

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VIII. EXPLORATORY STUDIES

One of the goals of this program was to maximize the production of oil from coal liquefaction. One way to increase oils, as discussed earlier in this report, is to remove heteroatoms from the liquefaction solvent. Another way is to select the right catalyst or combination of catalysts for liquefaction (see the Catalyst Selection section). Additionally, at the inception of this program, we thought that coal pretreatment and beneficiation would both enhance the activity and reactivity of coal, leading to enhanced oil production. Coal pretreatment was not successful, but coal beneficiation was very promising, as discussed earlier in the Coal Pretreatment and Beneficiation section.

In order to increase oil production beyond that achieved during the experiments discussed thus far, several exploratory experiments were also conducted. Since oil production was much higher with modified solvent (generated by treating base liquefaction solvent with anhydrous HCl followed by silica gel) than with base liquefaction solvent, most of the exploratory studies were carried out using modified solvent. The studies included (1) finding the optimum reaction conditions for coal liquefaction, (2) finding the right catalyst or combination of catalysts, and (3) studying the effect of recycling unconverted SRC. The results of these studies are discussed separately below.

OPTIMUM REACTION CONDITIONS

Most of the work discussed earlier was carried out at 425°C reaction temperature, 60-min reaction time, 850-psig initial (cold) hydrogen pressure, 1,000 strokes per min agitation, and a 2:1 solvent-to-coal ratio. In addition, a standard catalyst concentration of 500-ppm molybdenum based on coal was used; the catalyst was added as an oil-soluble compound like molybdenum octoate in order to achieve the highest dispersion in the reaction mixture.

Since dispersed molybdenum was more active than impregnated molybdenum and equivalent to iron (discussed earlier in the Catalyst Selection section), we decided to search for optimum reaction conditions using dispersed molybdenum catalyst. The reaction variables studied included reaction temperature, residence time, initial hydrogen pressure, solvent-to-coal ratio, and catalys concentration. The selection of the best conditions was based on higher oil yield, lower gas yield, and higher overall conversion, conditions that would unquestionably improve overall process economics. Results obtained from thes experiments are detailed below.

Reaction Temperature

The effect of reaction temperature was evaluated by increasing it from 425 to 440°C in the presence of 500-ppm molybdenum catalyst and modified solvent. Other reaction conditions were unchanged. As Table 63 shows, increasing the reaction temperature significantly increased the gas yield from 5.9 to 11.3%. However, both oil yield and coal conversion decreased, indicating an onset of retrogressive reaction at the higher temperature. Although not indicated in Table 63, further increasing the temperature to 450°C resulted in an even higher gas yield and lower coal conversion.

Several reasons can be proposed to explain this onset of retrogressive reaction at higher temperature. One possibility is that an increase in temperature increases the rate of thermal scission of coal molecules, thus increasing the overall need for hydrogen to stabilize the fragmented molecules. If hydrogen is not transferred to these fragments quickly, they will recombine to form coke. We know that, during coal liquefaction, hydrogen is first transferred from the gas phase to the liquid phase before it is transferred to fragmented molecules. Also, we know that catalysts will enhance the transfer of hydrogen both from the gas phase to the liquid phase and from the liquid phase to fragmented molecules. Therefore, apparently the rate of hydrogen transfer from the gas phase to the liquid phase, or from the liquid phase to the fragmented molecules, was not fast enough to keep up with the rate of formation of fragmented coal molecules at the higher temperature. This would result in the onset of retrogressive reaction and lower overall conversion.

TABLE 63

EFFECT OF REACTION TEMPERATURE[a]

	Temperature (°C)	
	425	440
Product distribution (wt % MAF coal)		
Gases	5.9	11.3
Oil	44.0	39.5
SRC	41.9	37.6
IOM	8.2	11.6
Conversion	91.8	88.4

[a] Reaction mixture:

Coal	3 g
Modified solvent	6 g
Catalyst	500-ppm molybdenum based on coal

Reaction conditions:

Time	60 min
Pressure	850 psig H_2 (cold)
Agitation	1,000 strokes per min

the production of gases nor SRC was greatly affected. These results indicate that all the negative features noted in noncatalytic liquefaction of beneficiated coal were nullified by the use of slurry catalyst.

Although the advantages of coal beneficiation are not obvious from our experimental results, they are if operation of the entire plant is considered. Coal benefication will reduce the overall solids loading to the solid/liquid separator and thereby improve its efficiency. Reduction in solids loading will also help in reducing the loss of SRC with solids, and will therefore increase the product recovery. Removal of mineral matter will also reduce plant abrasion and it will increase plant throughput because the feed being processed is more organic. All these features indirectly indicate the benefits of liquefying beneficiated (low mineral matter content) coal in the presence of slurry catalyst compared to liquefying noncleaned coal.

The transfer of hydrogen from the liquid phase to fragmented molecules can be altered simply by changing the amount of total hydrogen available for donatio by the solvent. This can be achieved by changing the solvent-to-coal ratio used in the liquefaction reaction. Likewise, the transfer of hydrogen from the gas phase to the liquid phase can be altered by changing the hydrogen partial pressure in the gas phase, which can be done simply by altering the initial pressure of hydrogen charged to the reactor. Therefore, several experiments were carried out to determine the limiting factor and also to explain the reasons for the onset of retrogressive reaction at higher temperature.

Solvent-to-Coal Ratio

The effect of hydrogen transfer from the liquid phase to fragmented coal molecules was investigated by varying the solvent-to-coal ratio from 2:1 to 1:2. Reducing this ratio should change not only the rate of hydrogen transfer but also the amount of initial hydrogen available for transfer. Therefore, if the liquefaction reaction was limited by the transfer of hydrogen from the liquid phase to fragmented molecules, reducing the solvent-to-coal ratio should enhance the extent of retrogressive reaction. However, this did not happen; reducing the ratio did not cause any significant change in liquefaction behavior, as evidenced by the product distribution summarized in Table 64. Hence, transfer of hydrogen from the liquid phase to fragmented molecules was apparently not the limiting factor in catalytic coal liquefaction.

Initial Hydrogen Pressure

The effect of hydrogen transfer from the gas phase to the liquid phase was evaluated by increasing the initial hydrogen pressure charged into the reactor from 850 to 1,200 psig at a solvent-to-coal ratio of 1:1. Increasing the initial hydrogen pressure should increase the effective hydrogen partial pressure in the reactor, the amount of hydrogen available for transfer, and the rate of transfer of hydrogen from the gas to liquid phase. Therefore, if

TABLE 64

EFFECT OF SOLVENT/COAL RATIO[a]

	Solvent/coal		
	2:1	1:1	1:2
Product distribution (wt % MAF coal)			
Gases	11.3	11.7	11.7
Oil	39.5	39.9	41.8
SRC	37.6	39.7	35.7
IOM	11.6	9.7	10.8
Conversion	88.4	91.3	89.2

---

[a] Reaction mixture:

Coal	3 g
Solvent	Modified
Catalyst	500-ppm Mo based on coal

Reaction conditions:

Time	60 min
Pressure	850 psig H_2 (cold)
Temperature	440°C
Agitation	1,000 strokes per min

the liquefaction reaction was limited by the transfer of hydrogen from the gas to liquid phase, the increase in the initial hydrogen pressure should improve coal liquefaction.

Indeed, increasing the initial hydrogen pressure from 850 to 1,200 psig significantly increased oil yield (Table 65). In addition, it increased coal conversion and slightly reduced the gas yield. Since 1,200-psig initial hydrogen pressure would result in approximately 2,000-psig total pressure at reaction conditions, no attempts were made to further increase the initial hydrogen pressure.

The significant increase in oil yield indicates that the catalytic coal liquefaction reaction might be more dependent upon the total amount of hydrogen available for reaction, rather than the rate of hydrogen transfer. However, this is only conjecture in the absence of any experimental verification. This point could be proven by undertaking a massive experimental program.

Catalyst Concentration

The effect of molybdenum concentration was evaluated in liquefaction tests using modified solvent. Metal concentration was varied from 0 to 500 ppm based on coal. The data in Table 66 show that both oil production and coal conversion increased significantly when molybdenum concentration increased from 0 to 125 and to 250 ppm. The increases in both oil yield and coal conversion, however, were marginal with a further increase in molybdenum concentration from 250 to 500 ppm, indicating no real benefit of using 500-ppm molybdenum in liquefaction, especially since a lower concentration would undoubtedly enhance the overall process economics. Therefore, a molybdenum concentration of 250 ppm based on coal was chosen as the standard concentration for establishing the optimum reaction conditions.

TABLE 65

EFFECT OF INITIAL HYDROGEN PRESSURE[a]

	Initial H_2 pressure (psig cold)	
	850	1,200
Product distribution (wt % MAF coal)		
Gases	11.7	11.2
Oil	39.9	53.4
SRC	39.7	29.4
IOM	8.7	6.0
Conversion	91.3	94.0

---

[a] Reaction mixture:

Coal	3 g
Solvent	3 g (modified solvent)
Catalyst	500-ppm Mo based on coal

Reaction conditions:

Temperature	440°C
Time	60 min
Agitation	1,000 strokes per min

TABLE 66

EFFECT OF CATALYST CONCENTRATION[a]

	Molybdenum concentration (ppm based on coal)			
	0	125	250	500
Product distribution (wt % MAF coal)				
Gases	10.8	9.8	10.9	11.2
Oil	33.8	41.5	50.9	53.4
SRC	33.3	32.9	31.6	29.4
IOM	22.1	15.8	6.6	6.0
Conversion	77.9	84.2	93.4	94.0

[a] Reaction mixture:

Coal	3 g
Solvent	3 g (modified solvent)

Reaction conditions:

Temperature	440°C
Time	60 min
Pressure	1,200 psig H_2
Agitation	1,000 strokes per min

Reaction Time

The effect of reaction time was evaluated in liquefaction tests by increasing it from 60 to 120 min. Once again, a solvent-to-coal ratio of 1:1, an initial hydrogen pressure of 1,200 psig, and molybdenum concentration of 250 ppm based on coal were used as standard conditions. Table 67 shows that both oil production and coal conversion decreased slightly with increasing reaction time. Gas yield, however, increased slightly. Overall, no real benefits were noted by increasing the reaction time.

Summary

The detailed study of the effect of reaction variables indicated that a reaction temperature of 440°C, residence time of 60 min, initial hydrogen pressure (cold) of 1,200 psig, agitation rate of 1,000 strokes per minute, solvent-to-coal ratio of 1:1, and a molybdenum catalyst concentration of 250 ppm based on coal gave higher oil yield and conversion than other reaction conditions. In fact, these reaction conditions were used to determine the effect of solvent modification on coal liquefaction (see the Solvent Modification section), and were classified as high-severity reaction conditions.

OPTIMUM CATALYST

The Catalyst Selection section showed that molybdenum, nickel, and iron catalyze the coal liquefaction reaction, whereas zinc, lead, copper, and cobalt were detrimental. In the previous section, we showed that increasing the molybdenum concentration from 125 to 250 ppm significantly increased both oil production and coal conversion. However, further increases in concentration to 500 ppm showed only marginal improvements, which would not justify the additional cost required to increase the molybdenum concentration from 250 to 500 ppm based on coal.

TABLE 67

EFFECT OF REACTION TIME[a]

	Reaction time (min)	
	60	120
Product distribution (wt % MAF coal)		
Gases	10.9	12.8
Oil	50.9	46.2
SRC	31.6	33.4
IOM	6.6	7.6
Conversion	93.4	92.4

[a] Reaction mixture:

Coal	3 g
Solvent	3 g
Catalyst	250 ppm Mo based on coal

Reaction conditions:

Temperature	440°C
Pressure	1,200 psig H_2
Agitation	1,000 strokes per min

In an attempt to further increase oil production, the activities of nickel and iron were tested with modified solvent using the optimum reaction conditions just described. The activity of catalyst combinations was also tested, and the results of these tests are described below.

Dispersed Metals

The catalytic activities of molybdenum, nickel, and iron during liquefaction with modified solvent were evaluated. Since molybdenum and nickel are expensive metals, they were used at a low concentration of 250 ppm based on coal, whereas inexpensive iron was used at a concentration of 0.5% (5,000 ppm) based on coal. All three metals tested were added in the form of oil-soluble metal compounds. The reaction conditions and solvent-to-coal ratio used in these experiments were those selected from our exploratory studies (as described earlier).

Data on molybdenum were obtained during the exploratory studies on reaction conditions and are summarized in Table 68 for easy reference.

Increasing the nickel concentration from 125 to 250 ppm did not show any dramatic improvement. In addition, the use of nickel at both 125 and 250 ppm resulted in much less oil and coal conversion than molybdenum at the same concentrations. Adding 0.5% iron, however, resulted in more oils and higher coal conversion than noted with nickel. In fact, both oil production and coal conversion with iron were very similar to those noted with 250-ppm molybdenum (see Table 68). Based on these data, iron and molybdenum are essentially suitable catalysts and selection should depend on cost. Using nickel rather than iron or molybdenum would not be advantageous.

Combinations of Metals

Several catalyst combinations were tested to either improve oil production or reduce the overall cost of catalyst in coal liquefaction. The data summarized in Table 69 show that combining 125-ppm Mo with 0.5% Fe increased oil production and coal conversion over both 125-ppm Mo and 0.5% Fe when used alone. Both oil production and coal conversion with this combination were similar to those noted with 250-ppm Mo, indicating that part of the Mo could

TABLE 68

EFFECT OF METAL CATALYSTS[a]

	Catalyst				
	Molybdenum		Nickel		0.5%
	125 ppm	250 ppm	125 ppm	250 ppm	iron
Product distribution (wt % MAF coal)					
Gases	9.8	10.9	12.2	12.2	12.5
Oil	41.5	50.9	37.8	34.5	47.5
SRC	32.9	31.6	29.8	35.6	31.3
IOM	15.8	6.6	20.2	17.7	8.7
Conversion	84.2	93.4	79.8	82.3	91.3

[a] Reaction mixture:

Coal	3 g
Modified solvent	3 g

Reaction conditions:

Temperature	440°C
Time	60 min
Pressure	1,200 psig H_2
Agitation	1,000 strokes per min

TABLE 69

EFFECT OF CATALYST COMBINATION

Catalyst	125-ppm Mo	0.5% Fe	125-ppm Mo + 0.5% Fe	250 ppm Mo	250-ppm Mo + 0.5% Fe	250-ppm Ni	250-ppm Ni + 0.5% Fe
Product distribution (wt % MAF coal)							
Gases	9.8	12.5	10.8	10.9	11.2	12.2	10.9
Oil	41.5	47.5	50.1	50.9	51.2	34.5	54.4
SRC	32.9	31.3	32.6	31.6	32.0	35.6	27.8
IOM	15.8	8.7	6.5	6.6	5.6	17.7	6.9
Conversion	84.2	91.3	93.5	93.4	94.4	82.3	93.1

[a] Reaction mixture:

Coal	3 g
Modified solvent	3 g

Reaction conditions:

Temperature	440°C
Time	60 min
Pressure	1,200 psig H_2 (cold)
Agitation	1,000 strokes per min

be replaced by Fe catalyst without severely affecting the liquefaction performance. Interestingly enough, combining 250-ppm Mo and 0.5% Fe only marginally improved both oil production and coal conversion over those noted with 250-ppm Mo. These data clearly show the economic importance of selecting the right amount of catalyst for liquefaction. Like combinations of Fe and Mo, a combination of 250-ppm Ni and 0.5% Fe showed considerably higher oil yield and coal conversion than noted from each individually (Table 69).

One can conclude from the above results that the oil yield and coal conversion obtained with 250-ppm Mo are close to the maximum values that can be achieved in catalytic coal liquefaction. Minor improvements in both oil yield and coal conversion, however, can be made by combining two or more metal catalysts. The use and selection of the right amount of catalysts individually or in combination would greatly depend on economics.

EFFECT OF SRC RECYCLE

In an attempt to increase oil production, we also studied the impact of recycling unconverted SRC on coal liquefaction. LSRC recycle, studied extensively at the Wilsonville Advanced Coal Liquefaction Facility, was reported to significantly improve liquefaction performance of various coals, in addition to resolving a number of operational problems. However, no determination was made on the effect of LSRC recycle on either oil yield or coal conversion. Therefore, several experiments were carried out to investigate the effect of SRC recycle on oil production using both base liquefaction and modified solvents in the presence and absence of a catalyst. In all the experiments, the amounts of coal and solvent were fixed at 3 g each, and the amount of SRC added was varied. The results of these experiments are discussed below.

Noncatalytic Liquefaction

Several experiments were performed to investigate the effect of recycling SRC on the liquefaction of Illinois #6 coal using both base liquefaction and modified solvents; results are summarized in Table 70. With 13% SRC recycle, oil yield increased from 29 to 39% and from 34 to 39% in the presence of base

TABLE 70

EFFECT OF SRC RECYCLE ON NONCATALYTIC LIQUEFACTION[a]

	SRC/solvent ratio					
	Base liquefaction solvent			Modified solvent		
	0	0.13	0.50	0	0.13	0.47
Product distribution (wt % MAF coal)						
Gases	11.7	10.4	13.3	10.8	10.5	10.5
Oil	29.2	38.5	53.3	33.8	38.7	44.6
SRC	35.8	23.0	3.9	33.3	27.1	7.0
IOM	23.3	28.1	29.5	22.1	23.7	37.9
Conversion	76.7	71.9	70.5	77.9	76.3	62.1

[a] Reaction mixture:

Coal	3 g
Solvent	3 g

Reaction conditions:

Temperature	440°C
H_2 pressure	1,200 psig coal
Time	60 min
Agitation	1,000 strokes per min

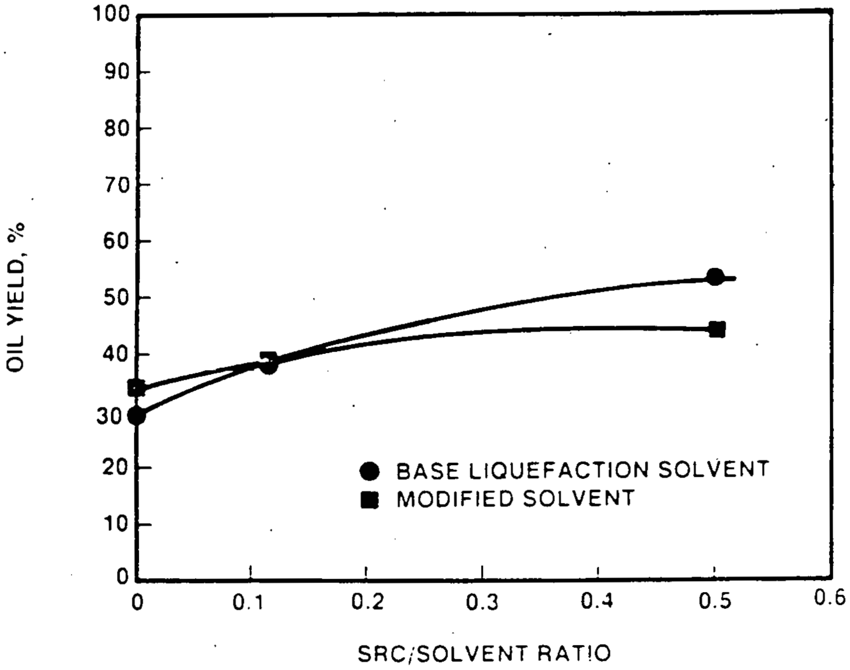
liquefaction and modified solvents, respectively (see Table 70 and Figure 11). However, overall coal conversion decreased with SRC recycle, much more so with base liquefaction solvent than with modified solvent. Increasing the level of SRC recycle to 50% further increased oil yield, but the increase was considerably greater with base liquefaction solvent than with modified solvent (Table 70 and Figure 11). On the other hand, coal conversion further decreased with an increasing level of SRC recycle, dramatically so with modified solvent. Apparently, all the advantages of modifying the solvent are lost by recycling this large amount of SRC. One can conclude that significant improvement in oil yield is achievable by recycling SRC, but at the expense of overall coal conversion. Furthermore, noncatalytic liquefaction of coal with SRC recycle may yield as much oil as noted with 250-ppm molybdenum catalyst without SRC recycle, but at the expense of considerable loss in coal conversion.

Catalytic Liquefaction

Several experiments were carried out with SRC recycle in the presence of 250-ppm molybdenum based on coal to study the effect of SRC recycle in catalytic coal liquefaction. The reaction mixture and conditions were again very similar to those used in noncatalytic liquefaction experiments.

Recycle of SRC using both base liquefaction and modified solvents significantly increased oil yield, as shown in Table 71 and Figure 12. The difference in oil yields obtained was the greatest without SRC recycle, but decreased consistently with an increase in the level of SRC recycle. However, oil yield obtained with modified solvent was always higher than that noted with base liquefaction solvent. Overall coal conversion, which decreased dramatically with SRC recycle in noncatalytic liquefaction, decreased marginally with SRC recycle in the presence of a catalyst (see Table 71 and Figure 12). Therefore, the recycle of SRC in the presence of a catalyst significantly increases oil production without a severe penalty in terms of coal conversion.

FIGURE 11
EFFECT OF SRC RECYCLE ON NONCATALYTIC LIQUEFACTION



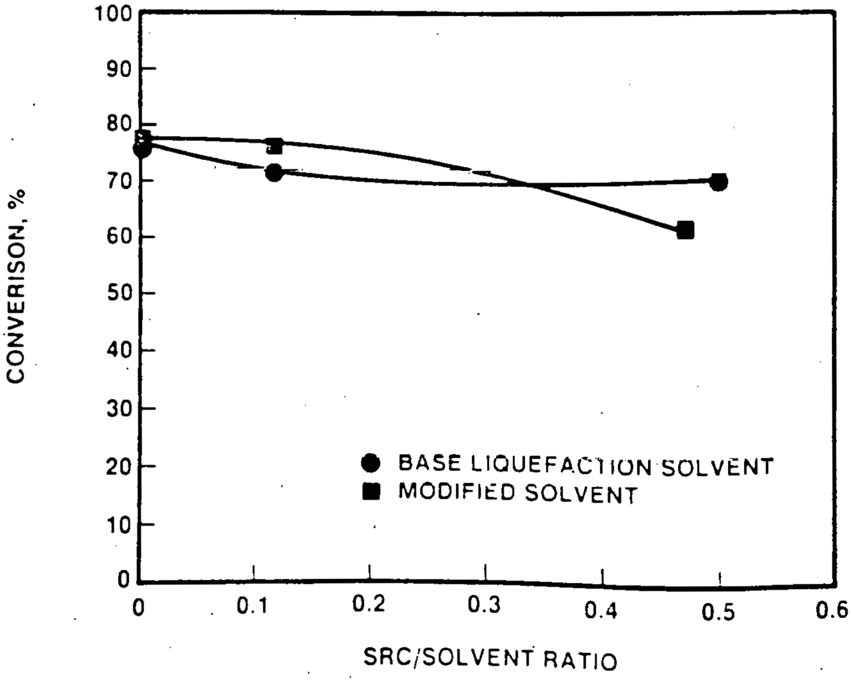


TABLE 71

EFFECT OF SRC RECYCLE ON CATALYTIC LIQUEFACTION[a]

	SRC/solvent ratio									
	Base liquefaction solvent					Modified solvent				
	0	0.07	0.13	0.27	0.50	0	0.07	0.13	0.27	0
Product distribution (wt % MAF coal)										
Gases	10.8	10.5	10.6	10.9	10.8	10.9	10.2	9.3	10.0	13
Oil	44.0	44.7	51.3	59.2	68.8	50.9	55.1	54.7	61.8	69
SRC	39.8	35.9	30.2	16.5	8.2	31.6	27.8	26.0	18.4	5
IOM	5.4	8.9	7.9	13.4	12.2	5.6	6.9	10.0	9.8	11
Conversion	94.6	91.1	92.1	86.6	87.8	93.4	93.1	90.0	90.2	88

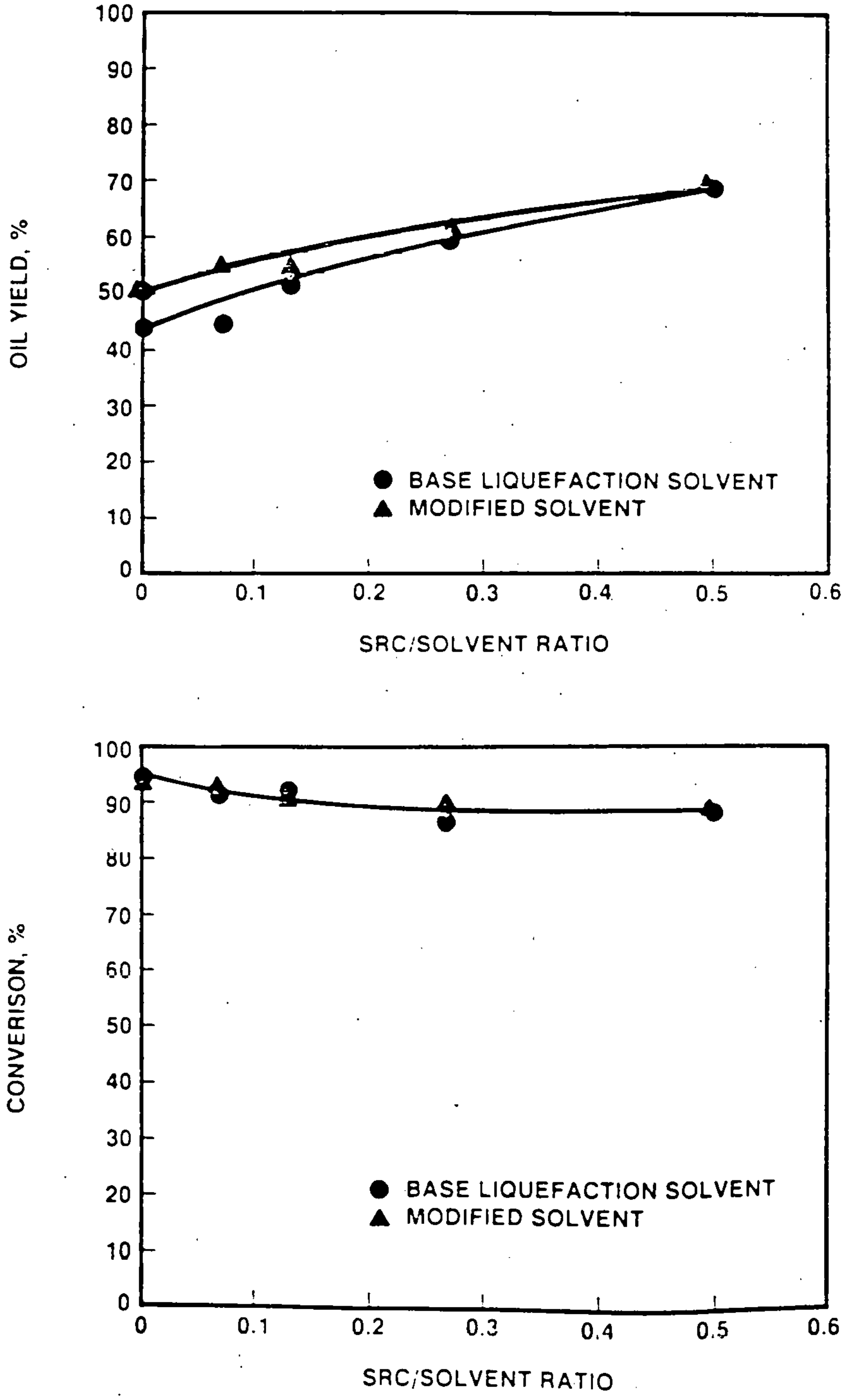
[a] Reaction mixture:

Coal	3 g
Solvent	3 g
Catalyst	250 ppm molybdenum based on coal

Reaction conditions:

Temperature	440°C
H_2 pressure	1,200 psig cold
Time	60 min
Agitation	1,000 strokes per min

FIGURE 12
EFFECT OF SRC RECYCLE ON CATALYTIC LIQUEFACTION



Effect of Catalyst Concentration

The effect of molybdenum concentration on coal liquefaction with SRC recycle was evaluated with both base liquefaction and modified solvents. The experimental results summarized in Table 72 show that increasing the concentration of molybdenum from 250 to 500 ppm based on coal increased oil yield with both solvents. However, the increase was much higher with modified solvent. Overall coal conversion also increased with increasing catalyst concentration using both base liquefaction and modified solvents.

Comparison of the data summarized in Tables 71 and 72 shows that the oil yield obtained with 250-ppm molybdenum along with recycle of 27% SRC can be increased from ~60 to ~70% with either solvent by increasing the amount of SRC recycle to 50% or by increasing the catalyst concentration from 250 to 500 ppm. Increasing SRC recycle slightly decreases coal conversion, whereas increasing catalyst concentration increases catalyst cost. Hence, cost-benefit analysis must be made before one of these two options is selected.

Summary

In summary, we conclude that SRC recycle undoubtedly increases oil yield in noncatalytic liquefaction, but at the expense of overall coal conversion. In contrast, SRC recycle in the presence of a catalyst increases oil yield while maintaining the coal conversion level. Thus, the advantages of SRC recycle are achievable only in the presence of a catalyst. Finally, our goal of higher oil production (close to 70% based on MAF coal) can be achieved either by recycling a large proportion of SRC or increasing the concentration of catalyst. Either way, a cost-benefit analysis must be made to select the best route.

TABLE 72

EFFECT OF CATALYST CONCENTRATION WITH SRC RECYCLE[a]

	Molybdenum concentration (ppm based on coal)			
	Base liquefaction solvent		Modified solvent	
	250	500	250	500
Product distribution (wt % MAF coal)				
Gases	10.9	10.1	10.0	10.7
Oil	59.2	66.7	61.8	70.1
SRC	16.5	17.0	18.4	12.5
IOM	13.4	6.2	9.8	6.7
Conversion	86.6	93.8	90.2	93.3

[a] Reaction mixture:

Coal	3 g
Solvent	3 g
SRC/solvent	0.27

Reaction conditions:

Temperature	440°C
H_2 pressure	1,200 psig cold
Time	60 min
Agitation	1,000 strokes per min

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APPENDIX 1

SOLVENT SEPARATION PROCEDURE

The purpose of this procedure is to provide rapid, precise fractionation of the gross coal conversion product into three subfractions defined by their solubility.

- Oils: pentane solubles
- SRC: pentane insoluble/methylene chloride - methanol soluble
- Residue: methylene chloride - methanol insoluble

This procedure was conducted at room temperature (25 ± 3°C), under nitrogen gas pressure, using solvents of the highest quality available. The sample may be liquid, solid, or a mixture, with less than 1% material boiling below 150°C.

EQUIPMENT REQUIRED

1. Branson Model 350 sonicator with 3/4-in. horn

2. Branson ultrasonic bath

3. Millipore 142 mm pressure filter with 300-mL capacity, #XX40-047-00, with 142 mm filter, 5 μm, FSLW-01420

4. Round-bottomed distilling flasks - 500-mL, 250-mL, two each

5. Rotoevaporator R, Fisher Scientific #9-548-151 (1979)

6. Vacuum pump and trap

7. Nitrogen gas (0-20 psi adjustable) pressure filter feed
   Nitrogen gas (0-20 psig adjustable) rotoevaporator feed
   Nitrogen liquid (1-2 L) freeze sample (dewar)

8. a) n-Pentane
   b) Methylene chloride
   c) Methanol

   Grade of solvent depends upon ultimate use of sample subfractions (Pesticide, Distilled in Glass, or HPLC grade)

9. Fume hood, 150-200-cfm air rate exchange

10. Cooling water or heater exchange for rotoevaporator condenser

11. Balance to read weights ±0.005 or better, with maximum load 200 g.

SAFETY FEATURES

Solvents must be used only under the fume hood and transferred from bottle to flask by hand pump. Protective gloves and overalls are required for laboratory work. Cleanup of spills on hands can be completed with Go-Jo, waterless hand cleaner, mild scrubbing, and water wash (warm). All normal safety precautions must be observed during the entire operation.

SAMPLE HANDLING

All the sample in the tubing-bomb reactor must be kept free of air (oxygen), heat, and light. Samples not ready for separation must be kept at 4°C under a blanket of nitrogen. The sample to be analyzed is removed from the refrigerator and its top cap unscrewed and mixed well in an ultrasonic bath. The sample is now ready for detailed solvent separation analysis.

PROCEDURE

The laboratory equipment is prepared in the following order:

(a) Ultrasonic unit with 3/4-in. horn adjusted and cleaned with methylene chloride.

(b) Millipore filter put in place after weighing dry filter element. Ensure that all O-rings fit well with no leaks (test with n-pentane under 10 psi). Use Teflon tape (3/4 in.) to wrap screw fittings and seals.

(c) Prepare rotoevaporator-bath temperature at 55-60°F for n-pentane; nitrogen flow rate should just cause 1/4-1/2 in. dimple in liquid of 250 mL flask.

(d) Cooling liquid for rotoevaporator condenser should be 10°C if heater exchanger used -10°C with MeOH.

Step 1: Thoroughly clean a 1000 mL heavy wall pyrex beaker.

Step 2: Add 25 mL of n-pentane to the tubing bomb reactor and mix the contents using an ultrasonic bath for 5 min. Pour the reactor contents into the 1000 mL beaker.

Step 3: Repeat step 2 four to five times until the liquid from the reactor is clear.

Step 4: To the mixture collected in the 1000-mL beaker add more n-pentane to bring the entire volume to 500 mL. Sonicate the entire mixture for 5 min at level 5.

Step 5: Allow mixture to settle (1-2 min). Decant supernatant into filter unit, refill beaker with n-pentane, and sonicate again for 3-5 min. Allow decant liquid to filter into a 500 mL flask - do not allow filter to dry from this time on.

Step 6: Repeat step 5 twice for a total of 2000 mL of n-pentane. If catch flask fills, transfer to rotoevaporator and begin to remove n-pentane under nitrogen at 60°C. Transfer the solids with small portions (25-50 mL) of pentane.

Do not discard beaker; hold for additional transfer of solvents to filter. This ensures removal of the maximum amount of material and reduces losses.

Step 7: Filter the solids, adding nitrogen pressure (5-10 psi) if needed. Add new pentane via original beaker as needed for a total of 2 L. This amount can be re-collected from the rotoevaporator unit during the continuous solvent removal steps.

Step 8: Continue solvent filtering until the filtrate is a very light yellow/green. At the end of pentane extraction, with 25 mL of pentane in the filter, add 100 mL of 10% methanol in methylene chloride and continue as in step 7 for 2.5 L. The new filtrate is collected in a new 500-mL flask (tare). Continue to transfer filtrate to rotovapor with a waterbath temperature of 75°C.

Step 9: Hold all pentane solubles collected through step 8 on the rotoevaporator for 2 min beyond the point when the last drop of condensed pentane is in the catch flask. Remove, clean, and dry the outside of the flask containing the oils (reddish) and weigh. Record:

Yield of oils: ------- grams

Step 10: Conduct methylene chloride/methanol extraction in the same way as Steps 7-9. Remove the methylene chloride/methanol solubles from the rotoevaporator when 10-20 mL of solution remains. Then vacuum-dry the flask. Record:

Yield of SRC: ------- grams

Step 11: Vacuum dry the residue retained on the filter paper. Gently remove filter paper with residue and weigh. Record:

Yield of residue: ------- grams

Step 12: Oils A

SRC B

Residue C

Gases D (determined by gas analysis)

- A + B + C + D = total recovered
- Original mass of sample charged = MS
- MS - total recovered = net loss or gain
- If gain of weight is observed, solvent is present in oils or other fraction.
- If loss of weight is observed, oils have volatile matter.
- Add net loss to mass of oils (A + net loss) and calculate over the material recovery.

		Recovered	Corrected	%
Report:	Oils	A	A + net loss	
	SRC	B	B	
	Residue	C	C	
	Gases	D	D	
	Total Recovered		MS	100%

This data is used to calculate the product distribution based on MAF coal.

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APPENDIX 2

AUTOCLAVE OPERATING AND CALCULATION PROCEDURES

An autoclave system was designed and assembled to provide a continuous supply of hydrogen to the liquefaction reaction. The detailed design of the autoclave is illustrated in Figure A-1 and detailed steps involved in the operation of the autoclave and calculations of the results are described below.

OPERATING PROCEDURE

1. Charge the autoclave with the reaction mixture consisting of 40 g of coal and 60 g of solvent. For catalytic runs, a predetermined amount of catalyst is also added.

2. Assemble the autoclave as shown in Figure A-1.

3. Leak-check the entire system using helium stepwise to 2500-psig pressure at room temperature.

4. If the system is leak tight, establish the flow of helium through the unit to purge the system as well as to remove any air trapped in the reactor system.

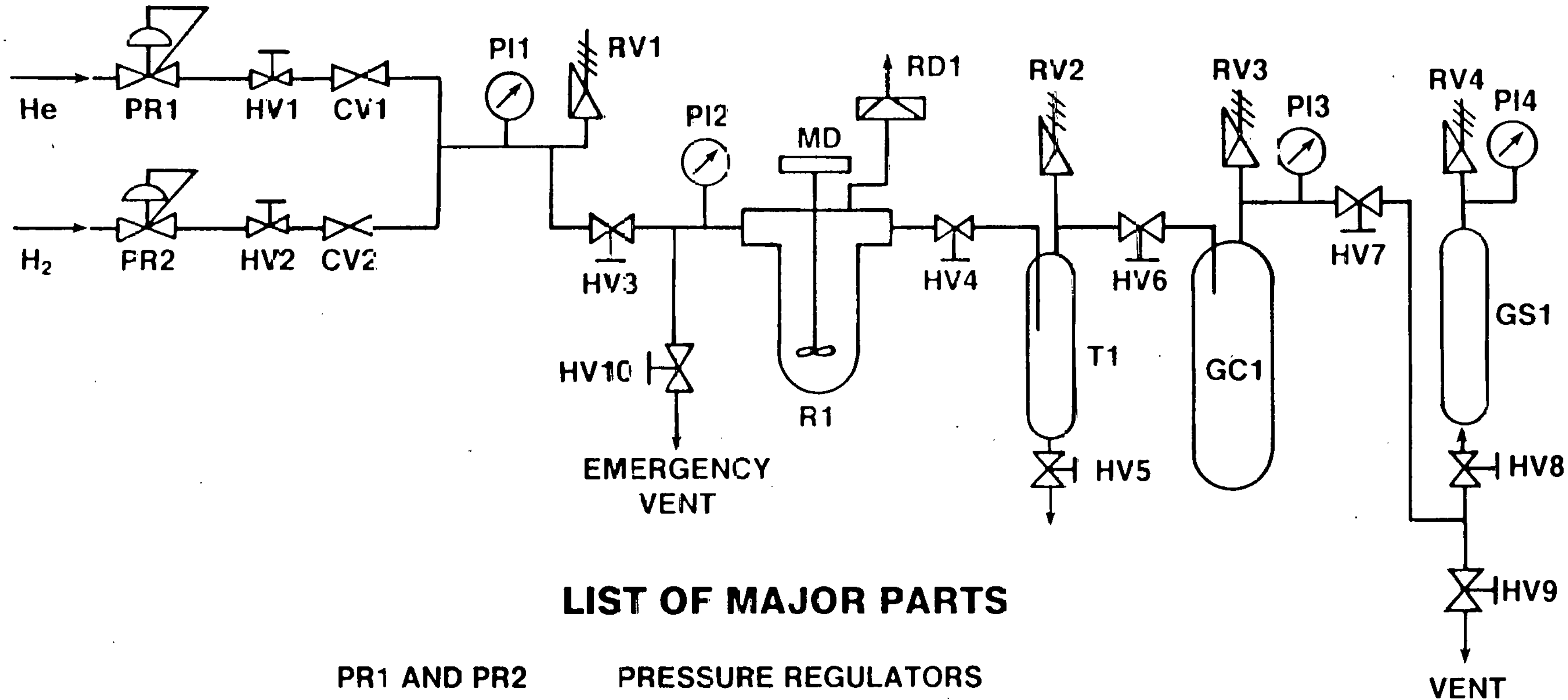
5. After purging the system with helium, turn on the stirrer of the autoclave and discontinue flow of helium.

6. Establish the flow of hydrogen and purge the system thoroughly with hydrogen.

7. Calibrate the system to determine the volume occupied by gases in the reactor, trap, gas collection, gas sample vessels, and transfer lines.

8. Isolate gas sample vessel, gas collection vessel, and trap by closing shutoff valves.

FIGURE A-1
SCHEMATIC OF 300-ML AUTOCLAVE REACTOR



LIST OF MAJOR PARTS

PR1 AND PR2	PRESSURE REGULATORS
HV1 TO HV10	HIGH-PRESSURE FLOW-CONTROL VALVES
CV1 AND CV2	CHECK VALVES
PI1 TO PI4	PRESSURE INDICATORS
RV1 TO RV4	RELIEF VALVES
R1	300-ML AUTOCLAVE REACTOR
MD	MAGNE-DRIVE UNIT
RD1	RUPTURE DISC
T1	COLD TRAP
GC1	GAS COLLECTION VESSEL
GS1	GAS SAMPLE BOMB

9. Pressurize the reactor to 1,000-psig with hydrogen.

10. Start heating the reactor. When the temperature in the reactor reaches 250°C, increase the hydrogen pressure to 2,000 psig and initiate the flow of hydrogen through the reactor to ensure more than enough availability of hydrogen for the reaction.

11. Collect the gases in the gas collection vessel.

12. When the reaction temperature reaches the desired value, set the reaction time to zero and carry the reaction for the desired period. After the desired reaction time, turn the heaters off and start cooling the reactor. In addition, discontinue the flow of hydrogen.

13. After some time, the temperature of the reactor will approach room temperature and the pressure in the reactor, trap, and gas collection vessel will equilibrate. Note the temperature and pressure.

14. Open appropriate valves to collect gas sample in the gas sample vessel for detailed gas analysis.

15. Collect organic material condensed in the trap and weigh it.

16. Open the autoclave system and collect all the material for further analysis.

17. Clean the system thoroughly for next run.

CALCULATION PROCEDURE

A number of steps are involved in determining the product distribution from the 300-mL semicontinuous (continuous flow of hydrogen to ensure sufficient supply of hydrogen for the reaction) autoclave reactor. These steps are described in detail below.

Step A

After the reaction, the flow of hydrogen is stopped and the autoclave is cooled down close to room temperature. At this time the final temperature and pressure are noted. In addition, a sample of gas is taken for C_1-C_5, CO, CO_2, H_2S, NH_3, and H_2 analysis. The volume occupied by gases is determined before the reaction by volume calibration. Knowing all these values, the weights of individual components in the gas phase are determined. The weight of total gases excluding hydrogen is determined.

Weight of gases excluding H_2 = A

Step B

The organic material condensed and collected in the trap is drained and weighed. The sample is then subjected to phase separation to determine the weight of water and oil, respectively.

Weight of water = B
Weight of oil = C

Step C

1. The autoclave is opened and all the material in it is recovered in a 1000-mL beaker. The entire unit is then thoroughly cleaned and washed with methylene chloride. The entire reaction product along with methylene chloride is then sonicated and filtered. The material remaining on the filter paper is liquefaction residue and it is vacuum-dried and weighed.

   Weight of liquefaction residue = D

2. The filtrate was rotoevaporated to remove methylene chloride. The concentrated filtrate containing product oil, process solvent, SRC, and part of the methylene chloride is subjected to two-step distillation.

3. The first step involves complete removal of methylene chloride by distilling the concentrated filtrate under vacuum at 60°C. Part of the very light oil product is lost with methylene chloride fraction, but it is assumed to be negligible.

4. After the removal of methylene chloride, the filtrate is distilled to recover product oil and process solvent. A temperature of 950°F (corrected temperature) is used as an end point. The distillate product (oil) and distillate bottoms (SRC) are then weighed.

Weight of distillate oil = E
Weight of SRC = F

Mass Balance

Feed

Weight of feed coal = X
Weight of feed solvent = Y
Total feed = X + Y

Product

Total gases = A
Water = B
Distillate oil = C + E
SRC = F
Residue = D
Total A + B + (C + E) + F + D

Note: The contribution due to hydrogen consumption is neglected in the calculation.

$$\text{Recovery} = \left[\frac{A + B + (C + E) + F + D}{X + Y}\right] \times 100$$

In most cases, the recovery is better than 98%. The losses are added to the distillate oil fraction to close the mass balance.

Product Distribution Calculation

Requirements: Ash in the coal = X_1
Moisture in the coal = X_2

Step 1

$$\text{Organic material in the coal} = X - (X_1 + X_2) \equiv OM$$

Net products	Weight	Wt % MAF coal
Total gases	A	(A/OM) x 100
Water	$B - X_2$	$[(B - X_2)/OM] \times 100$
Distillate oil	C + E - Y	[(C + E - Y/OM] x 100
SRC	F	(F/OM) x 100
Insoluble organic material (IOM)	$D - X_1$	$[(D - X_1)/OM] \times 100$

Conversion, % = 100 - wt % IOM

APPENDIX 3

COMPILATION OF RECORD OF INVENTION FORMS

DOE Form GC-213
(2-78)
DOE PR-9-9

U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

This Record of Invention is an important legal document and proper care in its early and complete preparation will save important time and inconvenience in the future. The Instructions* on the back should be read carefully before filling in the data

DOE Case No.

A. Inventor: 1. Name(s): Diwakar Garg. Edwin N. Givens and Frank K. Schweighardt

2. Title or Position: Principal Research Engr., M
R&D Safety & Special Servic
Research Associate.

3. Employed by: Air Products & Chemicals, Inc.

4. Permanent Address: P.O. Box 538, Allentown, PA 18105

B. Title of Invention (1*): "Improved Catalytic Coal Liquefaction Process"

C. Description of Invention (2*): The invention is an improved catalytic coal liquefaction proce which coal is converted predominantly to light gases and distillate products. The improved process concepts requires the removal of both basic nitrogen and phenolic pounds from the process solvent before recycling to the liquefaction reactor. In a it requires recycling of almost all the SRC generated during the liquefaction to th liquefaction reactor to promote higher liquefaction activity. The key distinctions both the removal of nitrogen and phenolic materials from the recycle solvent and th unconverted SRC to the liquefaction reactor.

D. Dates and Places of Inventions:

1. Conception by Inventor (3*) 10 September 1980 Allentown, PA At
2. First Sketch or Drawing At In Workbook Page
3. First Written Description 10 Sept. 1980 At Allentown, PA Idea Suggestion and Patent ~~Proposal~~ Page
4. Disclosure to Others (4*) Idea Suggestion and Patent Proposal: CG-0004, 10 September 1980, Allentown, PA
   a. 19 At
   b. 19 At
5. Completion of Model or Full Size Device At
6. First Test or Operation of Invention 23 September 1983 At Allentown, PA

E. Results of Tests and Extent of Use of Invention (5*)
The data show that catalytic processes are improved by simultaneous solvent treatment and SRC recycle.

F. Names of all Persons Having Knowledge of Facts Stated Und and E.:
William Collins
Steven A. Lindner
David L. Howells

G. Pertinent Reports (6*):
APCI Internal Report:
Idea Suggestion and Patent Proposal
#GG004, 10 September 1980

H. Other Closely Related Publications, Patents, and Patent Applications (7*):

U.S. 3,321,393	U.S. 3,700,584
U.A. 3,412,010	U.S. 3,519,555

I. Rights of U.S. Government:
Modification No. M006 of Contract No. DE-AC22-82PC50003, "Advanced Waiver Patent Clause."

J. Licenses or Assignments:
None

K. Contracts Involved:
Air Products and Chemicals, Inc.

Contract No.: DE-AC22-82PC50003

Date: 9/28

Contractor and Address
P.O. Box 533, Allentown, PA 18105

Type of Contract: [✓ Unclassified] Restricted Confidential Secret

L. Signature of Witness: Sheryl B. Del Giorno

Date: 11/8/84

Signature of Inventor(s):

Date:

Forwarded by (8*):
Application For a Patent Should be Filed

Date: 28 November 1984

(OVER)

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R-9-9

U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

Record of Invention is an important legal document and proper care in its early and complete preparation save important time and inconvenience in the future. The Instructions* on the back should be read carefully re filling in the data.

DOE Case No.

entor: 1. Name(s): obert N. Miller

2. Title or Position: Principal Research Chemist

Employed by: ir Products and Chemicals, Inc.

4. Permanent Address: P.O. Box 538, Allentown, PA 18105

le of Invention (1*): iquefaction of Coal Extracted with a Binary Solvent Mixture"

scription of Invention (2*): An improved coal liquefaction process is proposed wherein coal is ially extracted with a mixture comprised of two solvents, an aromatic hydrocarbon and lcohol. This binary solvent mixture removes small molecules in the coal thus its rnal structure is unexpectedly rendered more accessible to the H-donor solvent. The acted coal is subjected to liquefaction conditions to form a product with an improved yield over that obtained upon liquefaction of the original coal. The unique com- tion of binary solvents when used to extract coal renders the coal more reactive for iding oils upon liquefaction.

tes and Places of Inventions:

Conception by Inventor (3*) 25 March 1983 Allentown, PA At

First Sketch or Drawing At In Workbook Page

First Written Description 25 March 1983 At Allentown, PA In Workbook #7514 Page 3

Disclosure to Others (4*) At

a. Technical Idea/Patent Suggestion 3 Aug. 1983 At Allentown, PA
"Liquefaction of Solvent-Extracted Coal"

b. 19 At

Completion of Model or Full Size Device At

First Test or Operation of Invention 25 March 1983 At Allentown, PA

sults of Tests and Extent of Use of Invention (5*): rease in oil yield and an improved version over liquefaction of the original l.

F. Names of all Persons Having Knowledge of Facts Stated Under D. and E.: Bill Collins, Steve Lindner, Fran Gough

rtinent Reports (6*): 1 June 1983, 21 April 1983, 1 November 1983 written disclosure of experimental results was made to the tract Manager of DOE.

H. Other Closely Related Publications, Patents, and Patent Applications (7*): U.S. 4,089,638
U.S. 3,637,639 U.S. 4,272,356
U.S. 4,388,171

ghts of U.S. Government: Modification No. M006 of tract No. DE-AC22-83PC50-03 vanced Waiver Patent Clause."

J. Licenses or Assignments: None

ntracts Involved: ir Products and Chemicals, Inc.

Contract No.: DE-AC22-82PC50003

Date: 9/28/82

ntractor and Address: .O. Box 538, Allentown, PA 18105

Type of Contract: [✓ Unclassified] Restricted Confidential Secret

nature of Witness: rge B. DelGiorno

Date: 11/8/84

Signature of Inventor: Robert N. Miller

Date: 8 Nov. 84

warded by (8*): lication For A Patent Should Be Filed.

Date: 28 November 1984

(OVER)

DOE Form GC-213
(2-78)
DOE PR-5-9

U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

DOE Case No.

This Record of Invention is an important legal document and proper care in its early and complete preparation will save important time and inconvenience in the future. The Instructions* on the back should be read carefully before filling in the data

A. Inventor: 1. Name(s): Diwakar Garg
2. Title or Position: Principal Research Engineer

3. Employed by: Air Products and Chemicals, Inc.
4. Permanent Address: P.O. Box 538, Allentown, PA 18105

B. Title of Invention (1*): "Improved Catalytic Coal Hydroliquefaction Process"

C. Description of Invention (2*): A process for the liquefaction of coal in the presence of at le two catalysts impregnated on the coal to obtain both high conversion of coal and production of distillate oil. The key feature of the process is the unique combinat of the metal catalysts such as molybdenum, nickel, cobalt, and tungsten and the othe metal catalysts selected from Groups IB, IIB, IVB, VA, VIA, or VIIA of the period table. The second metal may be a weak hydrogenation catalyst or poison for coal liq faction. The distinguishing feature is the combination of catalysts which has not b applied or disclosed for coal liquefaction.

D. Dates and Places of Inventions:
1. Conception by Inventor (3*) 23 March 1983, Allentown, PA At
2. First Sketch or Drawing At In Workbook Page
3. First Written Description June 2, 1983 At Allentown Letter from D.Garg to A.R.Tarr ~~In Workbook~~ Page Auburn U
4. Disclosure to Others (4*) At
a. Technical Idea and Patent Suggestion 16 Sept. 1983, Allentown, PA 19 At
b. 19 At
5. Completion of Model or Full Size Device At
6. First Test or Operation of Invention 23 March 1983 At Allentown, PA

E. Results of Tests and Extent of Use of Invention (5*)
Successfully increased both coal conversion and distillate oil production.

F. Names of all Persons Having Knowledge of Facts Stated Unde and E.: A. R. Tarrer and Donald Cohela of Auburn University

G. Pertinent Reports (6*):
APCI Internal Report TIP #CJ-022B.

H. Other Closely Related Publications, Patents, and Patent Applications (7*): U.S. 3,183,180 U.S. 3,74
U.S. 3,532,617 U.S. 2,227,672
U.S. 3,619,404 137-P-US02786

I. Rights of U.S. Government: Modification No. M006 of Contract No. DE-AC22-82PC50003 "Advanced Waiver Patent Clause"

J. Licenses or Assignments:
None

K. Contracts Involved: Air Products and Chemicals, Inc.
Contract No.: DE-AC22-82PC50003
Date: 9/28

Contractor and Address
P.O. Box 538, Allentown, PA 18105

Type of Contract: [✓ Unclassified] Restricted Confidential Secret

L. Signature of Witness: Sheryl B. DelGiorno
Date: 11/8/84

Signature of Inventor(s):
Date:

Forwarded by (8*). Application For A Patent Should Be Filed.
Date: 28 November 1984

(OVER)

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U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

Record of Invention is an important legal document and proper care in its early and complete preparation save important time and inconvenience in the future. The Instructions* on the back should be read carefully ore filling in the data.

DOE Case No.

entor: 1. Name(s): Diwakar Garg. David S. Hoover and Robert N. Miller

2. Title or Position: Principal Research Engineer, Sr. Principal Research Chemist, and Principal Research Chemist.

Employed by: Air Products and Chemicals, Inc.

4. Permanent Address: P.O. Box 538, Allentown, PA 18105

le of Invention (1*): "Improved Coal Liquefaction Process"

scription of Invention (2*): An improved noncatalytic coal liquefaction process is presented in h coal is converted to light gases, distillate oil, solid SRC and a mineral residue h contains undissolved coal minerals and ash. The improvement involves soaking coal low heteroatom containing process solvent (modified solvent) derived from coal at peratures substantially below the typical coal liquefaction reaction temperature before jecting it to the liquefaction conditions. The soaking of coal in the modified solvent lted in an unexpected increase in both oil production and coal conversion which is the feature of the invention.

tes and Places of Inventions:

Conception by Inventor (3*) 22 June 1983 At Allentown, PA

First Sketch or Drawing ____ At ____ In Workbook ____ Page ____

First Written Description APCI Lab Notebook At Allentown, PA In Workbook #7535, #7508 Page 44-46, 31-32.

Disclosure to Others (4*) Corporate Idea & Patent Proposal Committee, APCI, Allentown, PA

a. 19 September 1983 19 At (Technical Idea & Patent Suggestion #CG-0231)

b. ____ 19 At ____

. Completion of Model or Full Size Device NA At ____

. First Test or Operation of Invention 22 June 1983 At APCI, Allentown, PA

esults of Tests and Extent of Use of Invention (5*): process successfully increased both oil duction and coal conversion.

F. Names of all Persons Having Knowledge of Facts Stated Under D. and E.:
Steve Lindner
Williams Collins

ertinent Reports (6*): I Internal Report TIP #CG-004

H. Other Closely Related Publications, Patents, and Patent Applications (7*): U.S. 4,028,221 U.S. 3,692,662 U.S. 3,791,957 U.S. 4,344,837 U.S. 4,250,014

ights of U.S. Government: Modification No. M006 of ontract No. DE-AC22-82PC50003 vanced Waiver Patent Clause."

J. Licenses or Assignments: None

ontracts Involved: Air Products and Chemicals, Inc.

Contract No.: DE-AC22-82-PC50003

Date: 9/28/82

ontractor and Address: P.O. Box 538, Allentown, PA 18105

Type of Contract: [✓ Unclassified] | Restricted | Confidential | Secret

gnature of Witness: heryl B. Del Gioiso

Date: 11/8/84

Signature of Inventor(s):

Date:

Robert N. Miller

8 Nov 84

orwarded by (8*): lication For a Patent Should Be Filed.

Date: 28 November 1984

(OVER)

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(2-78)
DOE PR-9-9

U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

DOE Case No.

This Record of Invention is an important legal document and proper care in its early and complete preparation will save important time and inconvenience in the future. The Instructions* on the back should be read carefully before filling in the data.

A. Inventor: 1. Name(s): David S. Hoover — 2. Title or Position: Sr. Principal Research Chemi
Diwakar Garg — Principal Research Engineer

3. Employed by: Air Products & Chemicals, Inc.
4. Permanent Address: P.O. Box 538, Allentown, PA 18105

B. Title of Invention (1*): "Improved Coal Liquefaction Process with Demineralized Feed"

C. Description of Invention (2*): This idea represents an improved coal liquefaction process wher the feed coal is substantially demineralized or "deep cleaned" by physical or chemic methods prior to liquefaction with dispersed catalysts. The demineralization techn substantially increases the activity of dispersed molybedenum catalysts over that s with typically cleaned coals. The advantages of practicing this process are: incr coal conversion, increased yields of distillate, reduced catalyst consumption and simplified solid separation facilities.

D. Dates and Places of Inventions:

1. Conception by Inventor (3*) 19 September 1983 At Allentown, PA
2. First Sketch or Drawing ______ At ______ In Workbook ______ Page
3. First Written Description 19 September 1984 At Allentown, PA In Workbook Patent Suggestion: APCI Form Page
4. Disclosure to Others (4*) 19 September 1983 At Allentown, PA (Patent Suggestion
   a. 22 April 1983 19 At Oral to DOE Contract Manager
   b. ______ 19 At ______
5. Completion of Model or Full Size Device ______ At ______
6. First Test or Operation of Invention March 19, 1983 At Allentown, PA

E. Results of Tests and Extent of Use of Invention (5*): This process results in increased coal conversion, increased yields of distillate, reduced catalyst consumption, and simplified ~~solid separation facilities.~~

F. Names of all Persons Having Knowledge of Facts Stated Und and E.: Steven A. Linder, Scott A. Sta Robert L. Iampietro, William S. Collins Frank K. Schweighardt.

G. Pertinent Reports (6*): None

H. Other Closely Related Publications, Patents, and Patent Applications (7*): U.S. 4,039,425 U.S. 4,397,732, U.S. 4,257,869

I. Rights of U.S. Government: Modification No. M006 of Contract No. DE-AC22-82PC50003

J. Licenses or Assignments: None

K. Contracts Involved: Air Products & Chemicals, Inc.
Contract No.: DE-AC22-83PC50003 — Date 9/2

Contractor and Address: P.O. Box 538, Allentown, PA 18105

Type of Contract: [✓ Unclassified] | Restricted | Confidential | Secret

L. Signature of Witness: Sheryl B. DelGiorno — Date: 11/8/84

Signature of Inventor(s): — Date

Forwarded by (8*): Application For A Patent Should Be Filed. — Date: 28 November 1984

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U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

Record of Invention is an important legal document and proper care in its early and complete preparation save important time and inconvenience in the future. The Instructions* on the back should be read carefully e filling in the data.

DOE Case No.

ntor: 1. Name(s): obert N. Miller, Diwakar Garg, and David S. Hoover

2. Title or Position: Principal Research Chemist, Principal Research Engineer, and Sr. Principal Research Chemist

Employed by: ir Products and Chemicals, Inc.

4. Permanent Address: P.O. Box 538, Allentown, PA 18105

e of Invention (1*): uefaction of Oxidized Coal with Modified Solvents"

scription of Invention (2*): A coal liquefaction process that is based on the discovery that ized coals can be liquefied without detrimental effects when the solvent that is used he H-donor vehicle in the liquefaction has been modified. The solvent modification, lving removal of a substantial portion of the -N and -O heteroatom constituents, ificantly improves the yield of distillate oils from liquefaction of oxidized coal pared to liquefaction using conventional solvents with fresh coal. The use of a roatom modified solvent to treat oxidized coal is the key feature.

tes and Places of Inventions:

Conception by Inventor (3*) 16 January 1984 At Allentown, PA

First Sketch or Drawing At In Workbook Page

First Written Description 16 January 1984 At Allentown, PA Technical Idea Suggestion, CG-0254 Page

Disclosure to Others (4*) F. K. Schweighardt, 16 January 1984, Allentown, PA At

a. 19 At

b. 19 At

Completion of Model or Full Size Device At

First Test or Operation of Invention experimental work 11 April 1983 to mid-December 1983 At Allentown, PA

esults of Tests and Extent of Use of Invention (5*): fficient experimental work has been concted under DOE Enhanced Catalysis contract demonstrate the validity of this process.

F. Names of all Persons Having Knowledge of Facts Stated Under D. and E.: D. L. Howells, S. A. Lindner, W. Collins

ertinent Reports (6*): CI Technical Idea/Patent Suggestion Report . CG-2054; Highlight Report DOE/TIC-50003- and in quarterly reports under below ref. contract

H. Other Closely Related Publications, Patents, and Patent Applications (7*): See Attachment A

ights of U.S. Government: dification No. M006 of Contract No. -AC22-82-PC50003 dvanced Waiver Patent Clause"

J. Licenses or Assignments: None

ontracts Involved: ir Products and Chemicals, Inc.

Contract No.: DE-AC22-82PC50003

Date: 9/28/82

ontractor and Address .O. Box 538, Allentown, PA 18105

Type of Contract: X Unclassified Restricted Confidential Secret

gnature of Witness: Sheryl B. DeGiorio

Date: 11-8-84

Signature of Inventor(s): Robert N. Miller

Date: 8 Nov. 84

orwarded by (8*): plication For A Patent Should Be Filed.

Date: 28 November 1984

(OVER)

Attachment A

Recent publications that have dealt with oxidation of coal and its relevance to liquefaction are as follows:

1. Neavel, R. C., "Liquefaction of Coal in Hydrogen-Donor and Non-Donor Vehicle," Fuel, 55, 237-242, 1976.
2. Chang, C. Y., Guin, J. A., Tarrer, A. R., "An Investigation of the Effect of Air-Oxidation on Coal Liquefaction," J. Chin. Chem. Soc., 23(3), 155-160, 1981.
3. EDS Coal Liquefaction Process Development, Phase V, Quarterly Tech. Progress Report, 1 July-30 September 1982, FE-2893-99, 49-51, 1983.

DOE Form GC-213
(2-78)
DOE PR-9-9

U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

This Record of Invention is an important legal document and proper care in its early and complete preparation will save important time and inconvenience in the future. The Instructions* on the back should be read carefully before filling in the data.

DOE Case No.

A. Inventor: 1. Name(s): Diwakar Garg and Swaminathan Sunder
2. Title or Position: Principal Research Engineer
Principal Research Engineer
3. Employed by: Air Products and Chemicals, Inc.
4. Permanent Address: P.O. Box 538, Allentown, PA

B. Title of Invention (1*): Base Enhanced Coal Liquefaction Process

C. Description of Invention (2*): This invention is an improved process for liquefying coal to pr
useful distillate oils and low ash and sulfur containing solvent refined coal (SRC
improvement consists of adding a base to a quinone (hydrogen transfer/hydrogen cat
catalyzed coal liquefaction process. This process results in a significant increa
both the overall coal conversion and oil yield. This invention utilizes the syner
between the quinones and bases in enhancing coal liquefaction. It is believed tha
this improvement will result in a decrease in the overall hydrogen consumption and
thus lead to a more economical process.

D. Dates and Places of Inventions:
1. Conception by Inventor (3*) 25 February 1984 At Allentown, PA
2. First Sketch or Drawing At In Workbook Page
3. First Written Description 25 February 1984 At Allentown, PA In Workbook #7941; pages 7-25, 30-3
#7348; pgs. 64-67, 76-78
#7508; pgs. 97-98, 103
#7706; pgs. 1-4, 7-8, 1
27-7
Page
4. Disclosure to Others (4*) At
a. Dr. D. S. Hoover and F. K. Schweighardt 19 At Allentown, PA
b. Technical Idea Suggestion 11 June 19 84 At Allentown, PA
5. Completion of Model or Full Size Device At
6. First Test or Operation of Invention 25 February 1984 At Allentown, PA

E. Results of Tests and Extent of Use of Invention (5*): This process results in a significant increase in both the overall coal conversion and oil yield.

F. Names of all Persons Having Knowledge of Facts Stated Unde and E.:
William Collins
Steve A. Lindner

G. Pertinent Reports (6*): None

H. Other Closely Related Publications, Patents, and Patent Applications (7*): U.S. Patent Numbers 4,049,535; 3,700,58
4,049,537; 4,051,012; 4,085,032; 4,085,

I. Rights of U.S. Government: Modification No. M006 of Contract No. DE-AC22-82PC50003 "Advanced Waiver Patent Clause"

J. Licenses or Assignments: None

K. Contracts Involved: Air Products and Chemicals, Inc.
Contract No.: DE-AC22-82PC50003
Date: 9/28
Contractor and Address: P.O. Box 538, Allentown, PA 18105
Type of Contract: [✓ Unclassified] | Restricted | Confidential | Secret

L. Signature of Witness: Sheryl B. DelGiorno
Date: 11/20/84
Signature of Inventor(s):
Date:

Forwarded by (8*): Application For a Patent Should Be Filed.
Date: 28 November 1984

(OVER)

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-9-9

U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

DOE Case No.

Record of Invention is an important legal document and proper care in its early and complete preparation ave important time and inconvenience in the future. The Instructions* on the back should be read carefully e filling in the data.

ntor: 1. Name(s): wakar Garg
2. Title or Position: Principal Research Engineer

ank K. Schweighardt
Research Associate

mployed by: r Products and Chemicals, Inc.
4. Permanent Address: P.O. Box 538, Allentown, PA 18105

of Invention (1*): proved Two-Stage Coal Liquefaction Process

ription of Invention (2*): This invention is a two stage coal liquefaction process in which coal nverted to light gases, distillate oil, low sulfur carbonaceous fuel, and a mineral due which contains undissolved coal macerals. The key feature of the process involves selection of the liquefaction solvent to give high yield of distillate oil. The efaction solvent may consist of either a distillate oil recovered from the products he liquefaction reactor or a distillate oil recovered from the primary products of a otreator or a mixture of the two.

es and Places of Inventions:

Conception by Inventor (3*) 26 September 1984 At Allentown, PA

First Sketch or Drawing ______ At ______ In Workbook ______ Page ______

First Written Description 26 September 1984 At Allentown, PA Technical Idea/Patent Suggestion Page ______

Disclosure to Others (4*) APCI-Idea and Patent Proposal Committee 26 September 1984

a. ______ 19 ______ At ______

b. ______ 19 ______ At ______

Completion of Model or Full Size Device ______ At ______

First Test or Operation of Invention ______ At ______

sults of Tests and Extent of Use of Invention (5*): s process will increase both coal consion and oil yield in coal liquefaction.

F. Names of all Persons Having Knowledge of Facts Stated Under D. and E.: Robert N. Miller

tinent Reports (6*): e

H. Other Closely Related Publications, Patents, and Patent Applications (7*):
U.S. 4,125,452
U.S. 4,081,351
U.S. 3,755,137
U.S. 1,838,547
U.S. 4,133,646

nts of U.S. Government: Modification No. M006 of tract No. DE-AC22-82PC50003, "Advanced ver Patent Clause"

J. Licenses or Assignments: None

ntracts Involved: ir Products and Chemicals, Inc.
Contract No.: DE-AC22-82PC50003
Date: 9-28-82

ntractor and Address: .O. Box 538, Allentown, PA 18105

Type of Contract: ☒ Unclassified ☐ Restricted ☐ Confidential ☐ Secret

nature of Witness:
Date: 4/27/84

Signature of Inventor(s):
Date: 11/27/84

warded by (8*): ication For a Patent Should Be Filed.
Date: 28 November 1984

(OVER)

DOE Form GC-213
(2-78)
DOE PR-9-9

U.S. DEPARTMENT OF ENERGY
OFFICE OF ASSISTANT GENERAL COUNSEL FOR PATENTS

RECORD OF INVENTION

DOE Case No.

This Record of Invention is an important legal document and proper care in its early and complete preparation will save important time and inconvenience in the future. The Instructions* on the back should be read carefully before filling in the data.

A. Inventor: 1. Name(s):
Diwakar Garg
David S. Hoover

2. Title or Position:
Principal Research Engineer
Sr. Principal Research Chem

3. Employed by:
Air Products and Chemicals, Inc.

4. Permanent Address:
P.O. Box 538, Allentown, PA 18105

B. Title of Invention (1*):
"Improved Deep Cleaned Coal Liquefaction Process with Catalyst Recycle"

C. Description of Invention (2*): This invention is an improved liquefaction process for the liqu
faction of deep cleaned coal with dispersed catalyst. The improvement consists of
recycling the liquefaction residue containing ash, undissolved coal, and spent catal
to further utilize the activity of the spent catalyst and to decrease the amount of
fresh catalyst required for liquefaction. Recycling of the liquefaction residue alo
with fresh catalyst results in unexpected improvements in both oil yield and overall
coal conversion. The unique feature of the process is the use of fresh catalyst in
attac

D. Dates and Places of Inventions:

1. Conception by Inventor (3*) 1 October 1984 At Allentown, PA
2. First Sketch or Drawing ______ At ______ In Workbook ______ Page
3. First Written Description 1 October 1984 At Allentown, PA Technical Idea/Patent Sugges ______ Page
4. Disclosure to Others (4*) 1 October 1984 to APCI - Idea At and Patent Proposal Committee
a. ______ 19 ______ At ______
b. ______ 19 ______ At ______
5. Completion of Model or Full Size Device ______ At ______
6. First Test or Operation of Invention ______ At ______

E. Results of Tests and Extent of Use of Invention (5*)
This process increases both overall conversion and oil yield and decreases catalyst consumption.

F. Names of all Persons Having Knowledge of Facts Stated Und and E.:
Robert N. Miller

G. Pertinent Reports (6*):
None

H. Other Closely Related Publications, Patents, and Patent Applications (7*):
U.S. 4,039,425 U.S. 4,397,732
U.S. 4,257,869

I. Rights of U.S. Government: Modification No. M006 of Contract No. DE-AC22-82PC50003 "Advanced Waiver Patent Clause"

J. Licenses or Assignments:
None

K. Contracts Involved:
Air Products and Chemicals, Inc.

Contract No.:
DE-AC22-82PC50003

Date
9/2

Contractor and Address
P.O. Box 538, Allentown, PA 18105

Type of Contract:
[✓ Unclassified] Restricted Confidential Secret

L. Signature of Witness:
Sheryl B DelGiorno

Date:
11/27/84

Signature of Inventor(s):

Date
11/2

Forwarded by (8*):
Application For a Patent Should Be Filed.

Date:
28 November 1984

(OVER)

DOE/PC/50003-38

EVALUATION OF THE EFFECT OF SOLVENT MODIFICATION AND COAL PRETREATMENT AND BENEFICIATION ON LIQUEFACTION

DOE