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Cooperative Research in Coal Liquefaction

**Final Report on DOE Contract
No. DE-FC22-90PC90029
Period: May 1, 1992 to April 30, 1993**

Submitted to the
U.S. Department of Energy

On Behalf of the
Consortium for Fossil Fuel Liquefaction Science

**University of Kentucky
University of Pittsburgh
University of Utah
West Virginia University
Auburn University**

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Edited by

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**Submitted by the University of Kentucky
On Behalf of the
Consortium for Fossil Fuel Liquefaction Science**

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ACQUISITION & ASSOCIATE DIV.

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SUMMARY

I. Iron-Based Catalysts for Coal Liquefaction

Research on sulfate and metal(Mo, Sn) promoted Fe_2O_3 catalysts^(1,2) in the current year focused on optimization of conditions. Parameters varied included temperature, solvent, solvent-to-coal ratio, and the effect of presulfiding versus in situ sulfiding. Oil yields were found to increase approximately proportionately with both temperature and solvent-to-coal ratio. The donor solvent, tetralin, proved to give better total conversion and oil yields than either 1-methylnaphthalene or Wilsonville recycle oil. However, the oil yield obtained using the Wilsonville recycle oil was almost as large as that using tetralin. In situ sulfiding gave higher yields than presulfiding the catalyst to pyrrhotite before liquefaction. Model compound reactions at relatively mild conditions(160-200 °C, 300-500 psig H_2) established that superacidity of anion-modified iron and tin oxide catalysts plays an important role in hydrocracking and alkylation of 1-phenyldecane.

A significant enhancement of both total liquefaction yields and oil yields from lignites and subbituminous coals has been achieved by incorporating iron into the coal matrix by cation exchange^(3,4). In this process, the iron enters the coal molecularly, replacing calcium cations bound to the oxygen anions in carboxyl groups. Mossbauer spectroscopy indicates a bimodal size distribution, with ~20-40% of the iron present in particles <25 Å in diameter, which may represent molecularly dispersed iron, and the balance contained in particles 50 to 100 Å in mean diameter. In recent experiments, it was shown that the cation-exchanged iron had significantly greater catalytic activity for liquefaction than the 30 Å Mach I catalyst.^(3,4)

A systematic study of the catalytic properties of the 30 Å iron oxyhydroxide (ferrihydrite) catalyst produced by Mach I, Inc. was carried out.⁽⁵⁾ Liquefaction studies of four coals were carried out and a number of model compound reactions were investigated. The coals investigated included Blind Canyon(DECS-6) and three Argonne premium coals, Illinois #6, Pocahontas #3, and Wyodak. For Blind Canyon coal, the effect of different solvents, catalyst loading, and the presence or absence of added sulfur were investigated. All four coals were liquefied at two temperatures both with and without the 30 Å catalyst plus added sulfur. All coals exhibited significant liquid yield improvements with the added catalyst, particularly Pocahontas #3, for which oil yields tripled, and total liquid yield more than doubled at 400 °C. The reduced catalyst, presumably to iron metal, showed much greater

activity for the hydrogenation of naphthalene than the sulfided catalyst. The activity decreased with reduction temperature, presumably due to catalyst sintering.

An aerosol reactor for the production of fine particle catalysts was constructed and tested. Mixtures of pyrite(PY) and pyrrhotite(PYH) were produced using a fuel injector to inject ferric acetate solution into a reaction chamber containing a nitrogen/hydrogen sulfide mixture at a pressure of 200 psig and temperature of 200 °C. In related work, PY/PYH catalysts were produced by hydrothermal disproportionation of ferric sulfide under a wide range of conditions. The aerosol product is a thin-shelled hollow sphere of catalyst made up of fine particles ~0.1 to several microns in diameter. These catalysts exhibited good catalytic activity in the liquefaction of Blind Canyon coal^(6,7) and in preliminary coliquefaction experiments on rubber tire tread material and coal.

A systematic investigation has been conducted of the synthesis of 5 - 20 nm diameter Fe-, Mo- and W-based particulate catalysts using a CO₂ laser pyrolysis technique. These catalysts include carbides (Fe₃C, Fe₇C₃, Mo₂C, W₂C), sulfides (Fe_{1-x}S), nitrides (Fe₃N, Fe₄N, Mo₂N, W₂N), oxides (Fe₃O₄, WO₃), and metals (α-Fe, γ-Fe). Commercial carbonyl compounds including Fe(CO)₅, W(CO)₆ and Mo(CO)₆ have been used as chemical precursors, and C₂H₄, H₂S, NH₃, and O₂ as reactant gases. The catalytic benefit of nanoscale Fe-carbide (Fe₇C₃) and Fe-sulfide (Fe_{1-x}S) catalysts produced by laser pyrolysis in the direct liquefaction of subbituminous coals has been investigated.^(8,9) The results have been compared to those determined for commercial Fe-oxide catalysts.

The CO₂ laser pyrolysis method has been extended to synthesize nanoscale carbon black particles, which might be used as catalysts or as a catalyst support for more expensive metals (e.g., Pt, Mo, etc) in coal liquefaction. These carbon particles are produced by pyrolyzing benzene (C₆H₆) with a small amount of Fe(CO)₅ as a catalyst. Furthermore, using our laser pyrolysis system, we have produced FeWO₄ by pyrolyzing a mixture of Fe(CO)₅, W(CO)₆, and O₂, which demonstrates for the first time that the CO₂ laser pyrolysis is also useful to produce stoichiometric, crystalline, and nanoscale *ternary* compounds. This is important since many mixed-valence ternary compounds (e.g. La_{2-x}Sr_xCuO₄) have been found to exhibit high catalytic activity.

The activity and selectivity of iron-based slurry-phase catalysts were investigated for the hydrogenation of pyrene and the hydrocracking of C-C bonds in several model compounds: 1-methylnaphthalene (1-MN), 2-hexylnaphthalene (2-HN), and 4-(1-naphthylmethyl-bibenzyl) (NMBB).⁽¹⁰⁾ Reactions were performed under typical coal liquefaction conditions. Higher reaction temperature and the presence of sulfur increased the hydrogenation of pyrene by the iron catalysts generated in situ. An in situ method of catalyst addition was most effective for pyrene hydrogenation for the iron catalysts, while molybdenum naphthenate showed increased activity with two-

stage processing. Both Fe and Mo catalysts showed low activity in reactions where the catalyst was generated ex situ. Combinations of Fe and Mo catalysts were synergistic for pyrene hydrogenation, although the amount of increase was dependent upon the particular iron precursor used. The Fe and Mo catalysts affected the hydrocracking of the three model species differently. Molybdenum naphthenate was more active for hydrocracking 2-HN and NMBB than any of the Fe catalysts but combining FeNaph with MoNaph was detrimental to the hydrocracking of these compounds. The selectivity of hydrocracking NMBB at specific bonding sites was affected by the presence and type of catalyst, presence of sulfur, and reaction time.

Water-soluble compounds containing molybdenum, tungsten, iron, cobalt and nickel were used as catalyst precursors for the catalytic hydroliquefaction of Blind Canyon coal in the absence of a solvent.⁽¹¹⁾ The coal was impregnated from solution, then vacuum dried at 55 °C and hydroliquefied in tubing bomb reactors at 400 °C, ~2,000 psi H₂. Tests of numerous iron and several nickel and molybdenum water-soluble catalyst precursors were completed using the same catalyst concentration (0.03 wt.%). Nickel hexahydrate and ammonium tetrathiomolybdate gave the best total liquid yields (~80%). While Mo gave the highest total liquid yield, the oil product was less volatile than that from Fe and Ni catalysts. This suggests that Mo is a good hydrogenation catalyst, but that Fe and Ni are better choices for hydrocracking of primary coal liquid products.

A number of methods of characterizing both the size and structure of iron-based catalysts have been fully developed.⁽¹²⁻¹⁸⁾ A new method of analyzing low temperature superparamagnetic Mossbauer relaxation spectra has been developed that provides a novel approach to determining the size distribution of ferric oxide and oxyhydroxide catalysts.⁽¹²⁾ For catalyst particles only a few nanometers in diameter, the recoilless fraction of the ⁵⁷Fe nuclei is markedly decreased by particle recoil on gamma ray absorption and by thermal agitation of the particles.⁽¹³⁾ X-ray absorption fine structure (XAFS) spectroscopy provides information both on the electronic state and radial distribution of ultrafine particles.^(14,18) Excellent TEM capabilities have been developed for direct measurement of size distributions and structure determination through electron microdiffraction.^(15,18) Electron probe microanalysis has been used to study the dispersion of iron, molybdenum and nickel in chemically impregnated coals and hydrotreated coals.⁽¹⁶⁾ Iron was found to be more uniformly dispersed through the coal particles after hydrotreatment than either molybdenum or nickel. XAFS spectroscopy has established that the surface iron atoms of ultrafine ferrihydrite catalysts are coordinate unsaturated sites.⁽¹⁴⁾ The tendency of these particles to agglomerate and transform to large particle hematite is dramatically increased by the chemisorption of water, as shown directly by TEM measurements of particle size distributions and structure.⁽¹⁵⁾ Magnetization measurements from 5 K to 300 K in zero-field-cooled and field-cooled cases are used to determine the region of superparamagnetism for nanoscale iron oxide and oxyhydroxide particles, followed by magnetization measurements up to 55kOe in the superparamagnetic state to

determine the particle size distribution.⁽¹⁷⁾ The use of all these methods, as well as more standard techniques such X-ray diffraction line broadening, has been compared in a comprehensive article summarizing a wide range of characterization studies for most the classes of iron-based catalysts under investigation in the Consortium.⁽¹⁸⁾

XAFS spectroscopy, transmission electron microscopy(TEM), and Mossbauer spectroscopy were to determine the structure of a 30 Å iron oxide catalyst manufactured by Mach I. It was found to have the ferrihydrite structure with coordinate unsaturated sites (CUS) at the particle surface.⁽¹⁴⁾ Chemisorbed moisture at these sites drastically increases agglomeration and transformation to large particle hematite at elevated temperatures.⁽¹⁵⁾ New ultrafine (~3-10 nm) binary ferrihydrite catalysts containing Si and Al have been synthesized using simple precipitation methods.⁽¹⁹⁾ The Si is believed to occur as SiO₄ at the particle surfaces.

II. Novel Coal Liquefaction Concepts

A unique coal liquefaction reactor system has been developed.⁽²⁰⁾ The jet loop reactor system permits better control of free radical generation/reaction and offers higher mass transfer rates than conventional reactors. It is now being used for the coprocessing of coal with waste oil.⁽²¹⁾ Improvements in conversion and selectivity are observed, relative to conventional reactors. The reactor provides a vehicle for evaluating coal slurries, coprocessing materials, and catalyst activity.

An investigation has been conducted of the comparative activity of soluble iron catalysts to that of solid iron catalysts in the multi-step Shabtai liquefaction procedure.⁽²²⁾ It was concluded that Fe₂O₃/SO₄ exhibited comparable activity to aqua complexes of salts such as Fe₂(SO₄)₃(H₂O)₅ and FeCl₃(H₂O)₆. Such solid nanoscale iron-based catalysts could therefore replace the soluble salts in the HT-BCD step of the treatment.

A high pressure(5-500 psig) multipurpose bioreactor was constructed and tested. A study with *D. desulfuricans* under normal and high pressure H₂ showed complete(~100%) reduction of fumarate within 24 hours.⁽²³⁾ Mossbauer spectroscopy verified the formation of ultrafine FeOOH from pyrite in coal by treatment with *Acidianus brierleyi*. The liquefaction yield was increased by this treatment by 14%.

A novel continuous-flow semi-batch liquefaction reactor has been designed and successfully tested. The advantage of this reactor over a batch liquefaction reactor is that light liquefaction products produced in the former can be removed by the flowing H₂, preventing further cracking or condensation reactions.

III. Fundamental Studies in Coal Liquefaction

A rapid HPLC method has been developed for separating the oil fraction of coal-derived liquids into aliphatic, aromatic and polar molecules.⁽²⁴⁾ Product concentrations are determined with an evaporative light scattering detector. Product fractions have been collected and concentrated for further analysis using GC/MS and SFC/MS methods.

Systematic procedures were developed for optimal waste management systems for coal liquefaction processes.⁽²⁵⁾ These procedures were used to identify cost effective solutions for two major environmental problems associated with coal liquefaction; desulfurization of gaseous emissions and dephenolization of aqueous wastes. The most cost-effective methods identified are desulfurization by hot potassium carbonate and a membrane-hybrid system for dephenolization. These methods have cost advantages over competing options that range from factors of ~ 3 to 10. The major source of CO₂ in a coal liquefaction plant is the Claus unit which converts H₂S to elemental sulfur. It is found that the cost of reducing CO₂ emissions to 500 ppm is almost negligible (~\$0.1 - 0.2/bbl), but the cost of achieving emissions limits ~10ppm is prohibitive (~\$10 - 15/bbl).

The ¹³C NMR research program of the CFFLS has focused in the current year on the development of two dimensional(2D) methods.^(26,27) Equipment has been constructed to perform a new class of experiments, referred as magic angle turning(MAT), involving very slow spinning at the magic angle. With the MAT experiment, the average or isotropic chemical shifts are obtained in one dimension and the separated powder patterns are found in the second dimension. This greatly increases the number of tensor components that can be extracted from the spectrum, thereby increasing the complexity of the samples that can be studied. This method has been applied to the Argonne premium coals with excellent results. In future work, it will be applied to polymeric waste material and to the products of coliquefaction of coal with such waste material.

In situ ESR studies have demonstrated a clear relationship between the addition of nanoscale iron-based catalysts and the free radical density.⁽²⁸⁾ Hydrocracking activity is evident from the formation of more free radicals at lower temperatures in the presence of such catalysts at temperatures up to ~400 °C in hydrogen. New experimental capabilities that have been developed and are now starting to be explored are the capability of high pressure, high temperature, in situ ESR, and the ability to add a catalyst, solvent or other reactant in situ during the ESR measurement.

An investigation of the catalytic dehydrogenation(CD) of coal and recycle solvents is being conducted to achieve insights into the chemistry of direct coal liquefaction(DCL) and to see whether CD can be used as a method for assessing the

activity of DCL catalysts.⁽²⁹⁾ Hydrogen transfer ability of different solvents by catalytic reaction with a hydrogen acceptor such as stilbene. Pyrrhotite was observed to be about six times less active than MoS₂ for catalytic dehydrogenation of 9,10-dihydroanthracene. This is approximately the ratio of the activities of these phases for DCL.

The development and testing of the high pressure TG/GC/MS system has been completed and several studies have been performed on coals, model polymers and waste polymers at hydrogen pressures up to 900 psi and with various catalysts provided by several Consortium members (viz. Professors Anderson, Shabtai and Wender).^(30,31) These experiments are starting to provide a wealth of new information on the mechanisms of heterogeneous catalysis, e.g., with regard to the role of radical vs. carbonium ion chemistry in hydropyrolysis or hydrogenolysis reactions and on the effect of hydrogen pressure and specific catalysts on hydrogasification (hydrogenation) reactions. The construction and testing of a microscale high pressure flow-through reactor coupled to a GC/MS system has been completed and the first on-line analyses of coal conversion products in a variety of different solvent environments at pressures up to 700 psi have been performed.

Molecular orbital calculations have been used to study the adsorption of toluene and 1-methylnaphthalene at various sites on FeS and related defect clusters and to calculate bond-breaking energies of the aromatic-aliphatic linkage.⁽³²⁾ As a preliminary explanation of the catalytic activity of FeS, it is proposed that the donation of electrons to the iron surface by the adsorbate leads to a decrease in the bond breaking energies relative to the gas phase.

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Task I

Iron-based Catalysts for Coal Liquefaction

Program Coordinators: Irving Wender and Gerald P. Huffman

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TASK I

Project I.1

SULFATE-PROMOTED METAL OXIDES AS DIRECT COAL LIQUEFACTION CATALYSTS

**Irving Wender, John W. Tierney, G.D. Holder
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Introduction

We have previously reported on the synthesis and characterization of a number of novel anion-modified sulfated and molybdated oxides and oxyhydroxides of iron (M_xO_y/SO_4 and M_xO_y/MoO_4)^{1,2,3}. These proved to be excellent catalysts for direct liquefaction of coal and coal-oil coprocessing reactions. Studies of these catalysts after reaction showed that the anionic modification of these iron oxide catalysts prevented their sintering at the high temperatures employed in coal liquefaction. When used in less than 0.5 -1.0 wt% Fe relative to coal and in the presence of a sulfur source, these catalyst precursors are effective for converting coal or coal-oil mixtures into light oils. In the past year, we have carried out several direct coal liquefaction experiments using Fe_2O_3 promoted by either sulfate, molybdate or tungstate anions and $Mo/Fe_2O_3/SO_4$ catalysts. We studied the effect of various reaction parameters on the total conversion and selectivity to oils. These included the effects of reaction temperature, reactor configuration, nature of the solvent, solvent-to-coal ratio and amount of sulfur added to the reaction mixture. We also presulfided some of the catalyst precursors and measured conversions in order to evaluate the possibility of catalyst reuse. Finally, we employed model compounds with anion modified metal oxides to improve our understanding of catalytic reaction pathways in direct coal liquefaction.

Experimental

All the direct coal liquefaction experiments were carried out using either a 27 cc horizontally shaken microreactor ('tubing bomb') or a 300 cc stirred autoclave

reactor. Temperatures of 375-425°C were used for coal liquefaction experiments with 800-1000 psig (cold) H₂ pressure. The normal reaction time was 60 minutes; reaction times between 5-120 minutes had been used for kinetic modelling. Coals used were obtained from the Argonne Premium Coal Sample Bank and from the Penn State Coal Sample Bank. Between 0.5-1.0 wt% of the anion-modified metal oxide catalysts (preheated to 450°C for 30 minutes before reaction) relative to coal were used in catalytic runs. Model compound reactions were all carried out in either the microreactor or in a 50 cc well-stirred microautoclave reactor.

Results and Discussion

Effects of Variation of Reaction Parameters on Total Conversion and Conversion to Oils

(i) *Effect of reaction temperature* : Three iron-based catalysts (Fe₂O₃, Fe₂O₃/SO₄, and Mo/Fe₂O₃/SO₄, all with added sulfur) were used for the direct liquefaction of Wyodak coal (0.17 % pyrite) at three different temperatures (375, 400 and 425°C) to determine the effect of reaction temperatures on the activities of these catalysts for coal conversion. As shown in Figure 1, the activities of the sulfated catalysts for the production of oils (n-pentane solubles) from coal increased proportionately in going from 375 to 425°C. Sulfated catalysts gave higher conversion and higher yields to oils than unsulfated iron oxide. Fifty ppm of Mo relative to coal, present in the Mo/Fe₂O₃/SO₄ catalyst, also had a significant effect on oil yields at 375°C.

(ii) *Effect of reactor configuration*: An important difference between the two reactor systems employed (the 27 cc microreactor and the 300 cc stirred autoclave) is the time required for heat-up and cooling. It takes about 35 minutes for the 300 cc autoclave to reach the reaction temperature (400°C and higher) and about 20 minutes to cool down to below 100°C after reaction. The microreactor can be heated up to reaction temperature in less than 5 minutes using a fluidized sand bath and cooled down immediately after reaction by quenching in cold water. Mass transfer effects may be different as the mixing phenomena are different in both systems. The results of the direct liquefaction of Argonne subbituminous Wyodak coal with tetralin (4:1 by weight to coal) as reaction solvent, and sulfated iron/tin oxide catalysts, using both the reactor systems, are shown in Figure 2. Both conversion and oil yields differ

by at most 6% and provide comparable results. The presence of excess amounts of donor solvent (tetralin), which provides a good dispersion medium for mixing and helps to maintain a H₂ rich atmosphere, may be responsible for the similar results observed from the two reactor configurations.

(iii) *Effect of solvent vehicle used and solvent-to-coal ratio:* Three solvents with different donor properties were used with sulfated iron oxide catalysts for direct liquefaction of Argonne Illinois No. 6 coal: Wilsonville recycle oil (V-1074), tetralin and 1-methylnaphthalene. The results are shown in Figure 3, from which it is evident that use of tetralin as the donor solvent gave the highest coal conversion and selectivity to oils. We believe that, in the presence of 1-methylnaphthalene, a non-donor solvent, the transformation of the initially added sulfated iron oxide precursor into its active catalytic form, pyrrhotite, is relatively slow. The effects of solvent-to-coal ratios on the conversion levels using sulfated iron oxide catalyst are shown in Figure 4. Conversion levels decrease with decreasing solvent-to-coal ratios. Since tetralin is a low-boiling solvent, much of it is in the vapor phase thus reducing the amount of liquid phase. Use of larger amounts of tetralin would hence provide a better dispersion and donor concentration in the liquid phase.

(iv) *Effect of amount of sulfur added to the reactor:* Sulfur is initially added to the reaction mixture; upon heating, the catalyst is transformed *in situ* to finely dispersed pyrrhotites (Fe_{1-x}S). The transformation may occur in the following way, where [Fe-O-S-H] is a transient

intermediate whose composition depends upon the reaction conditions. In the absence of sulfur, the coal conversions were slightly higher (5-6 wt%) than those obtained with a thermal blank run. When sulfur is added to the reactor to aid the *in situ* sulfidation of added catalysts, conversion levels increased by about 7-8 wt%. Sulfated iron oxide catalysts appear to perform more effectively with added sulfur.

(v) *Effect of presulfidation of the catalysts on coal conversion:* Presulfidation reactions were carried out at 400°C for 30 minutes in stirred autoclaves using tetralin as the reaction medium. A hydrogen donor is needed for rapid and complete catalyst transformation and the presence of carbonaceous material (from tetralin) on the

catalyst surface helps to maintain catalyst dispersion, mainly by inhibiting agglomeration⁴. The resulting iron catalyst was analyzed by X-ray diffraction, electron microscopy, and elemental analysis and was found to be primarily Fe_7S_8 ($\text{Fe}/\text{S} = 0.88$) with about 2 wt% of carbon deposited on its surface. This presulfided catalyst was then employed for the direct liquefaction of a low-pyrite Blind Canyon (DECS-17) coal, both with and without added sulfur. As shown in Figure 5, Fe_7S_8 gives conversions slightly better than those obtained with a thermal (only sulfur) blank run. Addition of elemental sulfur to the already presulfided catalyst improves its activity for coal liquefaction; it is about as active as the starting sulfated iron oxide with added sulfur. There seems to be no apparent advantage in presulfiding the catalyst. We believe that, not only pyrrhotites, but rather a combination of pyrrhotites and hydrogen sulfide is catalytically active for direct coal liquefaction.

Reactions with Model Compounds

To further understand the role of these catalysts in coal liquefaction, model compounds were used with these superacid anion-modified metal oxide catalysts at mild conditions to investigate the effect of superacidity of these catalysts during coal liquefaction. These reactions could provide an insight into acid-catalyzed reactions which may occur during the heat-up time involved in direct coal liquefaction. First, we used 5-benzyloxyindole as a model compound and reactions were conducted at temperatures of 250, 300 and 350°C with 1000 psig (cold) initial H_2 pressure. As expected, we observed cleavage of the C-O bond in 5-benzyloxyindole to form toluene in all the three reactions. But the GC-MS analysis of the pentane soluble products indicated no product other than toluene. This is probably because, after cleavage of the C-O bond in 5-benzyloxyindole, the remaining radical rapidly polymerizes to form a heavy product which is insoluble in pentane.

1-Phenyldecane was used as the model compound in most of our later reactions. Temperatures of 160-200°C and H_2 pressures (cold) of 300-500 psig were used in these experiments. A $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$ (1 wt%) catalyst preheated to 450°C for 30 minutes was added with 1-phenyldecane and the reaction was carried out in a horizontally shaken microreactor. After reaction time of 1 hour, the products were identified in a GC-MS and were later quantified using a gas chromatograph.

Though the overall conversion was low (about 10%), we found significant amounts of products formed due to alkylation of the benzene ring in 1-phenyldecane. The products ranged from singly substituted aromatics such as toluene to highly substituted multi-branched alkylbenzenes. The thermal reaction of 1-phenyldecane under these conditions produced no appreciable conversion. We attributed the hydrocracked and alkylated products to the acidity of the catalyst along with some hydrogenation ability. To further understand the role of catalyst acidity in these reactions, we synthesized a bimetallic Fe-Sn catalyst ($\text{SnO}_2/\text{Fe}_2\text{O}_3/\text{SO}_4$ containing equimolar amounts of SnO_2 and Fe_2O_3). This catalyst was earlier shown to have the highest acidity among all iron-based catalysts synthesized by our group⁵. This gave a slightly higher conversion of 1-phenyldecane than the Mo-Fe catalyst but the amount of alkylaromatics present in the products are yet to be analyzed. Preliminary experiments employing phenol and dodecane as the starting compounds with these catalysts gave products, a significant portion of which were alkylated phenols. Evidently, the superacidity of these catalysts is effective in alkylating aromatics whether or not a straight chain paraffin is attached to the aromatic ring. We plan to further investigate the role of catalyst acidity by using multiring compounds (with and without added sulfur) and then testing its effect on coal.

Major Findings

1. In the presence of sulfated iron-oxide catalysts and elemental sulfur, the coal conversion and the oil yields increased almost proportionately with increase in reaction temperature from 375°C to 425°C.
2. Tetralin proved to be a better coal liquefaction solvent than Wilsonville recycle oil (V-1074) or 1-methylnaphthalene in terms of both overall conversion and selectivity to oils. However, the amount of n-pentane soluble products (oils) obtained from the Wilsonville recycle oil and tetralin were almost the same.
3. As expected, the coal conversions and oil yields increased with increasing solvent-to-coal ratios. But the increase in conversions were less significant at high solvent-to-coal ratios.
4. Addition of increasing amounts of sulfur to the sulfated iron oxide catalysts during coal liquefaction runs increased the conversion and selectivity to oils.

Addition of more sulfur favors the *in situ* sulfidation of the sulfated iron oxide catalysts to form pyrrhotite, which is the active form of the catalyst.

5. Presulfiding the catalysts using tetralin as solvent in coal liquefaction did not show an apparent advantage, as the conversions and oil yields were almost the same as those obtained using sulfated iron oxide catalyst precursors.

6. Model compound reactions at relatively mild conditions (160-200°C, 300-500 psig H₂) showed that the superacidity of these anion-modified iron and tin oxide catalysts plays an important role in hydrocracking and alkylation of 1-phenyldecane.

Future Work

We plan to investigate the anion-modified metal oxide catalysts in order to understand the acid-catalyzed reactions which occur at mild conditions using different model compounds. The next step is to introduce sulfur (both in organic as well as inorganic forms) into the model compound reaction systems and study the effect of sulfur on the quality of the products. The eventual objective of this investigation is to understand the effect of superacidity of these catalysts in direct coal liquefaction.

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(Run Nos. KM-9, 4, 14, KM24, 19, 29, and KM39, 34, 44)

Figure 1 Effect of Reaction Temperature on the Activities of Sulfated Iron Oxides for Hydroliquefaction of Argonne Wyodak Coal at 1000 psig H₂, 1 hr Reaction Time.

(Run Nos. MR02, KM9, KM24, KM39, and A062-A066)

Figure 2 The Effect of Reactor Configuration on the Conversion Levels using Argonne Wyodak coal and Tetralin, with Sulfated Iron Oxide Catalysts at 400°C and 1000 psig (cold) H₂, 1 hr Reaction.

(Run Nos. A012, A059, and A060)

Figure 3 The Effect of Vehicle on Conversion Levels of Argonne Illinois No. 6 Coal using Sulfated Catalysts at 400°C, 1000 psig (cold) H₂, 1 hr Reaction.

(Run Nos. A012 and A056-A058)

Figure 4 The Effect of Solvent-to-Coal Ratios on Conversion Levels of Argonne Illinois No. 6 Coal using Sulfated Iron Oxide Catalysts at 400°C, 1000 psig (cold) H₂, 1 hr Reaction.

(Run Nos. A084-092)

Figure 5 Activities of the Fe₇S₈ Catalysts, Preformed by Sulfidation of Catalyst II, and of the Spent Sulfated Iron Oxide Catalyst for Hydroliquefaction of DECS-17 Coal at 400°C and 1000 psig H₂.

TASK I

Project I.2

LOW TEMPERATURE DEPOLYMERIZATION AND LIQUEFACTION OF PREMIUM COAL SAMPLES

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The main lines of research during the May 1992 - April 1993 period were as follows:

1. Hydrogenolytic activity studies of soluble vs solid Fe-based catalysts using coal-simulating compounds as feeds.
2. Comparative hydrogenolytic activity studies of soluble vs solid Fe-based catalysts as related to coal liquefaction efficiency in the HT-BCD depolymerization procedure.
3. Preliminary studies on the depolymerization and co-processing of waste polymers.

Following is a short description of results obtained in the above studies.

I.1.1. Hydrogenolytic Activity Studies of Soluble and Solid Fe-Containing Acid Catalysts using Coal-Simulating Model Compounds.

A comparative activity study of soluble vs solid Fe-containing acid catalysts for hydrogenolysis of coal-simulating model compounds, i.e., 2-isopropylnaphthalene (IPN), 1,2-dinaphthylethane (DNE) and diphenylmethane (DPM), was performed. The soluble catalysts were supported on inert SiO_2 and included aqua complexes of various salts, i.e., sulfate, acetate and chloride. The solid catalysts consisted of finely dispersed superacids, i.e., $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{ZrO}_2/\text{SO}_4^{2-}$. The activity of the soluble catalysts is ascribed to the aqua complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, which is pre-formed or formed *in situ* in the presence of water, and

could act as a protonic acid by ligand dissociation.

Table I.1.1 summarizes the values of the pseudo-first-order kinetic rate constants (k_1) for hydrodealkylation of 2-isopropylnaphthalene, IPN, to yield naphthalene and propane (see Figure I.1.1), as a function of catalyst type. Table I.1.1 also provides the values of the rate constants (k_2) for the competing ring hydrogenation of IPN to yield 2-isopropyl-1,2,3,4-tetrahydronaphthalene. Kinetic runs were performed at two different temperatures, i.e., 350 and 400°C. The k_1 values obtained were taken as a measure of the hydrogenolytic activity of the catalysts.

As seen, at 350°C the solid superacid catalysts 4 and 5 showed markedly higher activity for hydrogenolysis of IPN than the supported soluble catalysts 1 and 2. The difference in activity becomes larger with increase in reaction temperature from 350 to 400°C. The supported anhydrous $\text{Fe}(\text{CH}_3\text{COO})_3$ catalyst showed the lowest activity among the soluble Fe salt catalysts. Addition of a small amount of water to this catalyst (see footnote d, Table I.1.1) prior to reaction, resulted in some hydrogenolysis activity, which, however was lower than that of catalysts 1 and 2 that contain the pre-formed aqua complex $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. The latter has been previously indicated²³ as the precursor of active, protonic acid-generating species, e.g., $\text{H}^+[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^-$. The relatively low activity of catalyst 3, even in the presence of water, indicated that it is preferable to use pre-formed aqua complexes of Fe salts. The thermal stability of such catalysts between 250-400°C is presently being investigated in this laboratory. The very low values of the ring hydrogenation rate constants (k_2) with the supported soluble catalysts 1-3 indicated that the latter possess essentially no ring hydrogenation activity, viz., they act as selective, monofunctional hydrogenolysis catalysts. In contrast, the $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst 4 showed moderate ring hydrogenation activity, especially at

400°C ($k_2=0.30$). This would indicate that under reaction conditions (H_2 pressure; elevated temperature) the sulfated iron oxide may be converted to a bifunctional catalyst system containing not only a strongly acidic functional group, but also a moderately active ring hydrogenation co-catalytic component. This could explain the overall good efficiency of this catalyst under coal liquefaction conditions.

Parallel hydrogenolytic activity studies with diphenylmethane (DPM) as feed showed similar trends as those in Table I.1.1. However, the rate constants for hydrogenolytic cleavage of DPM (to yield benzene and toluene) were lower, due to the slower protonation rate of the monocyclic aromatic rings in DPM, as compared with that of the bicyclic arene system in IPN.

Another model reaction studied was hydrogenolysis of 1,2-dinaphthylethane, DNE (Figure. I.1.2, reaction a). This reaction is accompanied by competing thermolysis (Figure I.1.2, reaction b). The composition of products from this feed showed the simultaneous occurrence of the above two main competing reactions, i.e., normal protonic acid-catalyzed α -cleavage leading to naphthalene and ethylnaphthalene and thermal cleavage at the β -bibenzylic position, to yield methylnaphthalene. The bibenzylic position has a very low bond dissociation energy (<70 kcal/mol).

Table I.1.2 provides the kinetic data obtained for the hydrogenolysis of 1,2-dinaphthylethane. Hydrogenolytic α -cleavage rate constants, k_α , were calculated on the basis of the yield of naphthalene and ethylnaphthalene (plus dimethylnaphthalene isomers). Table I.1.2 includes also rate constants, k_β , for the thermal β -cleavage reaction which were calculated from the yield of methylnaphthalene. Kinetic runs were performed at 325 and 350°C. The k_α rate constants obtained at these two temperatures indicated basically similar

trends as those observed for hydrodealkylation of 2-isopropylnaphthalene at 350 and 400°C. Both at 325 and 350°C the solid superacid catalysts showed higher hydrogenolytic activities as compared with those of the supported soluble catalysts 1 and 2. At 325°C the activity of $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ was only moderately higher than that of the catalysts 1 and 2. However, the difference in activity of the two groups of catalysts increased markedly when the reaction temperature was elevated to 350°C. Differences in the k_β values for the thermal (noncatalytic) β -cleavage reaction were relatively small for all reaction runs at a given temperature. As expected, the k_β values were basically dependent only on the reaction temperature and the presence of a catalyst during the reaction had essentially no effect on the β -cleavage rate constants.

I.1.2. Comparative Hydrogenolytic Activity Studies of Soluble vs Solid Fe-Based Acid Catalysts as Related to Coal Liquefaction Efficiency.

The hydrogenolytic activity of the two types of catalysts, as reflected in their efficiency for coal depolymerization by the HT-BCD procedure, was also examined.

Table I.1.3 summarizes the total conversions of the Blind Canyon coal sample (DECS-17) into depolymerized, THF-soluble products obtained by HT-BCD treatment, using different acid catalysts in the HT reactor (a flow reactor system was used in this part of the study). As seen, using either the soluble aqua complexes of Fe salts (unsupported; impregnated in the coal) or solid superacids (in the form of fine dispersions with a mean diameter of approximately 130 Å; physical mixture with the coal) resulted in a very high level of depolymerization (92.4-94.5 wt.%, calculated on the (THF) pre-extracted DECS-17 coal sample; MAF basis). However, the impregnated aqua complexes can be applied as acid catalysts at a mild HT temperature (275-300°C) whereas the use of finely dispersed solid superacids in the HT treatment step requires temperatures of $\geq 340^\circ\text{C}$.

Table I.1.4 summarizes data on the distribution of the total HT-BCD products using various acid catalysts in the HT step of the coal depolymerization procedure. As seen, the yields of cyclohexane-solubles (oil fractions) using the impregnated aqua complexes as catalysts in the HT step are in the range of 63-69 wt %, whereas with the dispersed solid $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst the yield is somewhat lower (58.7 wt %).

The above described studies (Section I.1.1 and I.1.2) allow for the following conclusions:

Kinetic studies of acid-catalyzed hydrogenolysis of 2-isopropylnaphthalene, 1,2-dinaphthylethane and diphenylmethane show that (in the temperature range of 350-400°C) finely dispersed solid superacids, e.g., $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{ZrO}_2/\text{SO}_4^{2-}$, possess markedly higher hydrogenolytic activity as compared with that of soluble aqua complexes of Fe salts, e.g., Fe sulfate, chloride and acetate (supported on SiO_2).

In agreement with the above, it is found that finely dispersed solid superacids, in very low concentrations (0.1-0.5 wt.%), can be conveniently applied as hydrogenolysis catalysts in the HT step of the HT-BCD (mild hydrotreatment-base catalyzed hydrolysis) coal depolymerization process. The effective application of such superacid catalysts, e.g., $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, in this process, however, requires HT temperatures $\geq 340^\circ\text{C}$, which are considerably higher than those previously found as optimal for impregnated soluble Fe salts as hydrogenolysis catalysts (275-300°C).

I.1.4. Preliminary Studies on the Depolymerization and Co-Processing of Waste Polymers.

Preliminary experiments on co-processing of a HVB coal (DECS-17) with a rubber sample of the SBR type (and in parallel runs with a sample of polyethylene) were performed using (a) $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ as catalyst at 300°C and a H_2 pressure of 1500 psig, i.e., conditions similar to those usually employed in the HT step of the HT-BCD coal depolymerization

procedure; or (b) $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ as catalyst at 340°C and a H_2 pressure of 2600 psig. These runs were followed by the usual BCD treatment at 290°C (10% KOH in MeOH as catalyst-solvent system). In both two-step (HT-BCD) treatments the yield of THF-soluble products was nearly proportional to the amount of the coal (70%) in the coal-SBR mixture, indicating practically no reaction of the SBR feed component under the above relatively mild conditions. Similar results were obtained with polyethylene as polymer component of the feed.

To identify suitable catalyst and processing conditions for high-yield conversion of waste polymers into liquid products, experimental work is being initiated on the catalytic breakdown reactions of pure polymers of the following types: (a) polystyrene samples with well defined molecular weights in the range of 800 to 280,000; and (b) isotactic polypropylene.

The effect of various acid, base, and organometallic catalysts in a wide range of processing conditions will be determined.

Table I.1.1.
Kinetic Rate Constants for Hydrogenolysis (Hydrodealkylation) and
Ring Hydrogenation of 2-Isopropylnaphthalene (IPN) as a Function of
Catalyst Type^{a-d}

Catalyst		$k_1 \times 10^2$ (ml/g°min), <u>hydrodealkylation</u>		$66k_2 \times 10^2$ (ml/g°min), <u>ring hydrogenation</u>	
		350 C	400 C	350 C	400 C
FeCl ₃ .6H ₂ O/SiO ₂	(1)	3.9	31.5	0.2	0.7
Fe ₂ (SO ₄) ₃ .5H ₂ O/SiO ₂	(2)	2.4	10.6	0.4	1.3
Fe(CH ₃ COO) ₃ /SiO ₂ ^d	(3)	0.4	6.9	0.2	0.5
Fe ₂ O ₃ /SO ₄ ²⁻	(4)	6.2	99.2	4.2	30.0
ZrO ₂ /SO ₄ ²⁻	(5)	372.5	565.9	4.1	5.7

^a In each kinetic run was used 20 g (26.7 ml) of a 2.0% by weight solution of IPN in n-dodecane.

^b The amount of SiO₂-supported soluble catalysts 1, 2 and 3 used in each run was 4 g. The rate constants for these catalyst were calculated on a SiO₂-free basis. The amount of superacids 4 and 5 used in each run was 5000 ppm (0.5%).

^c Reaction conditions: H₂ pressure, 1500 psig; temperature, 350 or 400°C; microclave reactor volume, 50 ml; sampling time intervals, 5-10 min; total reaction time, 75 min.

^d A calculated amount of water, needed for *in situ* formation of the Fe(H₂O)₆³⁺ ion was added to this supported anhydrous salt, prior to reaction.

Table I.1.2
Kinetic Rate Constants for Hydrogenolysis of 1,2-dinaphthylethane as
a Function of Catalyst Type ^{a-c}

Catalyst		$k_{\alpha} \times 10^2$ (ml/g $^{\circ}$ min), hydrogenolysis (α -cleavage)		$k_{\beta} 10^4$ (min $^{-1}$), thermal cleavage (β -cleavage)	
		400 C	350 C	400 C	350 C
FeCl ₃ .6H ₂ O/SiO ₂	(1)	1.7	5.9	0.8	9.4
Fe ₂ (SO ₄) ₃ .5H ₂ O/SiO ₂	(2)	2.3	5.2	0.9	8.7
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Fe ₂ O ₃ /SO ₄ ²⁻	(3)	3.7	30.6	1.2	11.1
ZrO ₂ /SO ₄ ²⁻	(4)	37.4	89.9	1.1	9.8

^a In each kinetic run was used 25 g (28.8 ml) of a 2% by weight solution of DNE in toluene.

^b The amount of SiO₂-supported soluble catalysts 1 and 2 used in each run was 4 g. The rate constants for these catalysts were calculated on a SiO₂-free basis. The amount of superacids 4 and 5 used in each run was 5000 ppm (0.5%).

^c Reaction conditions: H₂ pressure, 1500 psig; temperatures, 325 and 350°C; microclave reactor volume, 50 ml; sampling time intervals, 5-10 min; total reaction time, 75 min.

Table I.1.3.
HT-BCD Treatment of Blind Canyon Coal (DECS-17) Using Different
Acid Catalysts in the HT Reactor^a

HT catalyst	Catalyst/feed ratio	HT temp., °C	Total HT-BCD conversion ^b
$\text{Fe}_2(\text{H}_2\text{O})_5(\text{SO}_4)_3$	1:9	300	92.7
$\text{Fe}(\text{H}_2\text{O})_6\text{Cl}_3$	1:9	300	94.1
$\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$	1:200	340	92.4
$\text{ZrO}_2/\text{SO}_4^{2-}$	1:200	340	94.5

^a In each run was used 10.0 g of coal-catalyst mixture. HT reaction conditions: H_2 pressure, 1500 psig; H_2 flow rate, 50 sccm; total reaction time, 2 h. BCD reaction conditions: catalyst-solvent system, 10% KOH solution in MeOH; temperature, 290°C; total reaction time, 1 h.

^b Total yield of THF solubles (MAF basis), calculated on the pre-extracted Blind Canyon coal feed. The total yield of THF pre-extracted was wt%.

Table I.1.4.
Effect of Different HT Step Catalysts on Product Distribution
of HT-BCD Treated Blind Canyon Coal (DECS-17)^a

HT catalyst	HT temp., C	<u>HT-BCD product distribution</u>	
		Oil fraction ^b , wt%	Oil fraction ^b , wt%
Fe ₂ (H ₂ O) ₅ (SO ₄) ₃	300	63.2	36.8
Fe(H ₂ O) ₆ Cl ₃	300	68.5	31.5
<hr/>			
Fe ₂ O ₃ /SO ₄ ²⁻	340	58.7	41.3
<p>^a In each run was used 10.0 g of coal-catalyst mixture, HT reaction conditions: H₂ pressure, 1500 psig; H₂ flow rate, 50 sccm; total reaction time, 2 h. BCD reaction conditions: catalyst-solvent system, 10% KOH solution in MeOH; temperature, 290°C; total reaction time, 1 h.</p> <p>^b Cyclohexane-solubles</p> <p>^c Cyclohexane-insolubles, THF-solubles.</p>

Figure I.1.1. Kinetic scheme of hydrodealkylation (k_1) and ring hydrogenation (k_2) of 2-isopropylnaphthalene (IPN).

Figure I.1.2. Kinetic scheme of competing (a) hydrogenolysis and (b) thermolysis reactions of 1,2-dinaphthylethane (DNE).

TASK I

Project I.3

GENERIC STRUCTURAL CHARACTERIZATION AND LIQUEFACTION RESEARCH

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Introduction

This project consists of both a structural characterization component and a component which deals with the synthesis, testing, and characterization of novel iron-based catalysts. Studies were also initiated near the end of the year of the coliquefaction of coal with plastics. These results of these various research components are summarized in sections I.3.1-I.3.4 below.

I.3.1 GENERIC STRUCTURAL CHARACTERIZATION RESEARCH

Excellent progress was made in developing accurate methods of characterizing the size and structure of iron-based catalysts. The methods used were Mossbauer spectroscopy, XAFS spectroscopy, and transmission electron microscopy. Most of the results have summarized in a number of recent and forthcoming publications,⁽¹⁻⁵⁾ and will not be repeated here. One of the current authors (Bhaswati Ganguly) completed her Ph.D. in physics in the current year; her thesis title was, "Mossbauer Studies of Iron-Based Ultrafine Coal Liquefaction Catalysts."

In addition to carrying out the basic research required to establish structural characterization methodology, we have also investigated numerous catalysts from other CFFLS groups and other groups involved in iron catalyst development in the DOE AR&TD program. These results have been reported directly to the investigators responsible for synthesizing the catalysts and some of them are discussed in other sections of this report.

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I.3.2 LIQUEFACTION OF LOW-RANK COAL CONTAINING CATION-EXCHANGED IRON

Introduction

Catalyst particle size has a strong effect on catalytic activity and selectivity during direct coal liquefaction. Fine particles are desirable because the majority of the atoms are coordinatively unsaturated and have a large percentage of surface sites that are readily accessible for chemisorption and catalysis. Ion-exchange procedure plays a very important role in many chemical processes, because of its simplicity, selectivity, and finally its wide scope. Ion-exchange in which an ion in coal such as calcium is replaced by a catalytic ion such as iron can yield an ultrafine particle size with an even distribution of catalytic ions. This constitutes a new class of catalyst stabilized in a state of high dispersion even at coal liquefaction conditions. The work during this period focused on investigation into the role of ion-exchanged iron during direct coal liquefaction (DCL) of two lignites and a subbituminous coal. The results indicate that iron ion-exchanged into the low-rank coals constitutes a catalyst in a state of dispersion ranging from molecular ions to particles a few nanometers in diameter^{1,2}.

Experimental

The coals used in this study are Beulah lignite (obtained from Department of Energy Coal Samples, DECS-11) and Hagel lignite (obtained from Penn. State Office of Coal, PSOC-1482) from the Fort Union region in North Dakota, and a subbituminous Black Thunder coal. The original iron contents of these coals are less than 0.5 percent. The coal samples were first ground to <200 mesh under a nitrogen atmosphere. The ion-exchange experiments were carried out in a 10 liter fermenter equipped with temperature and pH controllers. A freshly made 0.05M aqueous solution of ferric acetate was kept at a controlled pH of about 2.8 using sulfuric acid and a constant temperature of 333K. A slurry made from a 10:1 ratio by weight of dry coal to ferric acetate was stirred under a nitrogen atmosphere for 20 hrs. At the completion of the procedure, the ion-exchanged coals were repeatedly washed with

distilled water until the pH value of the filtrate for two consecutive washes was constant. The iron contents of the Beulah and Hagel lignites and Black Thunder coal after the ion-exchange process were 7.8%, 5.33%, and 3.8%, respectively. The efficiency of lower loadings of iron in the ion-exchanged coals during liquefaction was also investigated; samples of the same lignites were first demineralized in a manner similar to the procedure described by Bishop and Ward³ and then ion-exchanged to final iron contents of 0.93% for Beulah, and 0.88% for Hagel lignite.

Liquefaction Experiments

Two sets of coal liquefaction experiments were conducted. The first set of experiments was carried out with tubing bombs in a fluidized sand bath. This set of experiments was designed to investigate the effect of ion-exchanged iron catalysts on the total yield and product distribution in the liquefaction process. Control liquefaction experiments, using slurry mixtures of the same coal samples with a 30Å iron oxide (ferrihydrite) and with no catalyst, were run under the same conditions. The second set of experiments was designed to generate larger samples for the detailed characterization of the chemical structure and reactions of the added iron. The apparatus used to prepare the samples for these experiments was a one liter autoclave. This autoclave was connected at the top to a vessel for holding the sample prior to heating. At the bottom, four nitrogen-purged sampling lines were attached to the outlet valve of the autoclave to collect the liquefaction products directly from the autoclave without exposure to air. Liquefaction experiments were performed in the presence of excess tetralin and dimethyl disulfide (DMDS) as a sulfur donating species.

Mössbauer and XAFS Spectroscopy

Mössbauer spectra for the as-received, demineralized, and ion-exchanged coal samples were obtained using a conventional constant-acceleration-type Mössbauer spectrometer⁴. Calculation of the particle size distribution is described in detail elsewhere⁵. XAFS measurements were performed at beam line X-19A at the National Synchrotron Light Source in Brookhaven National Laboratory. Iron K-edge XAFS

spectra of the samples were obtained in transmission mode using a Si(111) double crystal monochromator.

Results and Discussion

The total conversion and product distribution of oils, asphaltenes, and preasphaltenes for Beulah, Hagel lignites, and Black Thunder coal from the tubing bomb liquefaction experiments at 673K for 60min are illustrated in Figure 1(a, b, and c). It can be seen that the asphaltene and oil conversion yields increased significantly for all ion-exchanged coals, with a sulfur donating species (DMDS) present. The preasphaltene yields, however, tend to decrease as a result of iron species incorporated into the coal. The variation in the product yields with the addition of a catalyst may be related to the conversion of preasphaltene and asphaltene as the reaction proceeds. It is evident from Figure 1 that the ion-exchanged iron is a more active catalyst than the 30Å ferrihydrite. Both the total conversion and the oil yield are substantially greater for the ion-exchanged iron than the 30Å catalyst at approximately the same concentrations. Elemental analyses of all three coals before and after the ion-exchange process indicate that the calcium content of these samples decreased by about 1.2% after treatment, while the concentration of other alkali and alkaline earth cations remains more or less constant. Thus, iron in ion-exchange process was exchanged primarily for calcium, yielded a highly dispersed catalytic iron species for coal liquefaction. Joseph et al.⁶ have shown that calcium decreases the conversion yields of coal during DCL.

Typical Mössbauer spectra of a coal containing cation-exchanged iron are shown in Figure 2. The spectra are fit with one or several magnetic components and quadrupole doublets (peak positions denoted by bar diagrams), and a superparamagnetic relaxation component (dashed curve). As discussed by Ganguly et al.⁵, at a given temperature, particles with diameter less than some critical value will give rise to a quadrupole doublet, particles with a diameter greater than some larger critical value will exhibit a six-peak magnetic hyperfine spectrum, and particles with diameters between these two values will give rise to superparamagnetic spectra. Approximate size distributions can be determined by

measuring the percentages of these three components as a function of temperature. A typical size distribution determined in this manner for the cation-exchanged Beulah lignite for two different iron contents is shown in Figure 3. It is seen that the size distribution is bimodal, with a significant fraction of the iron in particles finer than 30Å in diameter and highly dispersed particles in the 30-100Å size range. In addition, the size distribution patterns of the low-iron-content cation-exchanged coals indicate the formation of the fine (less than 30Å) iron-bearing fraction in larger relative amounts. These observations imply that there are two distinct forms of iron present in these samples. The iron in the finer particle size (less than 30Å) category may in fact be ferric iron that is molecularly dispersed and bonded to oxygen anions of the carboxyl groups in the coal, while particles in the 30-100Å size range result from hydrolysis and agglomeration of either iron acetate or ion-exchanged iron to form larger iron oxyhydroxide particles.

Both the x-ray absorption near edge structure (XANES) and the radial structure function (RSF) derived from the iron K-edge XAFS spectra of the cation-exchanged coals exhibit significant size related effects. Typical results are shown in Figure 4. The XANES of cation-exchanged coals (Hagel with 5.33% and 0.88% iron content) are compared to that of bulk iron oxyhydroxide (α -FeOOH) in Figure 4a, while the corresponding RSF are compared in Figure 4b. It is seen that the XANES of the cation-exchanged iron and goethite are quite similar, with the exception of an increase in the intensity of the small pre-edge peak. This occurs because a significant fraction of the iron atoms in the coals is no longer in centrosymmetric octahedral coordination, but in reduced coordination number sites, which causes the intensity of the pre-edge ($1s \rightarrow 3d$) transition to increase⁷. This is believed to be due to surface iron atoms in the goethite particles and/or to carboxyl-bound iron atoms. The RSFs of the cation-exchanged iron in coals and iron in goethite exhibit similar peaks, but the peaks corresponding to the iron shells are decreased in amplitude for the iron in the coal. During DCL most of the cation-exchanged iron reacts with H_2S/H_2 to form pyrrhotite. In most cases, however, a small iron oxide remnant remains.

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Figure 1. Comparison of liquefaction product yield for Beulah, Hagel lignites and Black Thunder coal.

Figure 2. Mössbauer spectra of iron ion-exchanged Beulah lignite at room temperature and at 12K.

Figure 3. Size distribution of iron ion-exchanged Beulah lignite with indicated iron percentages.

Figure 4. Comparison of (a) x-ray absorption near edge structure (XANES), and (b) radial structure function (RSF) of FeOOH and ion-exchanged Hegal lignite.

I.3.3 DEVELOPMENT OF BINARY FERRIHYDRITE CATALYSTS FOR DIRECT COAL LIQUEFACTION

Because of its unique small particle size and large surface area, the 30Å NANOCAT™ catalyst manufactured by Mach I, Inc. has attracted much attention among the researchers in the consortium. The work conducted by our group is summarized below:

1. Structure of the 30Å catalyst

The 30Å catalyst is actually ferrihydrite which is one of the eight major iron oxide/oxyhydroxide phases. The structure of ferrihydrite is still controversial. Using X-ray absorption fine structure (XAFS), we found that the structure is oxyhydroxide-like with iron octahedrally coordinated by oxygens and oxyhydroxy groups. Of more significance, a large percentage of surface iron ions are at coordinate unsaturated (CUS) sites with tetrahedral symmetry. Figure 1 shows the proposed structure.

2. Agglomeration and phase transition of the 30Å catalyst (ferrihydrite).

The iron oxide catalysts are in fact the catalyst precursor for coal liquefaction. Under reaction conditions, the catalyst may experience several stages of phase transformation before converting to Fe_{1-x}S phase. One major concern for the iron catalysts is whether they are able to maintain their dispersion under reaction conditions. At high temperature ferrihydrite decomposes to hematite. TEM micrographs show that the 30Å catalyst after annealing at temperatures between 250 - 350°C contains two phases, a hematite phase with large particle size ($d > 200\text{Å}$) and small, apparently unaltered 30Å particles. Substantially more and larger hematite particles are observed if the samples has been exposed to moisture in the air for several day prior to annealing [2]. The phenomenon can be interpreted on the basis of surface structure. Upon exposure to moisture, water molecules are chemisorbed at the catalyst surface and the small particles become linked by the chemisorbed water. At high temperature, these water molecules are detached from the particle joints, causing agglomeration of small particles and formation of $\alpha\text{-Fe}_2\text{O}_3$ phase with decreased surface area. Detailed papers have been prepared discussing both the structure [1] and the agglomeration and phase transition of the catalyst during

annealing.

3. Synthesis and characterization of the binary ferrihydrite catalysts

Since the CUS sites can adsorb water molecules, they may adsorb a second element (M) if it is present during precipitation, forming M-O-Fe species at the catalyst surface. With chemisorbed water molecules, the CUS sites become the crystal growth sites; but once the CUS sites are occupied by the second element, the crystal growth sites become blocked (Figure 2), and the catalyst may be able to maintain its dispersion at high temperatures.

We have succeeded in synthesizing a series of binary ferrihydrite catalysts by coprecipitating Al, Si, Zn, and Mo with ferric nitrate. The average particle sizes of the catalysts determined by TEM micrographs are 30 - 100Å. XRD, Mossbauer spectroscopy and XAFS results show that the catalysts are structurally identical to the 30Å catalyst. TEM micrographs of the catalysts show that the nanoscale particles are heavily aggregated, whereas the 30Å catalyst particles are well separated.

To examine the effect of the second component on catalyst agglomeration, the catalysts were annealed at 400°C for 5 hours in air, and the structure of the samples before and after annealing were examined by XRD. Figures 3 and 4 show the results for pure ferrihydrite, and the ferrihydrite catalysts with 5% Mo, 5% Si, and 50% Al.

Among the compounds used as second components for coprecipitation with ferric nitrate, SiO₂ is most effective in preventing catalyst agglomeration. With Si/Fe = 5%, no α -Fe₂O₃ phase was seen after annealing at 400°C for 5 hours in air (Figure 4).

With 5% of Mo, Al and Zn added to the ferric nitrate solution, crystalline α -Fe₂O₃ was observed after annealing. The particle sizes of the α -Fe₂O₃ phase estimated from the width of the XRD peaks are considerably smaller than that of pure ferrihydrite (30Å). No formation of α -Fe₂O₃ was seen with Al/Fe = 50%.

4. Coal liquefaction test results.

Preliminary direct coal liquefaction tests have been performed using a tubing bomb. The conditions and product analysis are shown in Table 1. The results show that the binary catalysts are as good as or better than the 30Å catalysts.

New tests with different experiment conditions and different catalyst composition are underway. A more complete summary of the results for the binary

ferrihydrite catalysts have been prepared for publication [4].

Publications

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3. J. Zhao, Z. Feng, F. E. Huggins, N. Shah, and G. P. Huffman, ACS, Fuel Chem. Div. Preprint, V38, 196 (1993)
4. Zhao, J., Feng, Z., Huggins, F. E., and Huffman, G. P., submitted to *Energy & Fuels*.

Table 1. Coal liquefaction experiment conditions and products analysis.

Coal: Blind Canyon (Decs-17)

Coal loading: 5 g

Tetralin/Coal = 2 : 1

Catalyst loading: Fe/Coal = 0.6%

S(DMDS)/Fe = 2 : 1

Reaction temp: 380°C

H₂ Pressure: 800 psi

Reaction time: 60 min

Liquefaction products analysis

Sample	Oil	Asphaltene	Preasphaltene	Gas	Total
30Å	18.7	42.9	9.0	2.4	73.0
ferrihydrite (M/Fe<0.01)	22.7	38.1	12.4	2.2	75.4
Si _{0.05} /ferrihydrite	23.8	40.6	7.6	2.3	74.3
Al _{0.5} /ferrihydrite	24.7	37.0	8.0	2.2	71.9

Figure 1. Proposed structural model for ferrihydrite (30Å catalyst).

Figure 2. Chemisorption at ferrihydrite surface.

Figure 3. XRD of the 30A and the binary ferrihydrite catalysts.

Figure 4. XRD of the binary catalysts after annealing.

I.3.4 COLIQUEFACTION OF COAL AND PLASTIC WASTES

Due to an ever increasing volume of plastic products, sanitary landfills can no longer continue to be the major means for plastic wastes disposal. In the United States, disposal of plastics comprises as much as 40% of the volume of landfills. Plastics recycling appears to be a possible alternative solution and has the potential for high growth. However, the recycling of plastics that takes place currently is not due to industry initiatives, but because of government edicts. In the United States, laws are in effect in states such as California, Oregon, and Wisconsin that require plastic bottles to be made of at least 25 wt% of recycled plastic. Similar laws in other states and federal laws are likely to follow.

In 1990, about 0.4 million tons of plastics in the form of soft drink bottles entered the municipal waste stream, of which 31.5% was recovered. However, out of seven million tons of total plastic wastes in the same year, only 3.7% was recycled. Conventional plastic recycling always faces the problem of contaminated and mixed plastic scrap, which cause difficulties in the recycling. Conventional pyrolysis, as an alternative for plastic waste recycling, usually results in unsaturated and unstable oils of low yield and low value that can be used only for combustion.

Considering current conditions and expected future trends, of all the options that exist for plastics recycling, liquefaction should be considered seriously. Liquefaction of plastic wastes can not only provide a solution for plastic disposal, but can also generate an environmentally acceptable transportation fuel.

Scientists from Consortium for Fossil Fuel Liquefaction Science (CFFLS) have initiated a broad range of studies on the feasibility of coliquefaction of plastic and rubber wastes with coal. To expedite these efforts, a bibliography has been completed and distributed to all interested CFFLS scientists to serve as a source of theoretical and practical references for many topics of interest. The listed information is based upon available data as of the end of January 1993, primarily from chemical and engineering databases. It contains an extensive array of general and technical data, condensed from about one thousand articles, that represent the most important and relevant guidelines. The references are listed in alphabetical order by title in two

parts, plastics and rubber. A key word classification is also included for further subdivision of topics. In addition, the abstracts of articles that are considered to be most relevant are enclosed.

In our preliminary experiments, liquefaction studies carried out on polyethylene and polyethylene terephthalate waste by one stage tubing bomb reactor in fluidized sand bath using two different catalysts. At temperatures range from 400°C to 450°C, residence times from 15 to 60 min., and a hydrogen pressure of 800 psi cold the effects of both catalysts on the depolymerization of plastic materials and on the oil yields were examined. Comparative experiments were performed for coliquefaction of mixture of a medium density polyethylene (PE) and Blind Canyon coal. Saturated oil, consisting of mainly straight chain alkanes and alkenes and some light hydrocarbon gases, was produced from liquefaction of both polyethylene, polyethylene terephthalate and the coal-polyethylene mixture. The residence time at which the reactions were completed is estimated to be 45 minutes in this experimental conditions. The results obtained summarized in Table I. Oil yields of 88 percent were obtained from liquefaction of polyethylene and 93 percent from liquefaction of polyethylene terephthalate during these experiments.

Table I. Experimental results obtained from liquefaction of plastics, and coliquefaction of plastic/coal mixtures.

Sample	Additives	Temperature(C)	Total Conv.%	Oil Conv.%
PET	HZSM-5	420	100	92
PE	HZSM-5	420	100	88
PET	HZSM-5	400	100	90
Milk jug	HZSM-5	420	100	86
Coke Bottles	HZSM-5	420	100	93
lignite:PE 1:3	Fe-exch.+DMDS	450	91	83
lignite:PE 1:2	Fe-exch.+DMDS	450	67	51
lignite:PE 1:1	Fe-exch.+DMDS	450	53	40
PE	Tetralin	450	100	33
BC Coal:PE 1:1	Tetralin	450	70	42
BC Coal:PE 1:1	30Å FeOOH+DMDS	450	48	26
PE	30Å FeOOH+DMDS	420	100	76

PE = polyethylene, PET = Polyethylene Terephthalate, DMDS = Dimethyl Disulfide
 BC = Blind Canyon coal, Fe-exch. = Iron ion-exchanged Beulah lignite

TASK I

Project I.4

METAL CATALYST DISPERSION AND COAL MODEL COMPOUND STUDIES

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Working in collaboration with Professor Larry L. Anderson, a microscopic investigation was carried out of the dispersion of iron and molybdenum catalysts in hydrotreated Blind Canyon, Wyodak and Pittsburgh #8 coals. Incipient wetness and ultrasonication were compared as the means of impregnating the coal particles before hydrotreatment. Dispersion of catalysts in the coal particles was determined before and after hydrotreatment by electron probe microanalysis (EPMA). In the case of demineralized Blind Canyon coal it was possible to quantitate the iron present in impregnated coal particles by using the mineral marcasite as the iron standard in the EPMA experiments. A concentration of approximately 0.14 wt% iron was found in the demineralized Blind Canyon coal after hydrotreatment.

Some of the results obtained in the catalytic hydrotreatment of demineralized Blind Canyon coal are shown in Table I.2.1. Demineralization was carried out under nitrogen using warm (about 60°C) solutions of concentrated hydrochloric acid followed by concentrated HF and then concentrated HCl. In the case of bimetallic catalysts impregnation was sequential from aqueous solutions first using ammonium tetrathiomolybdate followed by iron(III) chloride hexahydrate or nickel(II) nitrate hexahydrate. Samples were hydrotreated in a shaken tubing bomb reactor for one hour at 350°C and 2000 psig of H₂ (hot). Hydrotreated samples were then soxhlet extracted with tetrahydrofuran (THF) to determine amounts of solubles produced.

We found that bimetallic catalysts were more efficient than either metal alone in producing THF solubles. We also observed that even when loading with Fe/Ni promoters is substantially decreased, significant amounts of THF solubles are still found. In all cases the metals located on the outside of the coal particles before hydrotreatment were found (by EPMA) to have migrated to the interior of the particles during hydrotreatment. Iron was more uniformly dispersed through the interior of the coal particles after hydrotreatment than either Ni or Mo. These latter metals are observed (by EPMA) to clump somewhat inside the coal particles.

In a comparison of yields of THF solubles obtained from Blind Canyon, Wyodak and Pittsburgh #8 coals it was found that the best yield was obtained from the subbituminous Wyodak coal. A rationale for this result was proposed based on the correlation of coal rank and carbon content with the porosity of the coal structure.¹ These results were presented at the symposium on "Structure and Reactivity of Coals, Tar Sands and Oil Shale" at the San Francisco American Chemical Society meeting, April 5-10, 1992 and will be published in Fuel Processing Technology.²

Early in the contract year it was determined that hydrotreatment of a mixture of coal and waste rubber tires potentially has significant advantages over hydrotreatment of coal alone. The rationale for such a program has been described succinctly by Farcasiu.³ A number of waste rubber tires were collected and stored in our laboratory.

In order to obtain small rubber particles, to carry out rubber tire experiments, rubber samples were initially chopped by hand with razor blades to produce fine particles. We subsequently found that an SH-5 standard Dura-Cut (1/4 shank) carbide tipped bit from Ultra Tool International (Huntington Beach, California) in an electric hand drill produces fine rubber particles in shorter periods of time.

The ground rubber tire samples were placed in 1.4 cm I.D. glass tubes. The glass

tubes were then sealed and placed in a muffle furnace for 1 to 2 hours at 400°C. The tubes were then cooled and opened. Oils soluble in methylene chloride were extracted. Samples of the original tires, the oils produced and the residue were sent out for elemental analyses. The results are shown in Table I.2.2.

Oils extracted from the rubber tire samples were analyzed with a Nicolet FT-IR spectrometer. Infrared spectra for the oils indicated that the tires are very much alike in their functional group makeup. Oils extracted from samples made up of only sidewall material from the tires contain a weak stretch at 2300 wavenumbers which suggests the presence of either a $C \equiv C$ or a $C \equiv N$ stretch that is not seen for samples taken from the tread portion of the tire.

Proton NMR measurements (see Table I.2.3), made on a Varian XL-300 spectrometer, indicate that the tire oils extracted contain a higher percentage of aliphatic protons than of aromatic protons. No measurements were made on the sidewall samples. .

The glass tubes cannot withstand high gas pressures. A large percentage of the tubes ruptured during the heating process. Sample tubes also ruptured frequently after reaction when they were opened at room temperature spraying out sample. These high pressures are not observable with pure coal samples but are seen only upon the addition of rubber tire particles or waste polymers. This suggests that oils in the rubber tire are responsible for the gas produced. The glass tube experiments were eventually discontinued in favor of less convenient but safer experiments carried out in metal tubing bombs. The tubing bomb is mounted horizontally and shaken in a heated sand bath. In addition to greater safety, tubing bombs have the advantage of permitting the addition of hydrogen gas (that is not possible in our glass tube experiments.)

Samples of rubber tires and coal have been prepared with and without catalyst, hydrotreated and analyzed for THF soluble products. Amounts of each reactant have been

varied and two catalyst impregnation techniques have been implemented in seeking to maximize the recoverable THF soluble products from a combination of coal and waste rubber tire reactants. Each tubing bomb experiment was carried out at 1000 psi H₂ (cold) and 350° C for one hour. The results in Table I.2.4 show that the addition of ground rubber tires to coal enhances the amounts of THF solubles recovered compared to coal samples prepared with no waste rubber tire particles added. A further increase of THF soluble products is seen to arise from the addition of catalyst, particularly when using the incipient wetness technique to impregnate the sample with catalyst.

EPMA experiments are being carried out to determine what effect the rubber tire particles have on the dispersion of catalyst in the coal particles. At the request of M.M. Taghiei (University of Kentucky) we also did some EPMA experiments that demonstrated that an ion exchange process (iron substituting for calcium) can be used effectively to impregnate coal.

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Table I.2.1. Catalytic hydrotreatment of demineralized Blind Canyon coal			
		THF ^c	
Catalyst ^a	Impregnation ^b	Sol.	Insol.
0.05% Mo	U	40	52
0.05% Mo	I	42	52
1% Fe + 0.05% Mo	I	55	41
0.01% Fe + 0.05% Mo	I	50	43
1% Ni + 0.05% Mo	I	50	46
0.01% Ni + 0.05% Mo	I	52	45
^a Catalyst loadings are given in wt%. ^b Impregnation: U = ultrasound, I = incipient wetness. ^c Yields are given as % m.a.f. coal.			

Table I.2.2. Waste Rubber Tire Elemental Analyses ^a				
entry	tire	carbon%	hydrogen%	sulfur%
1	LRR	85.3	7.0	2.3
	oil	89.4	8.2	1.7
	residue	87.6	1.3	2.8
2	Michelin XA4	86.7	6.9	2.1
	oil	89.8	8.0	1.6
	residue	91.3	1.5	2.1
3	Radial 155SR12	86.3	7.2	2.2
	oil	-	-	-
	residue	89.0	1.4	2.6
4	Michelin XZX	87.2	6.9	2.2
	oil	88.4	9.9	1.3
	residue	89.4	0.9	2.7
5	EMPCO	87.4	6.7	1.7
	oil	89.0	9.1	1.2
	residue	89.6	0.9	2.4
6	B.F.Goodrich	76.6	6.6	1.7
	GT-200	88.5	10.0	1.1
	oil	75.2	0.9	2.6
7	LRR ^b	-	-	-
	oil	-	-	-
	residue	85.5	1.1	4.2

- a reaction conditions: 1 g of powdered tire in sealed glass tube, heated for two hours at 400°C, extracted with 25 ml of methylene chloride, solvent then removed with rotary evaporator.
- b 1 gram sample of powdered tire reacted with 1% by weight of ammonium tetrathiomolybdate.

Table I.2.3. Proton NMR Analyses^a of Waste Rubber Tire Samples

entry	tire	oil(mg)	aromatic/ aliphatic ^b	solid residue(mg)
1	LRR	244	30/70	460
2	Michelin XA4	275	36/64	466
3	Radial 155SR12	255	32/68	459
4	Michelin XZX	493	17/83	408
5	EMPCO	361	21/79	366
6	B.F. Goodrich GT-200	450	15/85	395
7 ^c	LRR	397	23/77	396

a reaction conditions: 1 g of powdered tire in sealed glass tube; heated for two hours at 400°C; extracted with 25 mL of methylene chloride; solvent then removed with rotary evaporator.

b relative NMR peak areas for aromatic and aliphatic protons in the oil

c sample included 1% by weight ammonium tetrathiomolybdate

Table I.2.4. Results of Reacting DECS-17 Coal with Waste Rubber Tires (WRT)

Coal %	WRT%	Catalyst	Yield of THF Solubles ^c
100	0	0	0.387 g
60	40	0	0.558 g
50	50	.01 g H ₂ O impreg. ^a	0.651 g
60	40	.01 g H ₂ O impreg. ^a	0.797 g
50	50	.01 g added dry ^a	0.551 g
60	40	.01 g H ₂ O impreg. ^b	0.602 g

^a Ammonium Tetrathiomolybdate

^b Wender's Sulfated Iron Oxide

^c Based on 1 gram of sample before hydrotreatment

TASK I

Project I.5

NOVEL TEST REACTORS FOR COAL LIQUEFACTION

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OBJECTIVE

The main objective of this project over the past year was the development and characterization of a semi-batch reactor with vapor flow-through and vertical agitation, and the use of this reactor to assess catalysts for coal liquefaction. Hydrogen was used as the vapor stream purge gas. An advantage of the continuous-flow semi-batch liquefaction reactor over a batch liquefaction reactor is that light liquefaction products produced in the former can be removed by the flowing H_2 from the reactor, thus preventing further cracking and condensation. The reactor is dynamically balanced so that vertical agitation at up to 500 rpm is possible. Temperatures up to 450°C are attainable by means of a fluidized, constant-temperature sand bath.

RESULTS

1. Initial Testing

The semi-batch liquefaction reactor system was initially built with some mechanical modifications such as the use of larger capacity mass flow meters and spring coil inlet/outlet tubing. Test runs were then carried out to study the effect of purge gas flow velocity. Ideally, the gas flow should sweep out light products of liquefaction but retain tetralin (the solvent) in the reactor. A mixture of tetralin (87 wt%) and iso-octane (13 wt%, b.p. = 100°C) was used to simulate the reactor contents during coal liquefaction. The test runs were made at 400°C, 1000 scc/min of nitrogen and hydrogen at 300 rpm (300 psig N_2 and 500 psig H_2 pressure, typical conditions for coal liquefaction). The results in Figure 1 show that most of the solvent is swept out of the reactor in 6 minutes (normal liquefaction runs take 30 to 60 minutes), indicating the solvent loss is far too severe. Tetralin, therefore, can not be retained

in the reactor during the entire liquefaction period. This problem resulted from the high reaction temperature and high gas velocity. Since high gas velocity is necessary for sweeping out the light products and the reaction temperature must be kept around 400°C, it was decided that a pre-reactor tetralin saturator was needed to compensate for the tetralin loss from the reactor.

2. Test of the Reactor with a Tetralin Saturator

A stainless steel saturator, with a volume of 230 ml, a jacket heater and an internal thermocouple was installed upstream of the preheater coil. A product- (and solvent-) trap of the same size as the saturator was installed downstream of the reactor. About 190 ml of tetralin was loaded into the saturator before the test runs. The test conditions were the same as those described earlier but the run time was kept to 30 minutes. The test results at a residence time (τ) of 0.9 min are shown in Figure 2. The objective of the test was to maintain 10 ml of tetralin in the reactor for the duration of the liquefaction run (30 min). As indicated by the data, this objective was not achieved. Although a large amount of tetralin passed through the reactor to the collector (162 g at the saturator temperature of 400°C), the amount retained in the reactor is small (1.4 g at the saturator temperature of 400°C). The small tetralin level in the reactor suggested that the feed H_2 from the saturator to the reactor was not fully saturated. It may also have resulted from the expansion of the reactor contents when the reactor temperature is suddenly increased, and the subsequent high linear velocity in the effluent. These combined effects entrained the tetralin out of the reactor. Therefore some modification of the reactor itself was necessary.

3. Test of the Reactor After Reactor Modification

The original coaxial inlet/outlet in the center of the reactor was replaced by a separate, small-diameter (1/4") inlet at one end and a larger-diameter (1/2") outlet at the center of the reactor (see Figure 3). Thus the minimal cross-sectional area for the outlet stream increased by greater than an order of magnitude, from 0.011 in² to 0.126 in². The linear velocity in the outlet tube, therefore, decreased to less than 9% of the original value. The test results shown in Figure 4 (the circles), together with the data in Figure 2 as a comparison, indicated that the objective of maintaining 10 ml tetralin in the reactor can be reached by adjusting the saturator

temperature to below 300°C. This also suggested that the tetralin entrainment occurs only in the reactor outlet tube, therefore an increase of the outlet tube diameter reduces the tetralin entrainment from the reactor. Since the vapor pressure of tetralin is small at temperatures below 300°C, the results also suggested that the use of the pre-saturator is not necessary for the modified reactor. Data shown in Figure 5, as circles, indicate that as long as the H₂ velocity is less than 780 scc/min ($\tau = 1.2$ min), the saturator is not needed and that 94% of the tetralin initially loaded can be retained in the reactor for a 30-minute experiment. However, for the H₂ flow of greater than 1000 scc/min loss of tetralin is significant.

In order to reduce H₂ residence time further, test runs were also made with the addition of stainless steel (SS) beads into the reactor to reduce the reactor volume. For the same H₂ velocity, the reduced reactor volume gives a shorter gas residence time while maintaining the lower linear velocity in the outlet tube, which in turn enhances the amount of tetralin retained in the reactor. Runs with addition of 149 and 187 g of SS beads showed (square and triangles in Figure 5, respectively) that a residence time as small as 0.5 minute can be reached at a H₂ flow rate of 1000 scc/min with only about 14% loss of tetralin after 30 minutes.

At this stage, the modified reactor system (Figure 6) is capable of handling high H₂ flow rates (1000 scc/min, for example) to give short gas residence times (0.5 min for 1000 scc/min gas flow, 400°C and 500 psig pressure) with minimal loss of tetralin. The results obtained in the semi-batch reactor, therefore, can be compared with those obtained from a batch reactor at the same reactor conditions. The study of the effect of gas flow on coal conversion, oil and gas yield now becomes possible.

4. Coal Liquefaction Experiments

Uncatalyzed coal liquefaction experiments were carried out using DECS-6 coal in the modified reactor. The reactor conditions are 400°C, 500 psig H₂ (hot), 1000-1240 scc H₂/min, 300 rpm agitation, and 30 minute reaction time. The coal-to-tetralin ratio was 4 g/7ml. The results for these tests are shown in Figure 7 and compared with the batch data obtained at the same conditions but with no H₂ flow. It is seen that the increase of H₂ flow decreases the total conversion of coal but does not alter the yield to oil and gas. In other words, fewer asphaltene are produced. The decrease in total conversion with the H₂ flow may be partially caused by the loss of tetralin. As discussed earlier, about 14% of the tetralin is swept out of

the reactor during a 30 minute run at these conditions. Prior results have shown that the effect of tetralin is mainly to increase the asphaltene yield for this coal under the same conditions. An additional reason for this finding may be due to a non-ideal flow pattern of hydrogen gas through the reactor. It was noted that upon completion of the reaction, the reactor region closest to the hydrogen gas inlet was dry of tetralin. Without the high concentration of hydrogen donor in this region, recombination reactions could be favored. Further work on the potential of non-ideal gas flow is on-going.

The insensitivity of the oil + gas yield to the H_2 flow is unexpected. If the main effect of the flowing H_2 is to eliminate retrogressive reactions of the light products, an increase in the oil+gas yield should be observed for the semi-batch operation. The results indicate that the reduction of the retrogressive reactions by the flowing H_2 is insignificant. However, it is also possible that the H_2 does not play a major role in the production of oils. Experiments made using N_2 instead of H_2 at the same conditions suggest that this hypothesis may be true (see Table 1), at least for uncatalyzed liquefaction at $400^\circ C$. Compared to the H_2 atmosphere, N_2 decreases the total conversion but the oil+gas yield remains relatively constant for both the batch and flow-through runs.

Table 1.
Effect of Gas Type on Coal Liquefaction
($400^\circ C$, 500 psig, 300 rpm, 30 min, coal/tetralin-4g/7ml)

flow, scc/min	0	0	996	996
Gas type	H_2	N_2	H_2	N_2
Conv., %	72	29	53	26
O+G, %	20	19	16	18

5. Gas Analysis

As shown in Figure 6, the reactor system has an on-line GC with a sampling valve. A small amount of the reactor effluent can be injected to the GC by switching the sampling valve. A chromatogram obtained at an analysis rate of 1 injection per minute is shown in

Figure 8. The reaction was quenched at 30 minutes but injections continued to show some products in the gas phase up to 15 minutes after reaction termination. The slight zigzag in peak height resulted from a slight volume difference between the two sample loops used for injection. By knowing the areas of the peaks, volume of the sample loops, pressure, temperature and the effluent flow rate, the total amount of gas produced can be determined. The chromatogram indicates that at 400°C most of the gas fraction of the products is produced during the early reaction period which may correspond to initial pyrolysis of the coal.

6. Residence Time Distribution Studies

Another useful and interesting aspect of this project was an attempt to obtain the residence time distribution (RTD) for the flow-through reactor. When applied to reaction conversion data, the RTD aids in the quantification of kinetic information. The ultimate purpose is to gain an insight into the actual flow patterns occurring in the reactor and into the kinetics of the liquefaction reaction. It is hoped that this will suggest means of improving the conversion to the desired products.

Experimental Procedure

A step change is introduced at the inlet of the system by switching the purge gas flow from hydrogen to helium, using a three-way valve. The response is measured separately at the inlet and the outlet of the reactor, so that the RTD for the reactor in isolation can be calculated. To measure and record the response with time, a thermal conductivity detector on a gas chromatograph is employed. Since the flow rate of the purge stream is much beyond

beyond the capacity of the GC, a gas sampling valve is incorporated in the line before the GC. This valve has two sample loops of equal volumes. By switching the valve position at equal intervals of time, a gas sample from an alternate loop is swept into the GC by the carrier gas. Thus the concentration of the outlet stream is sampled at regular intervals. The recording gives the concentration-time profile for the tracer (He), from which the so-called F curve and consequently the E curves (the RTD for the reactor) are determined.

Model Development

The reactor system is modeled as two units in series: an ideal plug-flow reactor (E_o) which is essentially a dead time and an ideal mixed reactor (E_{reactor}). The E curve, i.e., the RTD for the reactor, is calculated using the following relation for the scheme shown below.

Here $C_1 = C_{in} * E_o * E_{\text{reactor}}$ where '*' is the convolution integral:

$$C_{in} * E_o \triangleq \int_0^t C_{in}(t-t') E_o(t') dt'$$

This can be rearranged to give E_{reactor} as shown:

$$E_{\text{reactor}} = \frac{\frac{d}{dt} (F_1(t))}{F_o(t)} \quad \text{where, } F_o(t) = \frac{C_o(t)}{C_{in}(t)}, \quad F_1(t) = \frac{C_1(t)}{C_{in}(t)}$$

Here C_{in} represents the step change introduced, C_o and C_1 are measured at locations

immediately before and after the reactor respectively. Thus the reactor can be modelled as a two-parameter combination of ideal reactor behavior.

PLANNED FUTURE WORK

Thus far, preliminary RTD experiments indicate that the data are sufficiently accurate to obtain model parameters for the residence-time distribution model. In essence, this model accounts for nonidealities in the flow patterns of the reactor system. These nonidealities are superimposed on any actual kinetic data taken on this apparatus for actual liquefaction runs. Thus it is planned to sample the product gas in the outlet stream during the course of a liquefaction run, so as to obtain the time dependence of conversion to gaseous products. Using these data in conjunction with the RTD data, we will attempt to obtain the actual kinetics of the evolution of gas products in the liquefaction reaction.

400°C, 1000 cc/min of gas flow, 300 rpm

Solvent: 87% of tetralin and 13% of iso-octane

FIGURE 1. Results of solvent removal from the flow-through liquefaction reactor for a gas purge of 1000 scc/min at two different pressures with N₂ and H₂.

Reactor: 400°C, 500 psig, 1000 cc/min of H₂, 30 min
(Initial tetralin loading in reactor = 20 ml)

FIGURE 2. Results of solvent loss with tetralin-saturated H₂ gas purge.

FIGURE 3. Schematic representation of modified flow-through liquefaction reactor.

Reactor: 400°C, 500 psig, 1000 cc/min of H₂, 30 min

(Initial teralin loading in reactor = 20 ml)

Temperature of the Saturator [C]

FIGURE 4. Results of tests showing solvent-retention in the flow-through reactor before and after reactor modification.

FIGURE 5. Relationship of tetralin retention in the flow-through liquefaction reactor as a function of hydrogen gas velocity.

FIGURE 6. Schematic Diagram of Hydrogen-Purged, Semi-Batch Liquefaction Reactor

DECS-6, 400°C, 500 psig (hot), 300 rpm, 30 min
(coal=4 g, tetralin=7 ml)

FIGURE 7. Total conversion and oil-and-gas yield for coal liquefaction with and without hydrogen gas purge.

TASK I

Project I.6

FERRIC SULFIDE AS A PRECURSOR FOR COAL LIQUEFACTION CATALYSTS AND SURFACE STUDIES OF ACTIVITY AND SELECTIVITY

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OBJECTIVES

The major thrusts of the work during 1992-1993 were the construction and testing of the aerosol reactor and the development of the aerosol technique for making mixtures of pyrite (PY) and pyrrhotite (PH) using ferric sulfide precursor. Involved in the development work were the determination of the size and chemistry of the particles produced by the aerosol reactor, the determination of the factors which control particle size and chemistry, and the evaluation of some of the materials formed in the reactor for catalytic activity in coal liquefaction experiments. In related work, catalysts formed by hydrothermal disproportionation of ferric sulfide under a wide range of conditions had previously been characterized using surface and wet-chemical techniques. These results were assembled and compared with the activity of these catalysts to come up with an overall model for the processes going on during hydrothermal disproportionation under a wide range of conditions. Another significant thrust during this period was the surface characterization of catalysts prepared by other members of the consortium.

RESULTS

1. Reactor Construction. The reactor system for the production of microfine iron catalysts has been constructed. The system consists of four basic components: a pump, a fuel injector, the reactor body, and a scrubber. The relation between these four is shown in Figure 1.

The pump is driven by high-pressure air and is capable of pumping up to 1 ml of liquid per cycle at 8800 psi pressure. The cycle rate can be adjusted from 0.011 to 3.3 Hz. The fuel

injector has a pin pressure of 6000 psi. Details of the modifications of this component are given below. The reactor body is essentially a cylinder 1 m long and 250 mm in diameter. The reactor temperature can be raised to 250°C through external band heaters. A sealable flange joins the injector component to the reactor body and enables pressures of up to 300 psig to be maintained in the reactor. The scrubber removes all traces of objectionable species from the exit stream of the reactor before the stream is vented through the hood.

2. Test Runs. The results of our previous work have shown that ferric sulfide disproportionates to PH, PY and elemental sulfur at different ratios, depending upon the time, temperature and pressure of the disproportionation. Those experiments have been in hydrothermal-bomb reactors. One particular mixture, with a PH/PY ratio of 1, has been shown [1,2] to be an effective catalyst for coal liquefaction. This catalyst mixture has been obtained at disproportionation conditions of 200°C and 250 psia, well within the range of the aerosol reactor. Hence these conditions were used for the test runs.

Reactants used to make ferric sulfide for the hydrothermal-bomb reactor were ferric chloride and sodium sulfide. These could not be used in the aerosol reactor. Instead, ferric acetate and hydrogen sulfide were used as reactants in the aerosol reactor. (Using ferric acetate in the hydrothermal-bomb reactor does not result in a catalyst which is significantly different from one made with ferric chloride in the same reactor.) Ferric acetate was prepared by first making ferric hydroxide from ferric chloride and ammonium hydroxide. The precipitate was washed and rinsed with distilled-deionized water to remove the chloride salt and excess ammonium hydroxide. The ferric hydroxide precipitate was then stirred and heated with acetic acid. The experiments were carried out by pumping this solution through the injector into the aerosol reactor.

Before starting the pumping, the reactor was charged with 10 parts of nitrogen to one part of hydrogen sulfide at a pressure of 200 psig and heated to 200°C by the band heaters. During injection, the ferric acetate solution is converted to an aerosol with a droplet diameter of about 50 μ , as estimated from fuel-oil calculations. Ferric ions at the surface of the droplet react almost instantaneously with the hydrogen sulfide in the vapor phase, forming a crust of ferric sulfide on the surface of the droplet. Under the experimental conditions, the ferric sulfide is unstable, and disproportionates into PH and PY. Depending upon the system

pressure, water can be vaporized from the droplet, shrinking the diameter. Under the present conditions, the pressure is near the vapor pressure of water, so the evaporation of water is slowed. Thus the droplet configuration is maintained until all the ferric acetate in the droplet is reacted. The product is essentially a hollow sphere with a crust of PH and PY. This product settles to the bottom of the reactor, where it can be easily flushed out with water after the batch reaction is complete. The other products, acetic acid and steam, are vented from the reactor through a pressure-controlled check valve, and pass through the scrubber. Make-up gas for the reactor in the proper ratio is fed via mass-flow valves at the nitrogen and hydrogen sulfide sources.

In the early test runs, scanning electron microscopy (SEM) analysis of the products showed that many particles of relatively large size (greater than $20\text{ }\mu$) were present. These would correspond to aerosol droplet sizes much larger than $50\text{ }\mu$. Further, excess fluid was seen to be emitted from the leakoff port in the fuel injector, indicative of orifice plugging. In addition, the injector metals were heavily plated with iron sulfides during the reaction, and some pitting of injector parts was also noted. Between injections, the ferric acetate solution evaporated, and crystals of ferric sulfide that were formed prevented the tight re-seating of the injector pin. Hence, in addition to the $50\text{-}\mu$ droplets formed by the injector, large drops of solution escaped through the partially-opened orifice.

To avoid this problem, a new nozzle, constructed from 303 Stainless Steel (SS), was purchased. This is a hydraulic hollow-cone atomizer, not a fuel injector, so it has to be backed up by a pressure-check valve. The 303 SS is not reacted by the gases in the reactor during the batch run, and the system seems to be very effective in producing small particles.

3. Product Properties. Samples from the aerosol reactor with the new nozzle were collected and analyzed. SEM analysis shows that the particles are indeed spherical, as expected. They are also hollow. Some shells can be seen resulting from breakage of the hollow spheres. The diameter of the largest spheres is approximately $2\text{ }\mu$, but the surface of the spheres is composed of very fine crystals of size less than $0.1\text{ }\mu$. In addition, SEM indicates a significant quantity of spheres of overall diameter much smaller than $2\text{ }\mu$, which would result in a mean particle diameter of less than $1\text{ }\mu$. Some spheres have surfaces which appear to contain fissures, consistent with the escape of vapor during the shrinking process; other spheres seem

intact.

A second analysis of particle size was carried out using light scattering. A printout of the particle size distribution is reported in Table I. A normal distribution curve is obtained, with a mean diameter of 0.8 μ . This is consistent with the SEM analysis.

A helium pycnometer was used to determine the density of the spherical particles. Samples from several runs were separately examined. The density of every sample was significantly less than that of any known iron sulfide. The average value obtained was 3.78 g/ml, while typical bulk iron sulfides range in density from 4.5 to 5 g/ml. Further, the density of the particles was found to increase when samples were ground. These observations confirm that the particles are indeed hollow spheres.

The particles were chemically analyzed, using the selective acid dissolution technique used earlier by us to differentiate between PH and PY. The analysis shows that the iron sulfide mixtures produced by the aerosol reactor are indeed 50-50 mixtures of PY and PH, in agreement with the ratio corresponding to the sample produced in the hydrothermal-bomb reactor under the same conditions.

X-ray diffraction (XRD) studies of the aerosol products were carried out in the laboratory of Professor M.S. Seehra. The results (Figure 2) show clearly a diffraction pattern for PY but not for PH. This is also consistent with XRD analysis of the hydrothermally produced product. In fact, the XRD patterns are nearly identical. As in the hydrothermally produced material, the PH is small enough to be transparent or amorphous to X rays.

Surface area measurements of the aerosol products by BET indicate a value of 9.52 m^2/g . This is consistent with the average particle size reported above.

4. Controlling Factors. The temperature of the aerosol reactor is expected to control the rate of formation of ferric sulfide, but this is believed to be so rapid that temperature should have relatively little effect in this regard. However, the temperature should control the relative distribution of PH and PY, following the results for the hydrothermally produced material (summarized below). The effect of temperature has not yet been extensively studied in the aerosol reactor.

A preliminary study of the effect of reactor pressure has been carried out for the aerosol material. Particles produced at a lower pressure (100 psig as compared to 200 psig) have a

higher density, 4.6 g/ml as compared to 3.78 g/ml. The higher density falls in the range of bulk densities expected, implying that these particles are more solid (less hollow) than those obtained at the higher pressure. A lower reactor pressure can be expected to increase the rate of vaporization of water; if this rate is of the order of the rate of formation of the ferric sulfide, then more-solid particles can be expected to be obtained.

The effect of the concentration of the ferric acetate has also been preliminarily investigated. For a 0.1M solution, the maximum particle size was found to be 11.5 μ , whereas a similar measurement starting with a 0.01M solution yields 5 μ . A more-dilute solution of precursor corresponds to smaller amounts of ferric acetate (and ferric sulfide) per droplet, lower rates of reaction, and smaller particles.

5. Activity and Yield for Coal Liquefaction. Experiments have been run to test the activity and yield of the particles produced by the aerosol reactor. Liquefaction reactions were carried out at 350°C and 1000 psig hydrogen pressure for 1 h at a shaking speed of 500 rpm. The total conversion was found to be 70%, with a yield of 6.4% oil (+ gas). These numbers are comparable to those with the hydrothermally disproportionated catalyst

6. Hydrothermally Disproportionated Catalyst. Results from XRD, Auger electron spectroscopy (AES), and wet chemical analysis before and after liquefaction, have been combined with the phase diagram of the Fe-S system and the liquefaction results to obtain an overall picture of the hydrothermally disproportionated catalysts obtained under a wide range of preparation conditions. The full results have been summarized elsewhere [3]. However, the following comments can be made.

From the phase diagram [4], Fe_2S_3 is unstable, at least above 0°C. At 25°C, a solid mixture of PY (FeS_2) and greigite (Fe_3S_4) is expected to be thermodynamically stable. At 100°C and 200°C, solid mixtures of PY and monoclinic pyrrhotite (Fe_7S_8) are expected thermodynamically, while mixtures of PY and troilite (FeS) are expected above 250°C.

For the disproportionation of Fe_2S_3 for 1 h at room temperature, therefore, we expect the main reaction to be

After liquefaction at 350°C, the following change takes place in the disproportionated catalyst:

If the liquefaction is carried out at 400°C, the above reaction is followed by the increasingly important reaction:

For disproportionation at 100°C, the data are consistent with:

After liquefaction at 350°C using this catalyst,

whereas for liquefaction at 400°C,

Finally, disproportionation at 200°C requires elemental S to be a (net) reactant, following

After liquefaction at 350°C or 400°C,

As mentioned earlier, all these processes are consistent with data from wet chemical analyses before and after liquefaction, XRD and AES.

The effects of catalyst loading on the overall conversion and product yield for coal liquefaction were also investigated. These reactions were carried out using DECS-17 coal and the 200°C-disproportionated catalyst, presulfided with 0.1 ml CS₂. The reaction temperature was 350°C and 1000 psig (cold) of hydrogen was used in the batch reactor. For a batch time of 1 h, the results are summarized in Figure 3. Conversion and oil (+ gas) yield are seen to vary nonlinearly with catalyst loading. The conversion increases with loading up to approximately 0.6 percent Fe; at higher loadings, the conversion continues to increase, but to a lesser extent. At low catalyst loadings, the yield of oil (+ gas) is less than under non-

catalytic conditions. The yield is a minimum around 0.6 percent Fe loading, after which the yield increases. Clearly the catalyst not only converts coal to preasphaltenes and asphaltenes, but is also instrumental in converting oils into heavier products by retrograde reactions.

Such reactions are expected to be minimized in a flow-through reactor, where the contact time is of the order of seconds rather than 1h, as in the batch case. One such flow-through reactor is currently undergoing testing, as reported in Task I.6. Under such conditions, the optimum catalyst loading is expected to be around 1 percent, corresponding to the leveling-off of the steep conversion-loading curve of Figure 3.

7. Measurement of Gas Yields from Batch Reactors. In analyzing the products from liquefaction reactions to date, we have found that the minimum error is obtained when the amounts of unconverted coal and asphaltenes/preasphaltenes are measured directly, and the amounts of oil (+ gas) are obtained by difference. (Details of the procedure are given in, e.g., ref. [2].) However, this means that the amounts of oil and gas cannot be separately obtained. Visual examination has led us to believe that the amount of gas products is small, so that the yield can be taken as that of the oil alone, but to date this has not been verifiable. This year, we have developed a technique to quantify the amount of gas products formed after liquefaction, and have used this technique in a representative number of runs.

After the reactor is cooled to room temperature following the run, a specially-designed attachment is connected to the stem of the reactor, and the vapor flows through a collector maintained at liquid nitrogen temperatures. This condenses almost all of the vapor, except hydrogen. When all the vapor from the reactor has been passed through, the collector is sealed and heated, and the contents are flushed through a gas chromatograph with a thermal conductivity detector. Calibration of the detector signal allows us to quantify the nature and amount of each component in the vapor.

The results indicate that the vapor contains mainly C_2 species. Table II shows some quantitative results from liquefaction experiments. In all cases, the amount of gas is less than 15 percent of the total oil + gas yield, confirming our earlier expectation. The total amount of gas produced increases with increasing liquefaction temperature. The relative amounts of gas and oil are roughly constant with temperature. Further, both the total amount of gas and the amount relative to oil decrease with increasing reaction time. This latter observation is

consistent with the earlier comment regarding retrograde condensation of oil and gas to asphaltenes and preasphaltenes. The gas would appear to be preferentially condensed.

8. Surface Characterization of Other Consortium Catalysts. Research activities here focused on Auger electron spectroscopy (AES) analyses of sulfated iron oxide (SIO) catalyst particles. The samples were supplied by the University of Pittsburgh and were previously used by us in comparative studies of liquefaction. The samples were identified as $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ with 1% Mo.

No optical or SEM analyses were performed. However, it was evident that the SIO particles, like the hydrothermally disproportionated catalyst, were extremely small. Also like the hydrothermally disproportionated catalyst, the SIO catalyst was only lightly contaminated by carbon, as could be seen by AES. For both samples of the SIO catalyst, the O/Fe ratio ranges from a nominal 1.5 to 1.9. The S/Fe ratio was found to be 0.1 to 0.2. These contrast sharply with the hydrothermally disproportionated catalyst, where O/Fe was found to be 1 and S/Fe was found to be 2, with essentially half the S being associated with excess elemental sulfur left over from the disproportionation process.

Line-shape analyses showed that the Fe-MVV AES peak is consistent with that of the Fe_2O_3 standard. Because of the low intensity of the S-LVV peak, a meaningful analysis of the line shape of this portion was difficult to obtain.

Other activities in this thrust consisted of refurbishing the existing AES system, and developing new facilities for x-ray photoelectron spectroscopy (XPS). These activities are significant to the program for several reasons. Repairs to the existing AES system allow the electron gun to be operated at substantially lower beam currents, while maintaining an acceptable signal-to-noise level. This minimizes the damage induced by the electron beam, which can alter the surface composition and stoichiometry. Further, the XPS facility being developed will provide more clear-cut information on the chemical states of metal and sulfur species in the catalyst particles. This capability is essential as we move to catalysts with more complex compositions, as discussed below.

FUTURE WORK

The effect of solution concentration, injection pressure, reactor pressure and temperature

on the properties of the aerosol catalysts, particularly their size and density, will be investigated. Mixed metal catalysts will be produced by this technique. The physical and catalytic properties of these materials will be investigated. The surface characterization of aerosol catalysts, both those containing iron alone and those containing mixed metals, will be investigated. Co-liquefaction of coal with waste materials will be investigated.

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TABLE I

Particle Size Distribution of Aerosol Disproportionated Catalyst

Under, %	Size, μ
25	0.58
50	0.79
65	0.99
70	1.11
75	1.26
80	1.47
85	1.77
90	2.37
95	3.37
99	5.00

TABLE II

Liquefaction Results Including Separate Gas Yields
(DECS-6 Coal, 0.1 ml CS₂, 1000 psig H₂, 500 rpm)

Temp °C	Time h	Conversion %	Asphaltene %	Oil %	Gas %
350	0.5	55.7	43.8	10.3	1.6
	1.0	57.2	46.6	9.9	0.76
400	0.5	88.2	60.2	24.8	3.2
	1.0	92.8	60.1	30.0	2.7

Figure 1. Schematic of system for aerosol catalyst manufacture.

Figure 2. X-ray diffraction pattern for aerosol catalyst.

Figure 3. Effect of loading (of 200°C-hydrothermally disproportionated catalyst) on conversion and oil (+ gas) yield

TASK I

Project I.7

LASER PYROLYSIS PRODUCTION OF NANOSCALE CATALYSTS FOR COAL LIQUEFACTION

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Summary

In this past year, we have systematically investigated the synthesis of 5 - 20 nm dia. Fe-, Mo- and W-based particulate catalysts using a CO₂ laser pyrolysis technique. These catalysts include carbides(Fe₃C, Fe₇C₃, Mo₂C, W₂C), sulfides(Fe_{1-x}S), nitrides(Fe₃N, Fe₄N, Mo₂N, W₂N), oxides(Fe₃O₄, WO₃), and metals(α -Fe, γ -Fe). Commercial carbonyl compounds including Fe(CO)₅, W(CO)₆ and Mo(CO)₆ have been used as chemical precursors, and C₂H₄, H₂S, NH₃, and O₂ as reactant gases. Our success in the synthesis of these catalysts demonstrates that other ceramic catalysts containing V, Hf, etc, whose carbonyl compounds are readily available, can also be prepared using the CO₂ laser pyrolysis technique.

We have also extended our CO₂ laser pyrolysis to synthesize nanoscale carbon black particles, which might be used as catalysts or as a catalyst support for more expensive metals (e. g., Pt, Mo, etc.) in coal liquefaction. These carbon particles are produced by pyrolyzing benzene(C₆H₆) with a small amount of Fe(CO)₅ as a catalyst. Furthermore, using our laser pyrolysis system, we have produced FeWO₄ by pyrolyzing a mixture of Fe(CO)₅, W(CO)₆, and O₂, which demonstrates for the first time that the CO₂ laser pyrolysis is also useful to produce stoichiometric, crystalline, and nanoscale *ternary* compounds. This is important since many mixed-valence ternary compounds (e. g. La_{2-x}Sr_xCuO₄) have been found to exhibit high catalytic activity.

We have also carried out a study to determine the catalytic benefit of nanoscale Fe-carbide(Fe₇C₃) and Fe-sulfide(Fe_{1-x}S) catalysts in the direct liquefaction of subbituminous coal. The results have been compared to those determined for commercial Fe-oxide(Fe₂O₃) catalysts.

I. Synthesis and characterization of Fe-, Mo- and W-based nanoscale catalysts

Our upgraded laser pyrolysis system¹ is shown schematically in Fig. 1. Liquid Fe(CO)₅ is contained in a glass trap, whereas solid Mo(CO)₆ or W(CO)₆ is loaded into a sublimation cell developed this year whose temperature can be regulated between 25 and 500 °C. Reactant gases including C₂H₄, NH₃, H₂S, and O₂, (or their mixture) either bubble through Fe(CO)₅ liquid, or flow through heated Mo(CO)₆ and W(CO)₆ powder, and then flow vertically out of a stainless

steel nozzle along with the vapors of these precursors, and intersect a horizontal beam from a CO₂ laser beam (Laser Photonics Model 150). The reaction is initiated and sustained by the heat generated from resonant absorption of CO₂ laser energy by either a reactant gas such as ethylene (C₂H₄) or ammonia (NH₃), which have strong rotational-vibrational bands that match one of ~100 CO₂ laser lines. We display absorption spectra of C₂H₄ and NH₃, and emission spectra of our CO₂ laser in Fig. 2. Important reaction parameters include total chamber pressure, laser power density, reactant gas flow rate, vapor pressure of chemical precursors and reactant gas nozzle diameter. The particles form as a result of the thermal decomposition of metal carbonyl, e. g. Fe(CO)₅ → Fe + (CO)₅, and the subsequent reaction of metal ions with the reactant gases. The detailed synthesis process has been described in our paper.

a. Fe-based catalysts(α-Fe, γ-Fe, Fe₃C, Fe₇C₃, Fe₃N, Fe₄N, Fe₃O₄)

In Fig. 3, we display XRD data (dots) for nanocrystalline α-Fe(3a), Fe₃C(3b) and Fe₇C₃(3c) generated in our laser pyrolysis system by pyrolyzing a mixture of Fe(CO)₅ and C₂H₄. The data, corrected for the instrumental zero shift in 2θ, were collected using Cu(K_α) radiation using a Phillips 3100 powder diffractometer. The solid lines in the figure were calculated to fit the data using a Lorentzian lineshape for the diffraction peaks and an exponential term $\beta e^{-\gamma x}$ for the background. The values used for the diffraction peak positions and peak areas were taken directly from a standard powder diffraction file. To fit approximately each diffraction scan, a single value for the Lorentzian line width (w, or the full width at half maximum-FWHM) was chosen for α-Fe, Fe₃C, Fe₇C₃ and Fe₃O₄, respectively. It is clear from the figure that the position and relative intensity of most peaks agree well with the standard powder data, indicating that our identification of the majority phase is correct.

Shown in Fig. 4 are the XRD results for a few batches of particles produced by pyrolyzing a mixture of Fe(CO)₅ and NH₃. The solid lines are composite curves calculated using sets of Lorentzian functions whose peak positions and intensities were taken from standard powder diffraction data files for each individual phases including α-Fe, γ-Fe, Fe₃N, and Fe₄N. Note the changes in the XRD pattern as the relative amount of α-Fe, γ-Fe, Fe₃N, and Fe₄N varies with NH₃ flow rate. This indicates that the relative amount of individual phase is controllable by adjusting reaction conditions, similar to what we have observed in the synthesis of single phase Fe-carbides.

In Fig. 5, we display XRD results for nearly single phase Fe-sulfide (Fe_{1-x}S)(5a) and Fe-oxide(Fe₃O₄)(5b) particles obtained by pyrolyzing mixtures {C₂H₄+Fe(CO)₅+H₂S} and {C₂H₄+Fe(CO)₅+O₂}, respectively. In both synthesis processes, the reaction parameters were adjusted so that C₂H₄ does not decompose, yet serves as an absorbing gas subsequently providing heat to the reaction. This is necessary since the other two gases, (i. e., H₂S or O₂) do not couple to the CO₂ laser energy. The fact that C₂H₄ does not decompose for example in the production of Fe_{1-x}S (W₂N) is supported by Fig. 5, in which we do not observe any diffraction lines associated with crystalline carbide phases. Furthermore, we have studied Fe_{1-x}S particles using Raman scattering in which we have not found any peaks that may be associated with the presence of pyrolytic carbon in Fe_{1-x}S particles.

b. Mo and W-based catalysts(Mo_2C , Mo_2N , W_2C , and W_2N)

In this section, we describe the synthesis of nanoscale Mo and W carbide and nitride catalysts from solid Mo- and W-carbonyl precursors using our CO_2 laser pyrolysis system. Since these carbonyls are solids at room temperature and sublime only in the range $120 \sim 150^\circ\text{C}$, we have used our newly installed temperature regulated sublimation cell to generate Mo- or W-carbonyl vapors into the reaction zone. This cell attaches via a copper gasket to the bottom of the stainless steel six-way cross reactor. The concentration of Mo- or W-carbonyl vapors in the reaction zone is thus controlled by regulating the temperatures of the sublimation cell.

We show in Fig. 6 the XRD results of Mo-carbide(Mo_2C)(Fig. 6a) and W-carbide(W_2C)(Fig. 6b) particles synthesized by pyrolyzing a vapor phase mixture of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ with C_2H_4 , respectively. In Fig. 7, we plot XRD data for Mo-nitride(Mo_2N)(7a) and W-nitride(W_2N)(7b) particles obtained by pyrolyzing a vapor phase mixture of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ with NH_3 , respectively. The sharp lines in Fig. 7b are associated with the large $\text{W}(\text{CO})_6$ crystalline particles condensed onto the glass trap from unreacted W-carbonyl vapor. In Fig. 7, diffraction line intensity differences between our data and those in the standard powder diffraction data file might indicate stoichiometric differences, or structural defects, in our laser pyrolysis produced particles which may in fact lead to interesting new properties.

Shown in Fig. 8 are the TEM images taken for Mo_2C , W_2C , Mo_2N , and W_2N particles whose XRD spectra have been given in Fig. 7. These particles are spherical and fairly uniform in particle size. The particle size determined from these images is larger than the crystalline size estimated from XRD results using DS equation, indicating that disorder exist within each particle. A heat treatment experiment is underway to see at what temperatures this disorder can be removed.

Raman scattering experiments to look for pyrolytic carbon were carried out on both W_2C and W_2N nano-particles. The dominant structure in W_2C spectra is the broad doublet with peaks centered at 1375 and 1580 cm^{-1} . This doublet is the well known result for a disordered pyrolytic carbon. It is clear from the figure that pyrolytic carbon does not exist in the nitride particles. This result is consistent with our previous study on the Fe-carbides and Fe-nitrides, where pyrolytic carbon has only been observed in the case of carbides. This is further supporting our conclusion that surface pyrolytic carbon on our nanoparticles, as observed in the carbides, comes from the thermal decomposition of C_2H_4 onto the particle surface, instead of from the CO derived from the carbonyl species.

c. Nanoscale WO_3 and ternary compound FeWO_4

In Fig. 10(a), we show the XRD data for nanoscale WO_3 particles obtained by pyrolyzing a mixture of $\text{W}(\text{CO})_6$, O_2 and C_2H_4 . Vertical lines in the figure represent standard powder diffraction data file for WO_3 . Agreement between line positions and intensities of our data and standard file identifies the crystalline phase. However, as synthesized, the particles exhibit a bluish color, indicating an oxygen deficiency. By a simple heat treatment at 300°C in flowing O_2 for 5 hours, the particles were transformed into stoichiometric WO_3 which exhibit yellow color at 300°C and yellow-greenish color at room-temperature.

In Fig. 10(b), we show XRD data of the as synthesized particles produced by using the same sets of reaction parameter values used in the synthesis of Fe_3O_4 (Fig. 5a), except for the presence of a controlled amount of $\text{W}(\text{CO})_6$ vapor in the reaction zone. In a comparison with the XRD spectra for Fe_3O_4 given previously in Fig. 5a, we note that majority of additional diffraction lines can be identified as due to the appearance of a FeWO_4 phase. Thus, we have demonstrated for the first time that a *crystalline ternary* compound can be obtained using this technique with appropriate sets of reaction parameters.

d. Nanoscale carbon black particles

Carbon black particles were produced by pyrolyzing a vapor phase mixture of $\text{Fe}(\text{CO})_5$ and C_6H_6 introduced into reaction zone by bubbling C_2H_4 through a solution of $\text{C}_6\text{H}_6:\text{Fe}(\text{CO})_5 = 50:1$ (by volume) in the glass container. The C_2H_4 flow rate was regulated to be ~ 100 sccm. Using $\sim 15,000 \text{ W/mm}^2$ incident power density in the reaction zone, a bright white flame was observed. If no $\text{Fe}(\text{CO})_5$ is present in the stream, almost no soot is produced. From our previous work, if no benzene is present (only C_2H_4 and $\text{Fe}(\text{CO})_5$), then Fe-carbides are formed. We therefore speculate that $\text{Fe}(\text{CO})_5$ in the presence of both C_2H_4 and C_6H_6 acts as a catalyst, dehydrogenating the benzene and forcing the benzene molecule to fragment in the pyrolysis flame, leading to carbon soot formation. The chemical role of the C_2H_4 may not be important, other than to allow heat energy from the laser to be pumped into the reaction. A 0.5g/hour production rate of carbon black was obtained under the conditions described above.

Subsequent to the synthesis, standard elemental analyses were applied to our carbon black samples for Fe, C, N, and H. The results of this analysis yield a composition $\text{C}_{10}\text{Fe}_{0.01}\text{H}_{1.2}\text{N}_{0.1}$. It should be noted that the C:H ratio is ~ 8 , close to the ideal value ~ 10 predicted for acetylene black using a polycondensation model, and this value is lower than that obtained for a typical acetylene black, which has C:H ~ 40 . The C:Fe ratio was also measured using electron microprobe analysis (EDX), resulting in C:Fe ~ 700 , consistent with the value ~ 1000 obtained from the elemental analysis.

Shown in Fig. 11 are the high resolution TEM data taken using a JOEL 4000 electron microscope on "as synthesized" (11a, 11b) and heat treated (2800°C in Ar) (11c, 11d) carbon blacks produced by laser pyrolysis. As shown in Fig. 11a, untreated carbon black particles present, on average, a well developed spherical shape, with an average particle diameter on the order of 20 nm. Typical of acetylene black, significant agglomeration was observed. It is difficult to determine to what extent the particles might be fused, however. Fig. 11b is a magnified image within particle. Although the formation of very primitive carbon planes is observable in some regions of selected particles, most carbon black particles appear to exhibit an image of a highly disordered graphitic carbon (see the discussion of the x-ray results below).

Using the standard N_2 BET technique, we determined a value $50 \text{ m}^2/\text{g}$ surface area for the "as-synthesized" carbon black. This value is slightly lower than $70 \text{ m}^2/\text{g}$ reported for a typical acetylene black, and is lower than the theoretical surface total surface area for a 20 nm spherical particles ($150 \text{ m}^2/\text{g}$). Consistent with this observation of a lower surface area, is that no significant cracking of the particle surface or accessible internal pores are apparent in the TEM photos (Fig. 11b) and that agglomeration (with possible fusion) of the particles is also observed.

Furthermore, the carbon black samples subjected to 2800 °C HTT in Ar show clear evidence for graphitization, consistent with lattice fringes from parallel carbon planes and the associated lattice plane spacing (Fig. 11d). As shown in Fig. 11c and 11d, heat treated particles, in many cases, exhibit parallel carbon layers in polygonal shapes about a hollow center. This suggests that crystallization is initiated at the particle surface. Finally, we did not observe any evidence for the presence of Fe or Fe carbides as small particles within the carbon black particle, or, in particular, at the particle core, or as a separate nanoparticle. This is consistent with the small amount of Fe observed in the carbon black (0.5wt %), suggesting that the Fe may be atomically dispersed throughout the soot.

Shown in Fig. 12 are XRD results obtained with a Rigaku powder diffraction unit using Cu K α radiation. Results for "as synthesized" (Fig. 12a) and low temperature HTT (900 °C in N $_2$) (Fig. 12b) carbon black samples are presented. The low HTT sample was produced with a higher than normal amount of Fe(CO) $_5$. As a result, this sample exhibited x-ray diffraction peaks associated with the existence of nanocrystalline α -Fe and γ -Fe, as indicated. The diffraction peaks for the "as synthesized" sample are similar in width to that of a typical acetylene black. Broad peaks are observed and indexed according to a convention for acetylene blacks based on graphite: in decreasing intensity, they are the 002, 10, and 11 diffraction lines, respectively. The average lattice constant along the c-axis, as determined from the 002 peak position, is found to be 3.65 Å, somewhat larger than normally observed (<3.5 Å) for acetylene black. A significant shift of 002 peak is observed after a 900 °C HTT in N $_2$ for 24 hrs (Fig. 12b), where again from the 002 peak, the lattice constant has decreased to 3.48 Å, closer to that of a typical acetylene black (3.43 Å).

II. Studies of relative activity of nanoscale iron oxide, iron carbide, and iron sulfide catalyst precursors for the liquefaction of a subbituminous coal

a. Experiment

Three nanoscale iron-based catalysts were utilized in this study. Iron carbide and iron sulfide were obtained using our laser pyrolysis system. The XRD spectrum of the particles confirmed the production of Fe $_{(1-x)}$ S. Table 1 shows the reaction parameters used for the production of the pyrrhotite particles. The iron sulfide particles were paramagnetic, therefore the ferromagnet was removed and the particles were separated from the gas stream by the teflon filter. The as-formed particles were less pyrophoric than the iron carbide phase but still required passivation prior to removing from the trap. The third catalyst used in this study, a superfine iron oxide (SFIO), was provided by Mach I Inc. and was reported to be a 30 Å diameter α -Fe $_2$ O $_3$ particle. The properties of the three catalyst used in this study, as determined by XRD and nitrogen BET adsorption measurements, are presented in Table 2.

Liquefaction experiments were carried out in 50 ml horizontal microautoclave reactors, a configuration that reduces mass transfer limitations. The reactors were agitated at 400 cycles/minute in a heated fluidized sand bath. This allowed the rapid (<2 minutes) attainment of reaction temperature and thereby minimized errors associated with long heat-up times. The microautoclaves were loaded with 3 g of a subbituminous Black Thunder coal and 5 g of tetralin, used as a hydrogen donor solvent. An analysis of the coal is shown in Table 3. Catalyst loadings

of 0.7 and 1.4 wt % Fe on as-received coal were used, corresponding to 1 and 2 wt % Fe on maf coal respectively, and dimethyldisulfide (DMDS) was added as a sulfiding agent in these runs. The reactors were sealed purged and pressurized to 1000 psig (cold) with hydrogen.

A set of blank liquefaction experiments were carried out in the absence of coal to determine the effect of sulfur on the iron carbide particles under liquefaction conditions. A microautoclave reactor was loaded with 0.2 g of Fe₇C₃, 5g tetralin, and DMDS at twice the stoichiometric loading needed to form FeS₂, and reacted at 385 °C for 30 minutes. The residue from the run was collected and analyzed by XRD.

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

The amount of solvent dehydrogenation was calculated from the naphthalene/tetralin ratio determined by GC analysis of the pentane soluble fraction. The H/C ratio of the PA&A fraction was determined by elemental analysis. The phase of the catalyst, as well as the average crystallite diameter, was determined from XRD spectrum. Surface area was measured using a nitrogen BET adsorption method.

b. Results and Discussion

Due to the small size of the SFIO particles, which severely limited the use of traditional characterization techniques such as XRD, there is some speculation on the actual phase. One recent study, using Mössbauer and XAFS spectroscopies, reported that the major phase is ferrihydrite². Another study has identified the major phase as γ -Fe₂O₃ based on energy-dispersive X-ray and microdiffraction³. This material is reported to be extremely sensitive to moisture and to tend to form large (~150 Å) particles of α -Fe₂O₃⁴. For the purposes of this study the SFIO will be considered to be Fe₂O₃ for the calculations of conversion and iron loadings.

The iron carbide formed by the laser pyrolysis technique was passivated prior to exposure to air. XPS studies of the passivated material indicated that some of the surface of the particles becomes oxidized, while XRD shows the bulk remained in the carbide phase. Similarly, the iron sulfide particles also were passivated though they were less pyrophoric than the carbide particles.

The results of the nitrogen BET adsorption measurements showed that there was very little porosity associated with any of the materials used in this study. Therefore, unlike supported catalysts, in which much of the surface area is associated with small micropores, the bulk of the active sites were on the external surface area and therefore readily accessible to the coal. The

results of the catalyst precursor characterization studies, shown in Table 2, indicate that the SFIO contained the smallest particles (3 nm diameter) and consequently the highest surface area (195 m²/g). The XRD spectra indicate that the diameter of the iron sulfide and iron carbide were very similar (14 and 17 nm respectively), although their surface areas differed significantly (42 and 95 m²/g respectively), reasons for which are not clear.

While it has been shown that iron oxide, in the presence of sufficient sulfur, will transform to pyrrhotite under liquefaction conditions ⁵, the behavior of the iron carbide was not known. The results of the blank runs showed that the transformation to pyrrhotite was complete within 30 minutes at 385°C, indicating that the iron carbide does not possess the stability reported to exist for molybdenum and tungsten carbides ⁶⁻⁸. While the pyrrhotite does not undergo a phase change it is possible that the stoichiometry will change as a function of the sulfur concentration in the system^{9,5}.

The results of the liquefaction experiments, summarized in Table 4, indicate that, at the high severity conditions and a catalyst precursor loading of 0.7 wt % Fe on as-received coal, all three precursors yielded nearly identical catalytic effects resulting in an increase in the total conversion from 81 wt% for the thermal runs to 87 wt % for the catalytic runs. The enhanced total conversion, shown in Figure 13, appears to be due solely to the increase in oil yield while the PA&A and gas yields show no significant deviation from the thermal baseline. Increasing the iron concentration to 1.4 wt % showed some further increase in total conversion for each precursor with Fe₇C₃ at 89 wt%, Fe_(1-x)S at 87 wt%, and SFIO at 88 wt %. Again, the increase is due mainly to an increase in oil yield. As shown in Figure 14, in the case of the Fe_(1-x)S and the SFIO precursors, slight decreases in the PA&A yield were also observed.

Liquefaction experiments were conducted at the low severity conditions to minimize thermal effects and to maximize the effect of the catalyst precursors. Further, since it had been shown that both the carbide and the oxide precursors transform to a sulfide phase under liquefaction conditions, the longer reaction time used in the high severity experiments may have also obscured the distinctions between the catalyst precursors.

The results, shown in Figure 15, indicate that at the low severity conditions there are only minor differences in catalytic activity for an iron loading of 0.7 wt %. The Fe_(1-x)S showed the highest activity with a total conversion, 52.6 wt %, followed by SFIO at 52.2 wt %, Fe₇C₃ at 50.3 wt %, compared to a thermal conversion of 46.2 wt %. The changes were mostly apparent as increases in PA&A with little change in the oil or gas yields. This indicates that there is little difference in the effect of the three iron based catalyst precursors on the conversions regardless of the form of the added precursor.

The amount of hydrogen consumption showed a strong dependence on the phase of the catalyst precursor, particularly at high severity. Under low severity conditions, at a loading of 0.7 wt % Fe, the effect of precursor phase on the amount of total hydrogen uptake is minimal, each showing a similar increase over the thermal baseline. The increase of severity to 415 °C for 60 minutes shows a marked increase in the total hydrogen consumption, as shown in Figure 16, with the Fe_(1-x)S and Fe₇C₃ precursors showing similar behavior. The SFIO, at these conditions, caused significantly greater total hydrogen uptake. The hydrogen consumed from the gas phase follows

the trend $\text{thermal} < \text{Fe}_7\text{C}_3 < \text{Fe}_{(1-x)}\text{S} \ll \text{SFIO}$ while the solvent dehydrogenation followed the opposite, though less distinct, trend. The higher gaseous hydrogen consumption and lower solvent dehydrogenation indicates a higher hydrogenation activity for the SFIO. This is particularly interesting since the liquefaction yields showed the effect of these catalysts to be nearly identical. This would appear to indicate that bond cleavage, rather than the availability of labile hydrogen, was the main factor in limiting the total conversion. Increasing the iron concentration to 1.4 wt % has a significant impact on the total hydrogen consumption for the Fe_7C_3 and the $\text{Fe}_{(1-x)}\text{S}$ bringing them closer to the uptake of the SFIO, which still causes significantly less solvent dehydrogenation, as shown in Figure 16.

The H/C ratio for the PA&A fraction showed that the additional uptake of hydrogen for the SFIO was, in part, incorporated into these products. The increase in H/C ratio with increasing SFIO concentration followed a trend similar to the hydrogen consumption, as shown in Figures 17 and 18, respectively. A similar propensity was also observed for Fe_7C_3 . This may be indicative of an increase in conversion from preasphaltenes to asphaltenes which was not discernable by the separation methods used in this study. However, the $\text{Fe}_{(1-x)}\text{S}$ at a catalyst loading of 1.4 wt % Fe showed a decrease in H/C ratio to near that of the thermal reaction. This may indicate that, for the $\text{Fe}_{(1-x)}\text{S}$, the increased hydrogen consumed was primarily utilized in improving the quality, though not the quantity, of the oil fraction. Confidence in this data was high due to the fact that the runs were made in duplicate with a standard deviation of less than $\pm 3.5\%$.

The final phase of the iron based catalysts in a coal liquefaction process is pyrrhotite, provided that sufficient sulfur is present to allow that transformation. As previously noted, the conversion of the carbide phase occurs within 30 minutes at 385 °C. The conversion of the catalyst precursor may occur by reduction of the surface oxide or carbide followed by sulfidation of the reduced iron sites¹⁰. The sulfur then diffuses into the particle as the internal oxygen or carbon diffuses to the surface where it reacts with the hydrogen. Since the activity of the particles is associated with active sites located on the surface, the various precursors probably exhibit similar catalytic effects very early in the reaction. This would explain the fact that the conversions obtained using pyrrhotite as the catalyst precursor were no more favorable than those obtained from the other precursors. Further, the activity of the SFIO for solvent hydrogenation is significantly higher than the $\text{Fe}_{(1-x)}\text{S}$ which was in turn slightly higher than Fe_7C_3 . Particularly for the high severity conditions, the difference in hydrogenation activity is probably related to the surface area, rather than the phase, of the precursor.

The study by Stohl¹¹ which reported that the surface area of the precursor had no correlation with the conversion agrees well with the findings of this study. However, while the surface area, or particle diameter, had no effect on the total conversion, the effect on hydrogenation was profound. The relation between solvent dehydrogenation and surface area, as determined from nitrogen BET measurements, shown in Figure 19, indicates that, particularly at higher severity, there is a distinct negative trend. Similarly, Figure 20 indicates an inverse correlation between the total hydrogen consumption and the particle diameter. This appears to indicate that the hydrogenation activity related to the catalyst precursors is much more closely related to the particle diameter, or amount of surface area available for reaction, than to the phase of the catalyst precursor.

The specific surface area, which is defined as the surface area per 100g maf coal, may be a measure of the catalytic sites available to the coal for reaction. Using this number, a plot for all experiments conducted at high severity may be constructed, as shown in Figure 21. The total hydrogen consumption increases rapidly at low specific surface areas followed by a plateau at higher specific surface areas. This may indicate a saturation condition above which increasing catalyst concentration will produce minimal benefit. This would explain the greater effect of increasing the catalyst loading for $\text{Fe}_{(1-x)}\text{S}$ and Fe_7C_3 compared to SFIO as shown in Figure 16. The greater specific surface area of the SFIO results in more rapid attainment of the saturation at lower concentrations, yielding minimal benefit for additional catalyst loading.

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

The effects of the different catalyst precursors on hydrogen consumption from the gas phase and the extent of solvent dehydrogenation were more pronounced. For the high severity conditions, at a catalyst loading of 0.7 wt % Fe, the total amount of hydrogen consumed followed the trend $\text{thermal} < \text{Fe}_7\text{C}_3 < \text{Fe}_{(1-x)}\text{S} < \text{SFIO}$. The amount of hydrogen consumed from the gas phase followed a similar trend while the amount of solvent dehydrogenation followed the opposite, though much less distinct, trend. The increase in hydrogenation activity correlates well with precursor particle diameter. This indicates that the difference in activity may not be a function of the phase of the catalyst precursor, but rather of the particle size, or available surface area.

The increase of the catalyst concentration to 1.4 wt % further increased the hydrogen consumption but narrowed the gap between the SFIO and the other two precursors. This may be explained as nearing a saturation of the specific surface area of catalyst available for reaction. As this plateau is approached, increasing the catalyst loading results in minimal additional benefit.

III. References

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Presentations and Publications Associated with the CFFLS Project (May, 1992 - May, 1993)

"Structural and Surface Studies of Nanocrystalline Iron Carbides", presentation, A. R. Sethuraman, A.M. Rubel, Xiang-Xin Bi, P. C. Eklund, G. T. Hager, F. J. Derbyshire and J. M. Stencel, Materials Research Society Meeting, San Francisco, CA, April 27 - May 1, 1992.

"In-Situ High Temperature X-Ray Diffraction Studies of Nanocrystalline Iron Carbides", presentation, A. R. Sethuraman, Xiang-Xin Bi, P. C. Eklund, J. M. Stencel, O. B. Cavin and C. R. Hubbard, Materials Research Society Meeting, San Francisco, CA, April 27 - May 1, 1992.

"Nanoscale Fe-based Catalysts for Coal Liquefaction", presentation, P. C. Eklund, Xiang-Xin Bi, F. J. Derbyshire, 6th Annual Technical Meeting of the Consortium for Fossil Fuel Liquefaction Science, Wheeling, WV, July 28 - 31, 1992.

"Synthesis and Physical Properties of Nanosize α -Fe, Fe_3C , Fe_7C_3 and Fe_2S Particles", presentation, Xiang-Xin Bi, S. Sinha and P. C. Eklund, Materials Research Society Meeting, Boston, Mass, Dec. 2 - 6, 1992.

"Nanoscale Fe-Based Catalysts from Laser Pyrolysis", presentation, P. C. Eklund, Xiang-Xin Bi, and F. J. Derbyshire, invited talk, Amer. Chem. Soc. meeting, Wash. D. C., 1992.

"Synthesis and Characterization of Laser Pyrolysis Produced Nanoscale Particles", poster, Xiang-Xin Bi, P. C. Eklund, T. Hager and F. J. Derbyshire, Gordon Research Conference (Hydrogen Carbon Science), Oahu, Hawaii, November 8 - 13, 1992.

"Carbide Catalysts: Laser Pyrolysis Synthesis and Catalytic Activity", presentation, J. M. Stencel, P. C. Eklund, Xiang-Xin Bi, B. H. Davis, G. T. Hager and F. J. Derbyshire, ICC Conference, Budapest, Hungary, July 19 - 24, 1992.

"Iron Ultrafine Particle Catalysts Formed by Laser Pyrolysis: Synthesis, Characterization and Coal Liquefaction Activity", J. M. Stencel, P. C. Eklund, Xiang-Xin Bi, and F. J. Derbyshire, *Catalysis Today*, **15**, 285(1992).

"Synthesis of Nanocrystalline Fe-based Particles by CO_2 Laser Pyrolysis", X.-X. Bi and P. C. Eklund, Proc. of Materials Research Society Meeting (Boston, Mass., Dec. 2 - 6, 1992).

"Laser Pyrolysis Production of Nanoscale Carbon Black", presentation, Xiang-Xin Bi, Wen-Tse Lee and P. C. Eklund, ACS meeting (Fuel Chemistry Division), Denver, Colorado, March 28 - April 2, 1993.

"Influence of Nanosize Fe_1-xS Particles on Coal liquefaction", presentation, G. T. Hager, Xiang-Xin Bi, P. C. Eklund and F. J. Derbyshire, submitted to ACS(Fuel Chemistry Division), Denver, Colorado, March 28 - April 2, 1993.

"Laser Pyrolysis Production of Nanoscale Carbon Black", X.-X. Bi, Wen-Tse Lee and P. C. Eklund, preprint of ACS meeting(Fuel Chemistry Division)(Denver, Colorado, March 28 - April 2, 1993).

"Nanocrystalline α -Fe, Fe_3C and Fe_7C_3 produced by CO_2 laser pyrolysis", X.-X. Bi, B. Ganguly, G. Huffman, E. Huggines, M. Endo, and P. C. Eklund, J. of Material Research, in press, 1993.

"Relative Activity of Nanoscale Iron Oxide, Iron Carbide, and Iron Sulfide Catalyst Precursors for the Liquefaction of a Subbituminous Coal", G. T. Hager, Xiang-Xin Bi, P. C. Eklund, E. N. Givens, and F. J. Derbyshire, submitted to *Energy&Fuel*, 1993.

Figure Captions:

Fig. 1 CO_2 laser pyrolysis system for the synthesis of nanoscale particles.

Fig. 2 Absorption lines of NH_3 (a) and C_2H_4 (b), and emission lines of our CW CO_2 laser(c).

Fig. 3 XRD data of nanoscale $\alpha\text{-Fe}$ (a) and Fe-carbide(Fe_3C (b), Fe_7C_3 (c)) particles obtained by pyrolyzing $\text{Fe}(\text{CO})_5$ with C_2H_4 . Solid lines are calculated using a set of Lorentzian lines whose peak positions and intensities are obtained from standard powder diffraction data files.

Fig. 4 Examples of X-ray diffraction data on preliminary Fe-N samples. Laser pyrolysis of $\text{Fe}(\text{CO})_5 + \text{NH}_3$ was used to produce nanoscale particles. The relative amount of Fe_3N and Fe_4N can be controlled by adjusting the reaction conditions. Solid lines are calculated as in Fig. 3 from standard powder diffraction data file using a variable which controls the relative amount of $\alpha\text{-Fe}$, $\gamma\text{-Fe}$, Fe_3N and Fe_4N . Relative percentage of each phase is given in the figure.

Fig. 5 XRD data of nanoscale Fe-oxide(Fe_3O_4 (a)) and Fe-sulfide(Fe_{1-x}S (b)) particles obtained by pyrolyzing $\text{Fe}(\text{CO})_5$ with O_2 and H_2S , respectively. Solid lines are calculated using a set of Lorentzian lines whose peak positions and intensities are obtained from standard powder diffraction data files.

Fig. 6 XRD data of nanoscale Mo-carbide(Mo_2C (a)) and W-carbide(W_2C (b)) particles obtained by pyrolyzing $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ with C_2H_4 , respectively. Solid lines are calculated using a set of Lorentzian lines whose peak positions and intensities are obtained from standard powder diffraction data files.

Fig. 7 XRD data of nanoscale Mo-nitride(Mo_2N (a)) and W-nitride(W_2N (b)) particles obtained by pyrolyzing $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ with NH_3 , respectively. Solid lines are calculated using a set of Lorentzian lines whose peak positions and intensities are obtained from standard powder diffraction data files.

Fig. 8(a) TEM images of nanoscale Mo-carbide(Mo_2C) particles.

Fig. 8(b) TEM images of nanoscale W-carbide(W_2C) particles.

Fig. 8(c) TEM images of nanoscale Mo-nitride(Mo_2N) particles.

Fig. 8(d) TEM images of nanoscale W-nitride(W_2N) particles.

Fig. 9 Raman spectra($\lambda=488$ nm, Ar, $T=300$ K) of W_2N and W_2C particles. The peaks that are indicated by the arrows are associated with pyrolytic carbon coating on the particle surface.

Fig. 10 (a) XRD data of W-oxide(WO_3) nanoscale particles by pyrolyzing $\text{W}(\text{CO})_6$ with O_2 . (b) A mixture of nanoscale phases containing the ternary phase FeWO_4 as obtained by adding $\text{W}(\text{CO})_6$ to the reaction zone. Vertical lines are from standard powder diffraction data files.

Fig. 11(a,b) High resolution TEM images for as synthesized carbon black particles from our laser pyrolysis system.

Fig. 11(c,d) High resolution TEM images for heat treated carbon black particles (2800 °C, in Ar)

Fig. 12 XRD data for as synthesized carbon black particles (a) and heat treated particles (b) (900 °C, in N₂). Vertical lines represent standard powder diffraction data file for α -Fe and γ -Fe.

Table 1. Typical Reaction Parameters used in Laser Pyrolysis

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

Table 2. Catalyst Characterization Data

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

Table 3. Analysis of Black Thunder Coal

Proximate	wt%	Ultimate	wt% dry	Sulfur	wt % maf
Moisture	22.4	Carbon	72.15	Total Sulfur	0.39
Ash	5.46	Hydrogen	4.34	Pyritic Sulfur	0.07
Volatile Matter	34.4	Nitrogen	1.23	Sulfate	0.09
Fixed Carbon	39.8	Sulfur	0.53	Organic Sulfur	0.30
		Oxygen (diff)	15.93		
		Ash	5.81		

Table 4. Summary of Coal Liquefaction Conversion Data

Catalyst	Loading	Severity ¹	% Total Conversion	% PA & A	% Oils	% Gas
None		Low	46.2	32.6	9.7	4.0
Fe _(1-x) S	0.7	Low	52.6	38.3	10.4	3.9
Fe ₇ C ₃	0.7	Low	50.3	35.7	10.4	4.2
SFIO	0.7	Low	52.2	38.7	9.4	4.1
None		High	80.6	44.6	29.3	6.8
Fe _(1-x) S	0.7	High	87.1	45.3	35.0	6.8
Fe ₇ C ₃	0.7	High	87.6	44.4	36.3	7.0
SFIO	0.7	High	87.0	45.2	34.6	7.2
Fe _(1-x) S	1.4	High	87.0	41.7	38.2	7.0
Fe ₇ C ₃	1.4	High	89.4	45.0	37.5	6.9
SFIO	1.4	High	88.1	42.5	38.3	7.3

¹ Low severity = 385°C for 15 minutes

High severity = 415°C for 60 minutes

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Figure 13 Effect of 0.7 wt% Fe Catalyst on Conversion at 415 C for 60 minutes

Figure 14 Effect of 1.4 wt% Fe Catalyst on Conversion at 415 C for 60 minutes

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

Figure 16 Effect of Catalyst on Hydrogen Consumption at High Severity

Figure 17 Effect of Catalyst Concentration on H/C ratio of PA&A fraction from high severity liquefaction experiments

Figure 18 Hydrogen Consumption as a Function of Catalyst Concentration

Figure 19 Effect of Surface Area on Solvent Dehydrogenation

Figure 20 Effect of Particle Diameter on Total Hydrogen Consumption

Figure 21 Effect of Specific Surface Area on Hydrogen Consumption

TASK I
Project I.8

**ACTIVITY AND SELECTIVITY OF SLURRY PHASE
IRON-BASED CATALYSTS FOR MODEL SYSTEMS**

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SUMMARY

The activity and selectivity of iron-based slurry-phase catalysts were investigated for the hydrogenation of pyrene and the hydrocracking of C-C bonds in several model compounds: 1-methylnaphthalene (1-MN), 2-hexylnaphthalene (2-HN), and 4-(1-naphthylmethyl)bibenzyl (NMBB). Reactions were performed under typical coal liquefaction conditions. Higher reaction temperature and the presence of sulfur increased the hydrogenation of pyrene by the iron catalysts generated in situ. An in situ method of catalyst addition was most effective for pyrene hydrogenation for the iron catalysts, while molybdenum naphthenate showed increased activity with two-stage processing. Both Fe and Mo catalysts showed low activity in reactions where the catalyst was generated ex situ. Combinations of Fe and Mo catalysts were synergistic for pyrene hydrogenation, although the amount of increase was dependent upon the particular iron precursor used. The Fe and Mo catalysts affected the hydrocracking of the three model species differently. Molybdenum naphthenate was more active for hydrocracking 2-HN and NMBB than any of the Fe catalysts but combining FeNaph with MoNaph was detrimental to the hydrocracking of these compounds. The selectivity of hydrocracking NMBB at specific bonding sites was affected by the presence and type of catalyst, presence of sulfur, and reaction time.

INTRODUCTION

Slurry-phase catalyst precursors that form finely divided catalysts during reactions have been shown to be active for coal liquefaction and coprocessing.¹⁻⁴ Addition of Fe catalysts in the form of finely divided Fe (III) oxides and Fe oxyhydroxides modified with either (SO_4^{2-}) or molybdate (MoO_4^{2-}) anions in coal liquefaction increased coal conversion and selectivities to n-pentane soluble products.⁴ A bimetallic catalyst that incorporated Mo with Fe, forming $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$ which consisted of 50 ppm Mo and 3500 ppm Fe, was active for coal conversion with a selectivity for oil.⁴ Other researchers⁵⁻⁸ have evaluated the catalytic activities of Fe present in different chemical forms in model coal reactions. Iron catalysts composed of $\text{Fe}(\text{CO})_5$ or $\text{Fe}(\text{CO})_5\text{-S}$ had high activity for hydrogenation (HYD) of aromatic species.⁴ Iron catalysts composed of Fe (III) oxides, sulfated Fe oxides, or FeOOH have also been shown to be active for hydrocracking (HYC) model compounds such as 4-(1-naphthylmethyl)bibenzyl (NMBB).⁶⁻⁸ Reactions of NMBB were performed in the presence of a H_2 donor solvent, 9,10-dihydrophenanthrene. Selective bond cleavage occurred, depending on the composition of the Fe catalyst and the presence of water in the system.⁸ A series of Fe catalysts generated by different means such as from oil-soluble iron pentacarbonyl, ultrafine ferric oxide and ferric oxyhydroxide, chemical impregnation of Fe catalysts into coal and cation exchange of iron species with coal have been analyzed using ^{57}Fe Mössbauer and X-ray absorption fine structure (XAFS) spectroscopy.⁹ The chemical structure of the different catalysts and particle sizes were determined.

The objective of this study was to determine the activity and selectivity of different Fe and Mo catalyst precursors for hydrogenating and hydrocracking model systems such as pyrene (PYR), 1-methylnaphthalene (1-MN), 2-hexylnaphthalene (2-HN), and NMBB at coal liquefaction conditions. These model species are representative of compound types present in coal and coal liquids. The catalyst precursors were examined individually and combinatorially using several different methods of dispersion: in situ, ex situ, and two-stage processing. The effect of S addition and reaction temperature on the reaction products was also evaluated.

EXPERIMENTAL

Materials. Chemicals used in the HYD and HYC reactions were PYR (99% purity), 1-MN (98% purity), and hexadecane (99% purity) obtained from Aldrich; 2-HN supplied by Dr. M. Farcasiu of the Pittsburgh Energy Technology Center and NMBB obtained from TCI America. The catalyst precursors used in the experiments were iron (III) acetylacetonate (FeAcAc) (15.9% Fe, 99% purity) from Eastman Kodak; iron (III) citrate hydrate (FeCH) (16.7% Fe, 98% purity) from Aldrich; iron (III) naphthenate (FeNaph) (6.0% Fe), iron (III) 2-ethylhexanoate (Fe 2-EH) (8.0 to 11.5% Fe), and iron (III) stearate (FeSTR) (9.0% Fe, 98% purity) from Strem; and molybdenum naphthenate (MoNaph) (6.0% Mo) from Shepherd Chemical. All the model compounds and catalyst precursors were used as received.

Reaction Procedures. Reaction methods used for dispersing the catalysts in the reactions were (1) in situ reaction where the catalyst precursor at a level of 900 to 1100 ppm active metal was added directly into the reaction system and reacted in the presence and absence of S; (2) ex situ reaction where the catalyst precursor reacted in the presence of the model compound was reclaimed, dried for 72 hr in a vacuum oven at 60 °C and reintroduced at a level of 900 to 1100 ppm active metal into a second reaction with PYR; (3) two-stage reaction where the catalyst precursor at a level of 900 to 1100 ppm active metal was added to hexadecane, H₂, and S and reacted for 30 min, then the model species was introduced into the reactor along with H₂ and reacted for another 30 min. The reactions were performed in ~20 cm³ stainless steel tubular microreactors. Reactions were conducted at 380, 400, or 425 °C for 30 or 60 min with a H₂ pressure of 1250 psig at ambient temperature and an agitation rate of 550 rpm. The solvent used in the reactions was hexadecane; however, because of interference with the analysis of reaction products, NMBB was reacted without a solvent. Reactions were performed both with and without S. When S was added, S was introduced as elemental S in a stoichiometric ratio of 3:1 sulfur:metal, based on the presumption that either Fe₃S₈ or MoS₂ was formed depending on the metal precursor used. Each reaction was at least duplicated; the standard deviations for both HYD and HYC reactions are given in the tables.

Pyrene Hydrogenation. Pyrene HYD reactions were performed using in situ, ex situ, and two-stage reaction methods. Two weight percent PYR in hexadecane was reacted at 380 and 425 °C for the in situ single-stage reactions. In addition, in situ reactions were performed at 380 °C using combined catalysts of Fe-based precursors and MoNaph. The total level of metal was kept constant at 900 to 1100 ppm for each reaction with Fe:Mo weight ratios of 75:25, 50:50, and 25:75 being used. For comparison, reactions with individual catalyst precursors introduced at metal levels of 750, 500, or 250 ppm of the active metal were also performed. Two different types of two-stage reactions were performed with FeNaph and MoNaph combined. In the Type 1 sequence, MoNaph, S, and H₂ were added together in the first stage while FeNaph, PYR, and H₂ were charged in the second stage. In the Type 2 sequence, MoNaph, FeNaph, S, and H₂ were added together in the first stage, and PYR and H₂ were introduced into the second stage. The reaction temperature for both sequences of reactions was 380 °C. The recoveries from the PYR HYD reactions varied but were typically in the range of 85 to 95%.

Hydrocracking Reactions. Hydrocracking reactions using 2 wt % 1-MN or 2-HN in hexadecane were performed at 425 °C for 30 min. 4-(1-Naphthylmethyl)bibenzyl was reacted at 400 °C without solvent for 30 min and 60 min for selected reactions. In situ and two-stage reactions were performed using 1-MN and 2-HN, while in situ reactions were performed using NMBB. In addition, reactions were carried out with combinations of Fe-catalyst precursors and MoNaph. The recoveries of 1-MN and 2-HN were usually in the 80 to 95% range with 2-HN giving the lower recoveries. The recoveries for NMBB were all above 90%.

Analysis. An analysis procedure using UV-visible spectroscopy was developed for measuring the amount of the organometallic complex that reacted under liquefaction conditions. The concentration of Fe or Mo complex present after a given reaction time with hexadecane present in the reactor was determined by UV-visible spectroscopy and was compared to the initial amount of complex introduced. Each Fe complex had to be treated differently in the experimental procedure because of their varying degrees of solubility in hexadecane. Hexadecane was used as the analysis solvent for FeNaph, Fe 2-EH,

and MoNaph; ethanol was the extraction and analysis solvent for FeCH; hot water was used to extract FeAcAc for analysis in ethanol.

Reaction products obtained from the HYD and HYC reactions were analyzed by gas chromatography using a Varian Model 3700 gas chromatograph equipped with FID detection and J&W DB5 30 m column. Quantitation was achieved by employing the internal standard method using p-xylene as the internal standard. The reaction products were identified by comparing retention times with those of authentic compounds and by identifying unknowns by GC-mass spectrometry using a VG70 EHF GC-mass spectrometer.

Definitions. Product slates were determined for each reaction from which the amount of HYD and HYC that occurred was calculated for each species. Percent HYD is defined as the moles of H₂ required to produce the liquid product as a percentage of the moles of H₂ required to hydrogenate the most hydrogenated product. The most hydrogenated liquid product from PYR was considered to be perhydropyrene, from 1-MN, 1-methyldecalin and from 2-HN, 2-hexyldecalin. Percent HYC is defined as the mole percent of the products that have undergone hydrocracking.

RESULTS AND DISCUSSION

Pyrene Hydrogenation Reactions

Pyrene was hydrogenated in the presence of five different slurry-phase Fe catalyst precursors at 380 and 425 °C in the presence and absence of S as presented in Table 1. The activity of the Fe catalyst precursors for PYR HYD was very low in the absence of S but the activity increased when S was added to the system. The hydrogenated products observed using the most active catalyst precursors, FeNaph and FeSTR, in the presence of S, were dihydropyrene (DHP), tetrahydropyrene (THP), and hexahydropyrene (HHP). When S was not present, DHP was the only product formed. The percent HYD obtained with the different Fe systems indicates their degree of activity. Iron naphthenate with S yielded the highest percent HYD at 380 °C giving 12% while at 425 °C FeNaph and FeSTR yielded similar HYD's of 11.5 and 11.9%, respectively. Iron acetylacetonate was the only other Fe catalyst precursor that yielded substantial HYD of 9.3% at 425 °C. Iron citrate hydrate and Fe2-EH yielded low HYD with sulfur at either reaction temperature.

Table 1. Activity of Iron Complexes for Pyrene Hydrogenation^a

% Hydrogenation					
	FeNaph	FeSTR	FeCH	FeAcAc	Fe2-EH
3:1 S:Fe Ratio					
380°C	12.0±0.3	5.2±0.2	1.0±0.1	0.6±0.1	0.0
425°C	11.5±0.6	11.9±0.4	NP ^b	9.3±0.1	1.4±0.1
No Sulfur					
380°C	0.3±0.0	0.0	0.0	0.2±0.0	0.0
425°C	1.7±0.0	0.0	NP	1.0±0.1	0.8±0.0

^a Reaction Conditions: 900-1100 ppm of Fe, 30 min, 1250 psig H₂ pressure at ambient conditions, 2 wt % PYR in hexadecane.

^b NP = not performed.

The solids from the in situ FeNaph reaction with S were analyzed by Mössbauer and XAFS spectroscopy by Dr. G.P. Huffman and Dr. F. E. Huggins of the University of Kentucky. Even though S was present in excess in the reactor, the solids formed were determined to be Fe oxyhydroxide, FeOOH, although a small amount of pyrrhotite might have been formed.¹⁰ The particle size of these solids was less than or equal to 70 Å.⁹

Reactions were also performed with MoNaph with and without S at 380 and 425 °C for 30 min. The presence of S in the reactor allowed the Mo to form finely divided MoS₂.^{10,11} The particle size of the MoS₂ was also less than or equal to 70 Å.⁹ The finely divided MoS₂ catalyst was an active catalyst for PYR HYD. At 380 °C, the PYR reaction with MoNaph and S yielded 34.6% HYD of PYR with HHP isomers being the primary products as well as a substantial amount of decahydropyrene (DCHP) being formed. When PYR was reacted at 380 °C with MoNaph but without S, 11.7% HYD of PYR occurred with DHP as the primary product and THP as the secondary product. At a higher reaction temperature of 425 °C, the reaction of MoNaph with S resulted in 23.7% HYD of PYR while the reaction without S gave 13.8% HYD. When excess S was present at 425 °C less HYD of PYR occurred. Thermodynamics limited the amount of PYR conversion since PYR was favored at higher reaction temperature.¹² Smaller amounts of partially saturated compounds were produced in the reaction at 425 °C than at 380 °C.

Concentration of Iron Complexes at Liquefaction Conditions. The Fe complexes of FeCH, FeNaph, FeAcAc, and Fe2-EH, each with an initial concentration of 1000 ppm Fe, were reacted at 380 °C with an initial H₂ charge of 1250 psig H₂ introduced at ambient temperature. The concentration of each Fe complex was determined by measuring the visible absorbance at two wavelengths and comparing the absorbance reading with a calibration curve for each complex obtained with the same solvent as was used with the reaction mixture. Each of the Fe complexes disappeared very quickly at liquefaction conditions. After 5 min of reaction, all of the Fe complexes were decomposed; in fact, all of them except FeNaph decomposed after 2 min of reaction. By contrast, MoNaph remained in solution longer; after 10 min of reaction, more than half of the MoNaph remained. However, MoNaph had totally decomposed after 15 min of reaction.

Comparison of Dispersion Methods for the Activity of FeNaph and MoNaph. Three methods of dispersion, in situ, ex situ, and two-stage batch processing, were used to test the effect of dispersion on the catalytic activity of catalysts generated from FeNaph and MoNaph with S. A comparison of the activity of FeNaph and MoNaph for PYR HYD using the in situ method showed that MoNaph plus S resulted in three times as much HYD as did FeNaph plus S. The more highly hydrogenated HHP was the primary product produced with MoNaph while DHP was the primary product from FeNaph. The ex situ method, in which the catalyst produced in an in situ experiment was dried, added to PYR and reacted in a H₂ atmosphere, resulted in much less activity for both FeNaph and MoNaph. The reaction with FeNaph did not convert any PYR while the reaction with MoNaph yielded about half the HYD observed in the in situ reaction.

Two-stage batch reactions were performed in which the catalyst precursor was introduced into hexadecane in the first stage and then reacted in the presence of S and H₂ at 380 °C. After 30 min, the reaction was quenched, gas released, and PYR and a new charge of H₂ were added. The system, including PYR, was then reacted again for 30 min. The two-stage reaction with FeNaph yielded about 6% conversion of PYR to DHP so that its activity was much less than that of the in situ generated catalyst. By contrast, the two-stage reaction with MoNaph yielded higher PYR HYD, 40.2%, compared to 34.6% for the in situ single-stage reaction. Also, substantially more DCHP was formed in the two-stage than in the single-stage in situ reaction. The catalytic activity of MoNaph increased with the two-stage treatment while FeNaph did not.

Effect of Dual Catalysts on Pyrene Hydrogenation. Reactions were performed in which Fe precursors were combined with MoNaph to determine if synergism occurred for PYR HYD. Reactions were performed with 1000 ppm of Fe complex or MoNaph individually and with combinations of ratios of 75:25, 50:50, and 25:75 Fe:Mo with the total active metal loading being 1000 ppm. Results from these reactions in terms of PYR HYD are presented in Table 2.

The dual catalysts of MoNaph with either FeNaph, FeSTR, FeAcAc, or FeCH all showed increased HYD of PYR for at least one combination. FeCH and FeAcAc yielded increased PYR HYD of ~41% at the 250 ppm Fe to 750 ppm Mo ratio compared to 34.6% HYD for 1000 ppm of MoNaph. A direct comparison at equivalent Mo loadings showed that MoNaph reacted individually at 750 ppm only

resulted in 27.8% HYD of PYR. FeSTR combined with MoNaph showed increased HYD of PYR compared to 1000 ppm of MoNaph at ratios of 500 ppm Fe to 500 ppm Mo giving 41.5% HYD and of 250 ppm Fe to 750 ppm Mo, 34.9% HYD. However, if both of these percent values were compared to MoNaph alone at equivalent levels, as shown in Table 2, then substantial increases in percent HYD were obtained. Iron naphthenate combined with MoNaph showed the greatest activity of the dual catalyst systems. At ratios of 750 ppm Fe to 250 ppm Mo and of 500 ppm Fe and 500 ppm Mo, the combination of FeNaph with MoNaph yielded more than 40% HYD of PYR which was more than that which occurred with 1000 ppm Mo and substantially more HYD than occurred with either 250 or 500 ppm of MoNaph.

Table 2. Effect of Combined Catalysts on the Hydrogenation of Pyrene^a

	1000 ppm Fe	750 ppm Fe 250 ppm Mo	500 ppm Fe 500 ppm Mo	250 ppm Fe 750 ppm Mo	1000 ppm Mo
% Hydrogenation with Mixtures of Fe and Mo Catalyst Precursors					
Fe Naph ^b	12.0±0.3	40.5±1.4	43.6±0.5	32.0±1.0	34.6±1.7
Fe STR	5.2±0.2	26.4±0.8	41.5±0.6	34.9±0.9	34.6±1.7
Fe AcAc	0.6±0.1	3.3±0.2	20.9±0.6	41.8±0.3	34.6±1.7
Fe 2-EH	0.0	7.5±1.0	11.0±1.0	17.1±0.8	34.6±1.7
Fe CH	1.0±0.1	6.3±0.2	29.8±0.3	41.4±0.3	34.6±1.7
% Hydrogenation with Individual Catalyst Precursor					
	1000 ppm	750 ppm	500 ppm	250 ppm	
Fe Naph	12.3±0.3	9.0±0.3	4.7±0.6	3.9±0.3	
Mo Naph	34.6±1.7	27.8±0.3	22.4±0.3	11.7±0.3	

^a Reaction Conditions: 990-1100 ppm metal, 1250 psig H₂ at ambient temperature, 3:1 S:Fe and S:Mo ratio 380°C, 30 min, 2 wt % PYR in hexadecane.

^b FeNaph = iron naphthenate; FeSTR = iron stearate; FeAcAc = iron acetylacetonate; Fe2-EH = iron 2-ethylhexanoate; FeCH = iron citrate hydrate; MoNaph = molybdenum naphthenate

Hence, the combined catalysts promoted reactions that increased the HYD of PYR compared to the single catalyst case. The solids obtained from the combined reactions of FeNaph with MoNaph were also analyzed by Mössbauer and XAFS spectroscopy. FeNaph formed FeSO₄ in the reaction with combined catalysts while Mo was coordinated with four oxygen atoms.¹⁰ The particle size of both particles was less than or equal to 70 Å.⁹ The Fe and Mo catalysts generated from FeNaph and MoNaph, respectively, were present in different forms when both metals were used simultaneously compared to when the individual metals were present in the PYR reactions. These differences may account for the synergism that occurred with both metals being present.

Effect of Two-Stage Processing on Pyrene Hydrogenation. Two-stage PYR HYD reactions were performed using the dual catalysts of FeNaph and MoNaph as presented in Table 3. The dual catalysts were introduced at a total active metal content of 1000 ppm with ratios of 75:25, 50:50, and 25:75 Fe:Mo. The two-stage reactions were performed in two ways: in Type 1 sequence, MoNaph was added to the first stage and FeNaph was added to the second stage; in Type 2 sequence, MoNaph and FeNaph were both added to the first stage. The reactions were also performed with each catalyst precursor individually so that the effect of the dual catalysts on the HYD of PYR could be compared

directly at the given Mo concentration level. All of the reactions with FeNaph reacted individually yielded low levels of PYR HYD.

Comparing the two-stage reactions using the Type 1 sequence to the Type 2 sequence showed that higher levels of HYD of PYR were obtained with Type 1. Increases in HYD were observed using the sequenced catalysts at both 500:500 and 250:750 Fe:Mo ratios compared to the simultaneous addition of catalysts at these combined catalyst loadings. However, the Type 2 reactions resulted in higher levels of HYD at 750:250 Fe:Mo ratio compared to Type 1. Both types resulted in at least two of the ratios having higher HYD of PYR than did the corresponding amount of MoNaph reacted individually.

Ex situ reactions were also performed with the dual catalyst system of FeNaph with MoNaph (Table 3). Almost no HYD of PYR occurred in these reactions. Evidently the removal of the catalyst from the reaction system and subsequent drying of the catalyst resulted in changes either in the catalyst structure or particle size that were detrimental to the HYD activity of the combined catalyst system.

Table 3. Effect of Two-Stage Processing and Ex Situ Reactions on Pyrene Hydrogenation^a

% Hydrogenation with Mixtures of FeNaph and MoNaph ^c					
	1000 ppm Fe	750 ppm Fe 250 ppm Mo	500 ppm Fe 500 ppm Mo	250 ppm Fe 750 ppm Mo	1000 ppm Mo
Two-Stage Reaction					
1. Mo added to 1st Stage Fe added to 2nd Stage	0.8±0.1	16.6±0.8	32.8±1.1	30.9±0.9	40.2±0.6
2. Mo & Fe added to 1st Stage	0.8±0.1	23.4±0.4	27.5±0.9	26.9±0.6	40.2±0.6
Ex Situ Reactions	0.0	0.5±0.2	0.8±0.3	NP ^b	18.1±1.1
% Hydrogenation with Individual Catalyst Precursors					
	1000 ppm	750 ppm	500 ppm	250 ppm	
Two-Stage Reactions					
FeNaph	0.8±0.1	1.6±0.3	1.3±0.2	0.7±0.1	
MoNaph	40.2±0.6	26.4±0.6	17.7±0.4	16.0±0.6	

^a Reaction Conditions: 250-1000 ppm FeNaph or MoNaph with a total catalyst loading of 1000 ppm, 380°C, 1250 psig H₂ at ambient temperature, 3:1 S:Fe or S:Mo ratio, 30 min, 2 wt% pyrene in hexadecane.

^b NP = not performed.

^c FeNaph = iron naphthenate; MoNaph = molybdenum naphthenate.

Hydrocracking Reactions

Reactions were performed in which the HYC activity of selected Fe complexes were tested. The model systems that were used included 1-MN, 2-HN, and NMBB which has been used extensively as model for HYC.⁶⁸ In each of the reactions, the bond, being tested for HYC was a C-C bond, which was present in different configurations and, hence, bond energies.

Hydrocracking Reactions of 1-Methylnaphthalene and 2-Hexylnaphthalene. The HYC activity of FeNaph and FeSTR for C-C bonds in 1-MN and 2-HN was tested at 425 °C as shown in Table 4. The HYD activity of these Fe catalyst precursors was also evaluated and compared to that obtained with MoNaph. Reactions were performed in situ with the individual and combined catalysts.

Baseline experiments were performed with naphthalene (NAP) to evaluate the effect of any catalytic activity of FeNaph or FeSTR on the aromatic ring structure. When reacted at 425 °C thermally, NAP did not react; however, when FeNaph and FeSTR were introduced with excess S, about 15 mol % tetralin (TET) was formed in the reaction. Only HYD occurred; no HYC of the aromatic ring was

observed. The products observed from 1-MN were primarily the HYD products of 5,6,7,8-tetrahydro-1-methylnaphthalene (5,6,7,8-1-HMN) and 1,2,3,4-tetrahydro-1-methylnaphthalene (1,2,3,4-1-HMN). The hydrocracked product, NAP, was the minor product, present at 2 to 3 mol %. Comparison of the product slate when MoNaph was used showed that substantially more of the hydrogenated products were formed yielding 39% 5,6,7,8-1-HMN and 25% 1,2,3,4-1-HMN, compared to the Fe catalysts where 11-12% 5,6,7,8-HMN and 3.6 to 5.3% 1,2,3,4-1-HMN were formed; however, no NAP was produced. For all of the catalysts, the 5,6,7,8-1-HMN isomer was the preferred product. If 1-methyldecalin is considered to be the most hydrogenated product, then the Fe complexes both yielded between 6 and 7% HYD of 1-MN but less than 3% HYC (Table 4). MoNaph yielded substantially more HYD of 1-MN at ~26%; however, no HYC of the methyl group from the aromatic ring occurred.

Table 4. Comparison of the Activity for the Hydrogenation and Hydrocracking of 1-Methylnaphthalene and 2-Hexylnaphthalene

Product Distribution (mole %)	Catalyst (1000 ppm)						Catalysts (500 ppm)	
	No Catalyst	FeSTR + S	FeNaph + S	MoNaph + S	Two Stage		FeNaph MoNaph + S	MoNaph + S
					FeNaph + S	MoNaph + S		
1-Methylnaphthalene								
% HYD	0.0	6.3±0.4	6.6±0.3	25.8±0.4	5.4±0.6	25.0±0.6	19.0±0.6	13.8±0.8
% HYC	0.0	2.2±0.3	2.7±0.4	0.0	3.5±0.6	2.5±0.6	3.5±0.5	0.0
2-Hexylnaphthalene								
% HYD	0.0	10.4±0.8	14.8±0.7	40.0±1.0	7.0±0.8	38.8±0.9	30.4±1.0	27.7±0.8
% HYC	0.0	9.6±0.2	13.1±0.9	36.4±0.3	6.1±0.3	35.0±1.2	23.7±1.0	25.2±0.4

* Reaction Conditions: 900-1100 ppm Fe or Mo, 1250 psig H₂, introduced at ambient temperature; 30 min, 425°C, S:Fe ratio 3:1, S:Mo ratio 3:1, 2 wt% 1-MN or 2-HN in hexadecane

Two-stage processing of FeNaph and MoNaph resulted in more HYC for both catalysts, producing more NAP. In both cases, the percent HYD of the products decreased slightly compared to the single stage in situ reaction. This lesser amount of HYD may have resulted from decreased catalytic activity because of exposure of the catalysts to air between the two stages.

Dual catalysts of FeNaph and MoNaph were combined at 500 ppm each and were reacted with 1-MN. For comparison, a reaction with 500 ppm MoNaph was also performed. The product distribution obtained from the dual catalyst system given in Table 4 showed characteristics of both MoNaph and FeNaph. Fairly high levels of HYD were obtained yielding 19% HYD with 5,6,7,8-1-HMN as the primary HYD product and 1,2,3,4-1-HMN as the secondary one. Hydrocracking also occurred yielding 3.5% HYC with NAP as the product. MoNaph at 500 ppm showed a lesser HYD of 13.8% and no HYC. The dual catalyst for 1-MN enhanced both HYD and HYC.

Hydrocracking of 2-Hexylnaphthalene. The same series of reactions was performed with 2-HN as with 1-MN (Table 4). Products obtained were 2-hexyltetralin (2-HT) and 2-ethyltetralin (2-ET). 2-Hexyltetralin was formed at a slightly higher amount than 2-ET regardless of the catalyst or reaction type. Of the two Fe catalyst precursors, FeNaph was more active for both HYD and HYC in the in situ reactions. However, MoNaph had the most activity yielding 40.0% HYD and 36.4% HYC compared to 14.8% HYD and 13.1% HYC with FeNaph. Two-stage reactions were detrimental to both HYD and HYC of FeNaph; about one-third less of each product was formed than in the in situ single-stage reaction. The reaction of 2-HN with MoNaph also experienced a decrease in the amount of HYD and HYC

occurring, but these decreases were quite small. The dual catalyst system of 500 ppm Fe and 500 ppm Mo resulted in slightly more HYD and slightly less HYC than the reaction with MoNaph at 500 ppm Mo.

Hydrocracking Reactions of 4-(1-Naphthylmethyl)bibenzyl. Reactions were performed using NMBB as a model HYC species for coal. Iron catalyst precursors, FeNaph, FeSTR, and FeAcAc, were reacted with NMBB in the presence and absence of S at 400 °C with no solvent; MoNaph was also used for comparison. All of the catalysts were introduced at an active metal loading of 1000 ppm. The primary products obtained from the reactions of NMBB were methylbibenzyl (MBB), NAP, bibenzyl (BB), and naphthyltolylmethane (NTM). Trace amounts of 1-MN, TET, p-xylene, and toluene were also identified in the reactions products when MoNaph was used.

As has been discussed previously in the literature,⁶ NMBB contains five different C-C bond sites, designated as *a*, *b*, *c*, *d*, and *e*, which are susceptible to hydrogenolysis. These bond sites are presented in Figure 1. Products that would be obtained from cleavage at the different bond sites are presented in Table 5. Thermal reactions of NMBB at 400 °C resulted in a small amount of HYC and yielded 1.9 mol % NTM and 3.0 mol % MBB; the percent HYC of the thermal reaction was $4.9 \pm 1.3\%$ which indicated a small thermal background. In the catalytic reactions, MBB and NAP were the predominant products.

Hydrocracking reactions were performed thermally, thermally with S, and catalytically with and without S as presented in Table 6. Most reactions were performed for 30 min; however, some of the in situ reactions with individual Fe and Mo precursors with sulfur were also performed for 60 min. The data from these reactions are given in terms of percent HYC which is the sum of the mole percents of all products that were hydrocracked. Percent bond cleavage of *a*, *b*, and *d* is the sum of the mole percents of those reaction products that were produced from cleavage of *a*, *b*, and *d*. Selectivity is defined as the cleavage of a given bond divided by the sum of the cleavage of bonds *a*, *b*, and *d*.

Figure 1. Cleavage Sites for 4-(1-Naphthylmethyl)bibenzyl.

Table 5. Possible Products from the Hydrocracking Reactions of 4-(1-Naphthylmethyl)bibenzyl

Bound Cleaved	Products Observed	Reaction Pathways
a	Methylbibenzyl, Naphthalene, Tetralin	1
b	Methylnaphthalene, Bibenzyl	2
c	Benzyl-naphthalene, Ethylbenzene	3
d	Naphthyltolylmethane, Toluene	4
e	Naphthyltolylethane, Benzene	5

Table 6. Selectivity of Iron and Molybdenum Catalysts for Hydrocracking 4-(1-Naphthylmethyl)bibenzyl

Catalyst Precursor	Reaction Time (min)	HYC (%)	Cleavage of a+b+d (%)	Selectivity x 100%		
				$\frac{a}{(a+b+d)}$	$\frac{a+b}{a+b+d}$	$\frac{d}{(a+b+d)}$
Thermal	30	4.9±1.3	4.9	61	61	39
Sulfur	30	9.3±2.7	7.3	64	67	33
FeNaph	30	5.5±1.0	4.6	74	74	26
FeNaph+S	30	13.5±1.4	10.4	79	86	14
FeAcAc+S	30	5.7±1.4	5.0	82	82	18
FeSTR+S	30	6.0±1.5	4.7	68	79	21
MoNaph	30	6.4±0.9	5.3	72	72	28
MoNaph+S ^a	30	28.5±2.1	21.0	87	94	6
MoNaph+S ^b	30	39.4±2.3	27.5	89	96	4
FeSTR+MoNaph+S ^c	30	8.9±1.4	6.7	69	81	19
FeNaph+MoNaph+S ^c	30	22.9±1.6	17.9	86	90	10
FeAcAc+MoNaph+S ^d	30	18.1±1.8	13.9	92	92	8
FeNaph+S	60	18.7±2.2	12.1	69	69	31
FeAcAc+S	60	9.9±2.0	6.4	56	56	44
FeSTR+S	60	7.8±1.5	5.2	62	62	38
MoNaph+S	60	47.3±3.8	34.8	89	95	5

^a 500 ppm Mo

^c 500 ppm Fe + 500 ppm Mo

^b 1000 ppm Mo

^d 250 ppm Fe + 750 ppm Mo

The thermal reaction showed a background HYC of 4.9% while the introduction of S nearly doubled the amount of HYC to 9.3%. The introduction of FeNaph and MoNaph without S resulted in low HYC of 5.5 and 6.0%, respectively. Addition of S increased the HYC from FeNaph to 13.5%. The other two Fe catalyst precursors used, FeAcAc and FeSTR, reacted with S gave low HYC of 5.7 and 6.0%, respectively. Increasing the reaction time to 60 min increased the amount of HYC observed for all three Fe catalyst precursors when reacted with S. The largest increase was observed with FeNaph, which increased from 13.5 to 18.7% HYC.

The percent HYC of NMBB with MoNaph and S at both 500 and 1000 ppm Mo resulted in substantial HYC of 28.5 and 39.4%, respectively; however, only trace amounts of HYD occurred. Increased reaction time of 60 min resulted in an increased HYC of 47.3%. Combinations of MoNaph with either

FeNaph and FeSTR at 500 ppm of each active metal catalyst and FeAcAc at 250 ppm Fe and 750 ppm Mo produced an increased HYC compared to the specific Fe catalyst. Iron naphthenate and FeAcAc showed the largest increases while FeSTR showed only a small increase. By contrast, if the percent HYC that occurred in the combined reactions is compared to that of MoNaph at the same loading level the percent HYC decreased. The largest decrease was observed for the reaction of FeSTR combined with MoNaph. Hence, the presence of the iron species in the reaction was detrimental to the HYC activity of MoNaph.

The percent HYC that has been discussed involved HYC of all C-C bonds observed during the reaction with the different catalyst precursors. The bond cleavage also given in the table is the addition of the mole percent of cleavage that occurred at sites *a*, *b*, and *d*. In every reaction except the thermal reaction without S, the sum of the cleavage at *a*, *b*, and *d* was less than the total HYC that occurred in the reaction.

The selectivity for HYC of NMBB at the two primary sites of cleavage *a* and *d* is shown in Table 6. For the 30 min reactions, the thermal reactions with and without S showed the lowest selectivity for cleavage at site *a* in the low 60% range. The reactions with iron precursors showed intermediate selectivity between 68 and 82%. Molybdenum naphthenate with S had the highest selectivity for cleavage at site *a* yielding 87 and 89% at 500 and 1000 ppm, respectively. Combining Fe precursors with MoNaph increased the selectivity for *a* to varying degrees for the different Fe species. The Fe precursors when reacted for a longer time of 60 min showed a decreased selectivity for *a* and a substantial increase in the selectivity for *d*. By contrast, the selectivity of MoNaph did not change with the increased reaction time.

The selectivity for cleavage appears to be dependent upon the reaction conditions and catalyst used. The selectivity for cleavage at sites *a+b* was less in the work performed by Farcasiu and Smith⁸ than in this study. For comparison the selectivity defined as *a+b* divided by the sum of *a+b+d* for the reactions performed in this study is also given in Table 6. Although the reaction temperatures were similar, the source of H₂ was different in the two sets of reactions; a H₂ donor was the source H₂ used by Farcasiu and Smith,⁸ while molecular H₂ at ~19 MPa was the source in this work. The catalyst form and particle size present in the reactor were also most likely different.

The primary factors that affected the selectivity for specific bond cleavage of C-C bonds in NMBB at these reaction conditions were (1) the presence or absence of a catalyst; (2) the type of active metal present in the catalyst; (3) the activity of catalyst generated in situ; (4) the presence or absence of S; and (5) reaction time. These same factors also strongly affected the amount of cleavage of bonds *a*, *b*, and *d* as well as the percent HYC.

SUMMARY

The activity of slurry-phase Fe-based catalysts for HYD of PYR was enhanced by the presence of S and higher reaction temperature. Of the five Fe precursors tested, FeNaph and FeSTR were the most active for hydrogenating PYR. The method of catalyst introduction affected the reactivity of the finely dispersed catalyst. Introducing the catalyst precursor directly into the reaction mixture was the most effective. Molybdenum naphthenate, used as a bench mark for catalytic activity, gave increased conversion and more highly saturated products of PYR compared to that achieved by the Fe catalysts. Combinations of MoNaph with the different Fe catalyst showed substantial increases in PYR HYD except for one Fe precursor. The practical value of using these combined catalysts is that more activity was achieved with a lesser amount of the more expensive Mo metal. The amount of HYC C-C bonds effected by the finely divided Fe catalyst generated in situ was different than that achieved by MoS₂ generated in situ. The finely divided Fe catalysts were not nearly as active as the finely divided MoS₂ and also had different selectivities for bond cleavage.

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NOMENCLATURE

1,2,3,4-1-HMN	= 1,2,3,4-tetrahydro-1-methylnaphthalene	FeCH	= iron citrate hydrate
1-MN	= 1-methylnaphthalene	FeNaph	= iron naphthenate
2-ET	= 2-ethyltetralin	FeSTR	= iron stearate
2-HN	= 2-hexylnaphthalene	HHP	= hexahdropyrene
2-HT	= 2-hexyltetralin	MBB	= methylbibenzyl
5,6,7,8-1-HMN	= 5,6,7,8-tetrahydro-1-methylnaphthalene	MoNaph	= molybdenum naphthenate
% HYC	= percent hydrocracking	NAP	= naphthalene
% HYD	= percent hydrogenation	NMBB	= 4-(1-naphthylmethyl)bibenzyl
BB	= bibenzyl	NTM	= naphthyltolylmethane
DCHP	= decahydropyrene	PYR	= pyrene
DHP	= dihydropyrene	TET	= tetralin
Fe2-EH	= iron 2-ethylhexanoate	THP	= tetrahydropyrene
FeAcAc	= iron acetylacetonate	XAFS	= X-ray absorption fine structure

Task II

Exploratory Research on Coal Conversion

Program Coordinators: Henk Meuzelaar and Mohindar Seehra

TASK II

Project II.1

COAL STRUCTURE/LIQUEFACTION YIELD CORRELATION BY MEANS OF ADVANCED NMR TECHNIQUES

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During the period of May 1, 1992 to April 30, 1993, our efforts focused on the development and testing of a number of techniques that can provide chemical shift information on polycyclic aromatic hydrocarbons, which serve as models of the structural features in the aromatic clusters found in coal. Obtaining the principal components of the chemical shift tensor for compounds with more than four distinct carbons using the standard static solid NMR techniques is often impossible due to overlap of the shielding patterns of each of the carbons. However, there have been many techniques developed to isolate the lineshape of a single carbon from the remaining carbons, either by separating the individual patterns in a two dimensional space or selectively observing only one carbon.

We recently published a paper on the application of variable angle sample spinning (VASS) technique to a series of substituted naphthalenes,¹ each with three different aromatic shift tensors. This work was also the focus of a talk presented at the International Conference on Coal Science in England during August 1991. A second paper, "Selective Saturation and Inversion of Multiple Resonances in High Resolution Solid State ¹³C Experiments using Slow Spinning CP/MAS and Tailored DANTE Pulse Sequence", was recently published.² This experiment employs rapid spinning of a solid sample at the magic angle. The chemical shift anisotropy (CSA) of each distinct carbon in a sample collapses into a relatively narrow line at the isotropic or average chemical shift. If the spinning speed is less than the width of the

shift pattern (the slow MAS condition) one does not obtain a single line but rather, one obtains a group of lines spaced about the central isotropic line at the interval of the spinning speed. By simulating the intensity pattern of this spinning sideband family, the components of the tensor can be retrieved. It is possible to isolate a shift pattern from only one carbon by selectively saturating the signals due to the remaining carbons in the sample. This has been done in the past; however, literature examples are limited to cases where only one or two resonances are either saturated or inverted.³ By taking advantage of the long ^{13}C T_1 values commonly encountered in solids, one can selectively saturate a number of resonances by sequentially applying several DANTE pulse sequences centered at different frequency offsets. In addition, it has been demonstrated that if one sideband of a spinning sideband family is selectively saturated the entire family is saturated.⁴ Therefore, a spectrum of only one or two families of spinning sidebands can be isolated from a sample that contains a number of resonances.

A probe to perform the magic angle hopping experiment, developed by Bax and Maciel in 1983,⁵ has been built in our laboratory. The magic angle hopping experiment separates the individual isotropic chemical shift patterns in a second dimension of a spectrum, removing overlap. By looking at slices in the 2-D space, individual shift patterns are obtained, making the retrieval of the tensor components simple. In the case of magic angle hopping, a static sample, held at the magic angle, is quickly jumped between three orientations 120° apart such that the sample spends one-third of its time at each position. This has the same averaging effect on the CSA as rapidly spinning at the magic angle. A static NMR probe coupled with a motor and encoder was assembled in our laboratory to rotate the sample between the three positions when a signal is received from the spectrometer.

The original magic angle hopping experiment has several shortcomings, preventing its

widespread use. A major problem was obtaining a motor to hop the sample very quickly, in a time short in comparison the spin lattice relaxation time of the sample. In addition, the original pulse sequence was phase modulated requiring the spectrum to be obtained in an obsolete mode intensity, leading to poor resolution in the second dimension.

In our laboratory we have used the same motor system and controller used in the commercial DAS system, which allows for each hop to be completed in less than 60 ms, compared to the 150 ms time reported in the Bax and Maciel paper. In addition, the experiment was modified to obtain the data in a hypercomplex manner (the techniques to do this were developed after 1983 for use in 2-D liquid NMR spectroscopic methods) in order to obtain a pure absorption mode spectrum, resulting in better resolution. These changes in the pulse sequence also lead to a gain in signal to noise over the previous experiment.⁶

A new experiment based on that developed by Z. Gan⁷ has been implemented in our laboratory. In Gan's experiment⁷ the hopping between the three positions is replaced by continuous spinning at the magic angle at a relatively low rate (in the range of 100 Hz). The evolution time of this 2-D technique is then divided into three segments, each consisting of one-third of a rotor cycle. Between these segments the prepared magnetization is stored along the magnetic field after evolving for one-third of the evolution time. As the evolution time is about an order of magnitude less than the time it takes the rotor to rotate 120°, the sample is essentially static during this evolution time.

The chemical shift, which is the sum of the isotropic and the CSA contribution, is different during each of these segments. However, the average of the chemical shift over the entire sequence is again only the isotropic chemical shift due to the fact that the chemical shift is a second rank tensor. The resulting 2-D spectrum is identical to that obtained in the magic angle hopping experiment. The advantage of this new method, however, is that the

need to mechanically hop the sample is removed. This experiment can be done on any magic angle spinning probe as long as a constant slow speed can be maintained. However, since most spinning systems are built for high speeds and are not stable enough for this experiment at lower speeds, this slow turning experiment can be difficult to perform on standard MAS probes since a very slight variation in the air pressure corresponds to a large change in the rotor spinning speed.

In our laboratory a very large volume (about 6 cm³) rotor system and a probe has been constructed. The maximum spinning speed of this system is several hundred Hz, and its speed is very constant (± 1 Hz) over 24 hours, the length of time needed for a typical experiment. In addition, the large sample volume allows for good signal to noise to be obtained in a relatively short time for a 2-D experiment.

Two important variations of the Gan experiment have been developed in our laboratory. The first, referred to as the "5 π pulse" experiment⁸ employs a constant evolution time synchronized to the rotor period during which 5 π pulses are applied. This two-dimensional experiment yields isotropic chemical shifts in the evolution dimension and undistorted slow-spinning-sideband chemical shift anisotropy powder patterns in the acquisition dimension. Peaks separated by only 1.07 ppm in 1,2,3-trimethoxybenzene are clearly resolved with this experiment.⁸ The success of the constant-time method would require that the spin system have relatively long T_2 values, but when this condition obtains the magnetization is used more effectively.

We have noted, however, that the Gan and 5- π pulse experiment produce spectral artifacts in the form of baseline distortions. We have therefore developed a 3- π pulse sequence (which we now call the Magic Angle Turning, MAT, experiment) which significantly improves the baseline. The pulse sequence employed by Gan is shown in Figure

III.2.1c. The 2D contour plot for 1,2,3-trimethoxybenzene (1,2,3-TMB) is shown in Figure III.2.2 together with the projection of the isotropic shifts onto the isotropic chemical shift axis. Note the baseline distortion in Figure III.2.2b. The 3-p MAT pulse sequence (Figure III.2.1a) was used to acquire the 2D contour plot of 1,2,3-TMB shown in Figure III.2.3a. The isotropic chemical shift projections (Figure III.2.3b) exhibit none of the baseline distortions seen in Figure III.2.2b. The resultant powder pattern for each carbon is seen in Figure III.2.3c. Variations of the basic 3-p MAT experiment can be used to suppress protonated carbons (dipolar dephasing, Figure III.2.1b) and display only protonated carbons (short contact time experiments) as seen in Figures III.2.4 and III.2.5.

The MAT experiment has been applied to coals and the spectra of Pocahontas coal (Argonne Premium Sample Bank) are shown in Figure III.2.6. In Figure III.2.7, the slices taken at various isotropic shift values illustrate the power of the MAT experiment in identifying carbons of various types by means of the CSA. The resultant CSA powder patterns along with the results obtained from the short contact time and the dipolar dephasing experiments are shown in Figure III.2.7. It is obvious that the overlapping of the powder patterns (Figure III.2.7b) of the protonated and nonprotonated aromatic carbons are successfully separated by the short contact time (Figure III.2.7c) experiment and the dipolar dephasing experiment (Figure III.2.7d).

Similar data have been obtained on all of the Argonne Premium Coal Samples. The aromaticity, f_a , obtained with the MAT experiment correlate very well with the data of Solum, et al.⁹ (see Table III.2.1).

To summarize, we now possess the capability in our laboratory to obtain the chemical shift tensor components in solids by several different 2-D methods. These 2-D methods greatly expand the molecules that are feasible to study, as we are no longer limited to looking

at only smaller aromatic systems with high degrees of symmetry in order to have only three or four magnetically inequivalent carbons. In particular, the 3- π MAT experiment looks very promising. We have successfully demonstrated that this experiment can be utilized for coal studies and we will shortly undertake a detailed analysis of the data that can be obtained with this new experimental technique.

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Table III.2.1
Aromaticities of Argonne Premium Coals
Obtained by the MAT Experiment

Coal	f_a (by MAT)	f_a (by CP/MAS) ^a
Pocahontas	0.86	0.86
Upper-Freeport	0.80	0.81
Stockton	0.73	0.75
Pittsburgh #8	0.75	0.72
Illinois #6	0.72	0.72
Blind Canyon	0.64	0.65
North Dakota Zap	0.67	0.65
Wyodak	0.62	0.63
a. Reference 9		

Figure III.2.1. The pulse sequences for the magic angle turning (MAT) experiment. τ is any integral number of rotor periods (except a multiple of three rotor periods). During the measurement, one rotor period was used.

- a) the $3\text{-}\pi$ MAT pulse sequence.
- b) the dipolar dephased $3\text{-}\pi$ MAT pulse sequence.
- c) the original MAT pulse sequence used by Gan where D is a time period determined by probe ring-down and receiver recovery.

Figure III.2.2. a) The 2D contour plot spectrum of 1,2,3-TMB obtained using the original MAT pulse sequence in Figure III.2.1c at a sample spinning rate of $44\pm 0.025\text{Hz}$. The dead time Δ is found to be $30\text{ }\mu\text{s}$ in this system. No line broadening was applied in either dimension. This spectrum was acquired using the following parameters: contact time 4 ms, recycle delay 8 s, t_1 increment $120\text{ }\mu\text{s}$ (three times the acquisition dimension), 110 increments acquired with 64 scans in each increment (i.e., 32 scans in each of the real and the imaginary FID for that t_1 time). Total experiment time was about 16 hours. The decoupler offset was set to the middle of the aromatic proton chemical shifts in order to improve the lineshape of the protonated aromatic carbons. b) the isotropic chemical shift spectrum which is the summed projection of the data onto the isotropic chemical shift axis.

Figure III.2.3. a) The 2D contour plot spectrum of 1,2,3-TMB obtained using the $3\text{-}\pi$ MAT pulse sequence in Figure III.2.2a at a sample spinning rate of $44\pm 0.025\text{Hz}$. The experimental parameters are the same as those for Figure III.2.2 except 140 increment was used and the total experiment time is about 20 hours. The time period Δ is chosen as $60\text{ }\mu\text{s}$. No line broadening was applied in either dimension. b) the isotropic chemical shift spectrum obtained from a. c) the resultant powder pattern for each carbon.

Figure III.2.4. a) The isotropic chemical shift projection spectrum for 1,2,3-TMB obtained by using the dipolar dephasing $3\text{-}\pi$ MAT pulse sequence in Figure III.2.2b with a dephasing time of $2^*DD=60\text{ }\mu\text{s}$ and $p_3=4\text{ms}$. The other experimental parameters are the same as those for Figure III.2.4. b) the resultant powder patterns for the nonprotonated aromatic as well as the methoxy carbons.

Figure III.2.5. a) The isotropic chemical shift projection spectrum for 1,2,3-TMB obtained by using the $3\text{-}\pi$ MAT sequence with a short contact time of $60\text{ }\mu\text{s}$.

Figure III.2.6. a) The 2D contour plot spectrum of Pocahontas coal obtained using the $3\text{-}\pi$ MAT pulse sequence at a sample spinning rate of $44\pm 0.025\text{Hz}$ with Δ chosen as $60\text{ }\mu\text{s}$. No line broadening was applied in both dimensions. The experimental parameters are: contact time 2 ms, recycle delay 2s, t_1 increment of $93.75\text{ }\mu\text{s}$ with 25 increment acquired, 512 scans per complex pair. The total measuring time is about 8 hours. b) the isotropic chemical shift spectrum.

Figure III.2.7. The powder patterns for several selected isotropic chemical shift positions in Pocahontas coal obtained by different MAT techniques. (a) and (b) were obtained from Figure III.2.6. (c) was obtained from a short contact time $3\text{-}\pi$ MAT experiment with a contact time of $50\text{ }\mu\text{s}$. (d) and (e) were obtained from a dipolar dephasing $3\text{-}\pi$ MAT experiment with a dipolar dephasing periods of $2^*DD=60\text{ }\mu\text{s}$ and $p_3=1.5\text{ms}$.

Figure III.2.1. The pulse sequences for the magic angle turning (MAT) experiment. τ is any integral number of rotor periods (except a multiple of three rotor periods). During the measurement, one rotor period was used.

- the 3π MAT pulse sequence.
- the dipolar dephased 3π MAT pulse sequence.
- the original MAT pulse sequence used by Gan where Δ is a time period determined by probe ring-down and receiver recovery.

Figure III.2.2. a) The 2D contour plot spectrum of 1,2,3-TMB obtained using the original MAT pulse sequence in Figure 1c at a sample spinning rate of 44 ± 0.025 Hz. The dead time Δ is found to be $30 \mu\text{s}$ in this system. No line broadening was applied in either dimension. This spectrum was acquired using the following parameters: contact time 4ms, recycle delay 8s, t_1 increment $120 \mu\text{s}$ (three times the acquisition dimension), 110 increments acquired with 64 scans in each increment (i.e., 32 scans in each of the real and the imaginary FID for that t_1 time). Total experiment time was about 16 hours. The decoupler offset was set to the middle of the aromatic proton chemical shifts in order to improve the lineshape of the protonated aromatic carbons.
 b) the isotropic chemical shift spectrum which is the summed projection of the data onto the isotropic chemical shift axis.

Figure III.2.3. a) The 2D contour plot spectrum of 1,2,3-TMB obtained using the 3π MAT pulse sequence in Figure 2a at a sample spinning rate of 44 ± 0.025 Hz. The experimental parameters are the same as those for Figure 2 except 140 increment was used and the total experiment time is about 20 hours. The time period Δ is chosen as $60 \mu\text{s}$. No line broadening was applied in either dimension.
 b) the isotropic chemical shift spectrum obtained from a.
 c) the resultant powder pattern for each carbon.

Figure III.2.4. a) The isotropic chemical shift projection spectrum for 1,2,3-TMB obtained by using the dipolar dephasing $3-\pi$ MAT pulse sequence in Figure 2b with a dephasing time of $2*DD=60\mu s$ and $p_3=4ms$. The other experimental parameters are the same as those for Figure 4. b) the resultant powder patterns for the nonprotonated aromatic as well as the methoxy carbons.

Figure III.2.5. a) The isotropic chemical shift projection spectrum for 1,2,3-TMB obtained by using the 3- π MAT sequence with a short contact time of 60 μ s.

Figure III.2.6. a) The 2D contour plot spectrum of Pocahontas coal obtained using the $3\text{-}\pi$ MAT pulse sequence at a sample spinning rate of $44 \pm 0.025 \text{ Hz}$ with Δ chosen as $60 \text{ }\mu\text{s}$. No line broadening was applied in both dimensions. The experimental parameters are: contact time 2 ms , recycle delay 2 s , t_1 increment of $93.75 \text{ }\mu\text{s}$ with 25 increment acquired, 512 scans per complex pair. The total measuring time is about 8 hours. b) the isotropic chemical shift spectrum.

Figure III.2.7. The powder patterns for several selected isotropic chemical shift positions in Pocahontas coal obtained by different MAT techniques.
 (a) and (b) were obtained from Figure 6.
 (c) was obtained from a short contact time $3-\pi$ MAT experiment with a contact time of $50\mu\text{s}$.
 (d) and (e) were obtained from a dipolar dephasing $3-\pi$ MAT experiment with a dipolar dephasing periods of $2*DD=60\mu\text{s}$ and $p_3=1.5\text{ms}$.

TASK II

Project II.2

MICROSCALE SIMULATION OF HIGH PRESSURE THERMAL AND CATALYTIC CONVERSION PROCESSES IN COAL AND WASTE POLYMERS WITH ON-LINE GC/MS

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Microscale Hydropyrolysis Simulation by High Pressure TG/GC/MS (Kui Liu, Wen Hu Du)

The high pressure TG/GC/MS system is shown in Figure IV.2.1. The quartz crucible holding the sample was modified as illustrated. The open hole in the bottom increases the sensitivity of the system by a factor 5-10, thus permitting the use of smaller samples. The thermal decomposition of Blind Canyon DECS-6 coal as well as of 1:1 mixtures of coal with polymer samples was studied under various conditions as listed in Table IV.2.I. The catalyst used was 1% Fe as iron chloride hexahydrate $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]$ promoted with 0.05% Mo in the form of ammonium tetrathiomolybdate $[(\text{NH}_4)_2\text{MoS}_4]$, as prepared and provided by Dr. Anderson and his co-workers. The thermogravimetric profiles in Figure IV.2.2 illustrate the effects of hydrogen and of catalyst on the decomposition of the original coal samples. The effect of hydrogen is clearly visible as a significant increase in volatiles evolution above 500 C. Adding catalyst to the coal increases the total weight loss (Table IV.2.1) by about 3-4% and, as expected, the volatiles evolution occurs at lower temperatures.

The total ion intensity profile of coal obtained in helium (thermolysis) be seen in Figure IV.2.3a indicating that the maximum rate of decomposition occurs at 480 C. Enlarging one sampling period, the total ion curve shows the separation of several compounds within the 1.22 min interval (Figure IV.2.3b). Although the resolution is insufficient in the

low MW range due to the relatively high column temperature (90 C), the extracted single ion chromatograms can be used for further analysis. Figures IV.2.3c and d show the abundance of characteristic alkenyl type (m/z 55) and alkyl type (m/z 57) fragment ions revealing the increase in alkene/alkane ratio with decreasing carbon atom number. The intensity profile of a typical alkyl phenol fragment ion (m/z 107) indicates (Figure IV.2.3e) that not only different compounds with different MW values (e.g. cresol vs. xlenol), but also certain isomers (e.g. ethyl phenol vs. dimethyl phenol) can be separated on the short column.

Figure IV.2.4 shows the effect of hydrogen reactant gas and a liquefaction catalyst on the evolution profiles of four characteristic coal conversion products. The TG curve (Figure IV.2.2) exhibits two main decomposition regions in a hydrogen atmosphere (350-520 C and ≥ 520 C). The rate of volatile evolution up to 520 C is similar in hydrogen and helium suggesting that hydrogen does not promote the devolatilization significantly in this temperature range. This assumption is confirmed by the intensity profiles of the individual ions in Figure IV.2.4. Although there are some variations in the evolution curves the overall difference does not seem to be significant in the lower temperature range. However, the formation of alkyl aromatic products (m/z 92, toluene and m/z 142, methyl naphthalene) is greatly enhanced at high temperatures in a hydrogen atmosphere. The liquefaction catalyst applied in hydrogen atmosphere increases the yield of each product. Some increase is observed in the high temperature release of alkyl aromatics in comparison with the uncatalyzed coal experiment in hydrogen. Furthermore, the catalyst promotes the formation of alkanes (as judged by the m/z 43 propyl fragment ion) and phenol (m/z 94) as well as of methyl naphthalenes at lower temperatures.

To the best of our knowledge, this is the first time that the effects of hydrogen and catalyst on coal conversion processes have been successfully observed by on-line

chromatographic and spectroscopic analysis of characteristic conversion products. Although many more experiments, (e.g. involving different coals and catalysts as well as comparisons with off-line analysis results from bench scale hydrolysis processes) need to be performed in order to validate this technique, our preliminary data with regard to specificity and reproducibility suggest that HPTG/GC/MS offers an attractive approach to screening of catalysts and, perhaps, optimization of reaction parameters. In order to determine the usefulness of the method for simulating conversion of coal/waste polymer mixtures several different polymers (polyethylenes, polystyrene) and a sample of tire rubber were analyzed in neat form, as illustrated by the TG profiles in Figure IV.2.5.

Figure IV.2.6 shows the average mass spectra of the volatiles evolved from 350 to 600 °C from coal and rubber as well as coal + rubber, with and without catalyst in a hydrogen atmosphere. The spectrum of the high volatile bituminous coal is dominated by alkenyl (m/z 41, 55, 69, 83, etc.), and alkyl (m/z 43, 57, 71, 85, etc.) type fragment ion series as well as aromatic hydrocarbons (m/z 78, benzene; m/z 91, toluene fragment ion) and phenols (m/z 94, phenol; m/z 107, cresol fragment ion). The rubber spectrum shows the formation of unsaturated hydrocarbon ions from the butadiene segments of rubber (e.g. m/z 67, methyl butadiene fragment ion) and aromatic hydrocarbons originating from the styrene moieties (e.g. m/z 91, toluene fragment ion; m/z 104, styrene). It should be noted that the oil additive of rubber may also release aromatic products. The spectra of the coal + rubber mixture (1:1 ratio) resemble the rubber spectrum at first sight because the rubber releases higher amounts of organic volatiles than the coal. The evaluation of average mass spectra is further complicated by the formation of several common products from coal and rubber (e.g. alkyl aromatics and alkenes). In spite of these difficulties it can be seen that the intensity of several ions is not additive and the presence of catalyst changes the product distribution.

More detailed information can be obtained about the effect of waste rubber and catalyst on coal hydropyrolysis by using time-resolved data. Figure IV.2.7 compares the evolution profiles of m/z 92 and m/z 94 from coal, rubber and the 1:1 mixture. The absolute intensities cannot be directly compared due to the different experimental conditions; therefore the intensities are scaled for equal height. The toluene evolution profile of the mixture (Figure IV.2.7a) appears to be the sum of the individual components. Other hydrocarbons exhibit similar behavior, however, it should be emphasized that this is not yet a quantitative comparison.

The spectra of both coal and rubber contain the m/z 94 ion, however, it represents two different compounds, phenol and heptatriene, respectively. Due to the chromatographic separation, the intensity profile of each product can be monitored separately in the mixture, as seen in Figure IV.2.7b. The heptatriene evolution occurs at about the same temperature from the rubber and the mixture. The rate of phenol formation from coal shows two maxima in hydrogen atmosphere (at about 450 C and 550 C). The presence of rubber significantly promotes the release of phenol in the lower temperature range (350-520 C).

Hydroliquefaction Microreactor with On-line GC/MS (Emma Jakob)

An obvious shortcoming of the above described HPTG/GC/MS instrument is that only coal conversion reactions in gaseous environments can be studied, thus precluding true hydro liquefaction experiments, e.g. in the presence of donor solvent. Consequently, we are now undertaking the development of a high pressure tubing reactor (HPTR) with on-line GC/MS capabilities. A similar reactor has been successfully used in our laboratory to study thermal cracking reactions in hydrocarbon jet fuels¹. A schematic diagram of the system is shown in Figure IV.2.8. The HPTR/GC/MS system can tolerate the supercritical (or subcritical) solvent

rich environments that are often encountered in coal liquefaction processes, and is easier to operate and maintain than the HPTR/GC/MS, albeit lacking the TG's capability to continuously measure remaining sample weight. The system can be operated at pressures up to 2000 psi, and temperatures up to 1000 C. The pressure of the reactor is maintained constant by a back pressure regulator. Catalytic coal liquefaction experiments with solvent such as tetralin and decalin are expected to start in the summer of 1993.

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TABLE IV.2.1
Weight Loss Data for High Pressure TG

	Fe, No Catalyst	Reactant Gas	Weight Loss, %
Coal	No	He	36.6
Coal	No	H ₂	54.6
Coal	Yes	H ₂	57.9
Coal & Rubber	No	H ₂	57.7
Coal & Rubber	Yes	H ₂	61.8
Coal & Polystyrene	No	H ₂	71.9
Coal & Plastic	No	H ₂	74.1
Coal & Polyethylene	No	H ₂	77.4
Rubber	No	He	66.6
Rubber	No	H ₂	67.5

FIGURE CAPTIONS

Figure IV.2.1. Schematic of the High Pressure TG/GC/MS system.

Figure IV.2.2. TG curves of coal and rubber under various conditions at high pressure (900 psi).

Figure IV.2.3. Thermal decomposition of coal in helium atmosphere. Total ion intensity a) in the whole temperature range; b) in a single sampling interval. Ion intensity of c) m/z 55, alkene; d) m/z 57, alkane; e) m/z 107, cresol fragment.

Figure IV.2.4. Effect of hydrogen and catalyst on the evolution profile of coal conversion products. a) m/z 43, propyl fragment, b) m/z 94, phenol; c) m/z 92, toluene; d) m/z 142 methyl naphthalene.

Figure IV.2.5. TG curves of 1:1 mixtures of coal with various polymers at high pressure (900 psi).

Figure IV.2.6. Average mass spectra of hydrolysis products of coal, rubber and coal + rubber with and without catalyst from 350 C to 600 C. (m/z 14, 28, 32, 40 are background peaks.)

Figure IV.2.7. Evolution profile of a) m/z 92, (toluene); b) m/z 94, (phenol and heptatriene) from the hydrolysis of coal, rubber and a 1:1 coal/rubber.

Figure IV.2.8. Schematic of the HPTR/GC/MS system under development for microscale simulation of hydroliquefaction reactions.

Figure IV.2.1. Schematic of the High Pressure TG/GC/MS system.

Figure IV.2.2. TG curves of coal and rubber under various conditions at high pressure (900 psi).

Figure IV.2.3. Thermal decomposition of coal in helium atmosphere. Total ion intensity a) in the whole temperature range; b) in a single sampling interval. Ion intensity of c) m/z 55, alkene; d) m/z 57, alkane; e) m/z 107, cresol fragment.

Figure IV.2.4. Effect of hydrogen and catalyst on the evolution profile of coal conversion products. a) m/z 43, propyl fragment, b) m/z 94, phenol; c) m/z 92, toluene; d) m/z 142 methyl naphthalene.

Figure IV.2.5. TG curves of 1:1 mixtures of coal with various polymers at high pressure (900 psi).

Figure IV.2.6. Average mass spectra of hydropyrolysis products of coal, rubber and coal + rubber with and without catalyst from 350 C to 600 C. (m/z 14, 28, 32, 40 are background peaks.)

Figure IV.2.7. Evolution profile of a) m/z 92, (toluene); b) m/z 94, (phenol and heptatriene) from the hydropyrolysis of coal, rubber and a 1:1 coal/rubber.

Figure IV.2.8. Schematic of the HPTR/GC/MS system under development for microscale simulation of hydroliquefaction reactions.

TASK II

Project II.3

CATALYTIC CRACKING, HYDROGENATION AND LIQUEFACTION OF COALS UNDER MILD CONDITIONS

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OBJECTIVES

For this period, the objectives of our project were as follows: (i) Determination of the particle size distribution of Fe-based coal liquefaction catalysts employing x-ray diffraction and squid magnetometry and (ii) Testing of these catalysts for liquefaction utilizing in-situ high temperature/high pressure electron spin resonance (ESR) spectroscopy. We also carried out some preliminary studies of coprocessing of coal with waste tires. Our research accomplishments in these tasks are presented below followed by a list of publications and conference presentations based on these studies.

SUMMARY OF RESULTS

(i) Catalyst characterization using x-ray diffraction and magnetometry:

The nine Fe-based catalysts used for these studies (provided by Dr. Wender's group) are listed in Table I. X-ray diffraction studies were carried out on a Rigaku diffractometer before and after drying the catalysts in air at 450°C for one hour. The positions of the Bragg peaks determine the chemical nature and widths of the peaks give the particle size. All the catalysts except Fe_7S_8 retained their chemical nature after drying, with only slight changes in particle size. On drying Fe_7S_8 showed conversion to $\alpha\text{-Fe}_2\text{O}_3$. For a particular catalyst, the particle sizes determined from different Bragg lines vary somewhat, perhaps due to the irregular shapes of the particles. The average of particle sizes obtained from all the prominent peaks along with the standard deviations (representing the spread of values from different Bragg peaks) for the catalysts are presented in Table I. Magnetization measurements from 5 K to 300 K in zero-field-cooled and field-cooled cases are used to determine the

region of superparamagnetism, followed by magnetization measurements up to 55 kOe in the superparamagnetic state to determine the particle-size distribution [1]. The mean value of the particle sizes obtained from the magnetization data is also included in Table I.

Table I. List of the anion-modified iron oxide catalysts, their preparation routes [10,11] and their particle sizes determined from x-ray diffraction analysis. (NSP= not superparamagnetic up to 300K)

Catalyst	preparation route	Particle size (Å)	
		x-ray	Magnetometry
Fe ₂ O ₃ /SO ₄ (1)	Homogeneous precipitation	110 ± 30	85 ± 5
Fe ₂ O ₃ /SO ₄ (2)	Rapid heterogen. precipitation	250 ± 35	NSP
Mo/Fe ₂ O ₃ /SO ₄	Homogeneous precipitation	140 ± 45	100 ± 5
Fe ₂ O ₃ /SnO ₂ /SO ₄	Heterogeneous precipitation	20 ± 5	95 ± 5
Fe ₂ O ₃ /MoO ₄	Heterogeneous precipitation	140 ± 20	100 ± 5
Fe ₂ O ₃ /WO ₄	Heterogeneous precipitation	290 ± 35	NSP
FeOOH/SO ₄	Homogeneous precipitation	75 ± 25	95 ± 10
Mo/FeOOH/SO ₄	Homogeneous precipitation	50 ± 20	100 ± 10
Fe ₇ S ₈		400 ± 100	NSP

(ii) In-situ ESR spectroscopy to test the activities of the catalysts:

All the nine catalysts were tested for their hydrocracking abilities of Blind Canyon coal using in-situ high temperature ESR spectroscopy of coal free radicals. The details of the technique and procedures have been given in earlier publications [2-4]. The premise of this approach is based on the generally accepted view that the DCL involves the interaction of thermally/catalytically generated free radicals in coals with the available hydrogen [5] and that at least some of these radicals are detected by in-situ ESR spectroscopy [6]. Furthermore pyrolysis and hydrogenolysis is expected to increase the free radical density N whereas hydrogenation (which involves capping of the free radicals by captured hydrogen) is expected to lower N [5-8]. Thus efficiency and activity of a catalyst could be monitored by its effect on the free radical density N under different experimental conditions and the obtained results compared with the results of the more traditional liquefaction experiments. These results, described below, show that in-situ ESR spectroscopy of free radicals provides a promising technique for the testing of Fe-based catalysts.

The loading of the coal for all the experiments were in the ratio, $\text{Fe/coal} = 1/99$, $\text{Fe/S} = 2$, and in some experiments the solvent, 9,10 dihydrophenanthrene (DHP), was also added in the ratio $\text{DHP/coal} = 2$. To determine the changes in mass during heating, thermogravimetric (TG) measurements using Metler TA 3000 system, were done for coal alone and coal mixed with elemental S and the catalysts. Fig 1. shows the remaining weight obtained from TG for coal alone, coal loaded with the catalyst $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$, and for coal loaded with the catalyst and sulfur. There is significant weight loss above 350°C , but the relative difference for the three cases is not significant. The TG data obtained for coal loaded with each of the catalysts is used in applying corrections for mass changes in the measurements of free radical densities (N is calculated per unit mass of the sample at the temperature of measurement.)

From ESR experiments the free radical densities are measured in-situ as a function of temperature in flowing hydrogen gas. The general features of the data are similar to those in bituminous coals [2-4] viz. a slight increase in N up to 100°C , followed by a decrease leading to a minimum near 300°C , and then a rapid increase in N due to thermal and catalytic cracking (stage 3). In some cases, at still higher temperatures, a fourth stage in which N again decreases with further increase in temperature also becomes evident [4].

We first consider the effect of a catalyst ($\text{Fe}_2\text{O}_3/\text{SO}_4(1)$) in the presence of elemental sulfur and DHP on the free radical density N of the Blind Canyon coal, at temperatures up to 550°C and in flowing H_2 gas, as shown in Fig. 2. As in earlier studies [2-4], the plotted $N = N_T(T/298)$ to take into account the Curie-law variation of the free radical density (N_T is the measured density at a temperature T and 298 K is the room temperature in degrees Kelvin). The results of Fig. 2 show that the addition of $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$ and S results in an increase in N , the free radical density, especially above about 300°C . On the other hand, addition of DHP lowers N up to 280°C and above this temperature, there is no significant effect of DHP. A separate TG experiment with DHP showed that all DHP suddenly boils off at 280°C (inset of Fig 1). This explains the null effect of DHP above 280°C and the lower N (compared to coal) below 280°C is due to hydrogenation of the free radicals by DHP. Since DHP boils off in flowing H_2 experiments, the experiments with the remaining catalysts were carried out without DHP. This also eliminates the dominant hydrogenation characteristics of DHP and it provides a convenient technique to test relative effects of various catalysts as discussed below.

From the experiments of N vs T carried out with the catalysts of Table I, we have selected three catalysts, $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$, $\text{Fe}_2\text{O}_3/\text{MoO}_4$, and FeOOH/SO_4 to present the typical results (Fig. 3) and the data on the Blind Canyon coal alone is also included for comparison purposes. This plot shows that in stage 3, above 300°C , the effect of the catalysts plus sulfur is to increase N at a given temperature, relative to the pure coal case. This additional increase in N can only be due to catalytic cracking in the presence of hydrogen and the magnitude of this effect is clearly different for different catalysts. This shows that this effect can be used to test the efficiency of different catalysts for hydrogenolysis or hydrocracking.

Most coal liquefaction experiments are carried out in the 350 to 450°C range and in our experiments reported here, significant changes in N are also observed in this region. To compare the catalytic cracking abilities of different catalysts, we compare the ratio $R = N_c/N_{\text{coal}}$ at 400°C , where N_c is the N value with a catalyst loading. If only thermal cracking is present, this ratio R will be unity. If $R < 1$, catalytic hydrogenation dominates and for $R > 1$, hydrogenolysis is occurring. This ratio R at 400°C for catalysts of Table I is plotted as a bar diagram in Fig. 4. Discussion of these results now follows.

The effects of the catalysts $\text{Fe}_2\text{O}_3/\text{SnO}_2/\text{SO}_4$ and $\text{Fe}_2\text{O}_3/\text{WO}_4$ on the free radical density N are similar to those of $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$ (shown in Fig 3) in that catalytic cracking begins at the lower temperature of 280°C and the ratio R at 400°C is quite high (~ 2.4). Consequently, these may be considered as good hydrocracking catalysts. The effects of Fe_7S_8 and $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$ on the variation of free radical density with temperature are similar to $\text{Fe}_2\text{O}_3/\text{MoO}_4$ (shown in Fig 3). Here the ratio R at $400^\circ\text{C} \sim 1.7$ indicating that hydrocracking abilities of these catalysts are lower than those of $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$, $\text{Fe}_2\text{O}_3/\text{SnO}_2/\text{SO}_4$ and $\text{Fe}_2\text{O}_3/\text{WO}_4$. On the other hand, the goethite based samples viz. FeOOH/SO_4 and $\text{FeOOH}/\text{Mo}/\text{SO}_4$ have essentially negligible catalytic activity and for these samples R is close to unity ($R=1.3$ for FeOOH/SO_4 and $R=1$ for $\text{FeOOH}/\text{Mo}/\text{SO}_4$) at all temperatures.

A major conclusion of the above results is that measurements of the free radical density N versus T and consequently the ratio R has provided a clear distinction between the effects of different catalysts. These conclusions can then be compared with the results of more traditional coal liquefaction experiments, whenever available. This comparison is discussed next using the results of Pradhan et al [9,10] who used these catalysts for the liquefaction of Blind Canyon coal at 400°C in 1000 psi of hydrogen and with tetralin as the donor solvent.

The work of Pradhan et al [9,10] showed that FeOOH-based catalysts in coal liquefaction experiments yield less oil as compared to experiments when Fe₂O₃-based catalysts are used. These findings are consistent with our results discussed above. Pradhan et al [9,10] attribute this difference to the fact that Fe₂O₃-based catalysts retain their small particle size better under liquefaction conditions while FeOOH agglomerates under these conditions. They also found that for the yield of oils, molybdated and tungstated hematite-based catalysts are better than sulfated iron oxides. Our ESR based results show Fe₂O₃/SO₄(1), Fe₂O₃/WO₄, and Fe₂O₃/SnO₂/SO₄ have the high R ratio of about 2.4 for hydrocracking, followed by R ~1.7 for Fe₂O₃/MoO₄, Mo/Fe₂O₃/SO₄ and Fe₇S₈. Although there is a general consistency among the two sets of experiments, we caution that hydrogenation effects of the catalysts, if present, would tend to lower the free radical density and hence the ratio R. Mo and W can form sulfides under liquefaction conditions which are strong hydrogenation catalysts, besides the hydrocracking abilities of the starting catalysts. This may be the reason for some of the minor discrepancies between the two sets of experiments. In our future work, we plan to test these catalysts with a hydrogen donor such as DHP under 600 psi pressure of hydrogen. With such experiments, we hope to separate the hydrocracking and hydrogenation effects.

The results presented here have demonstrated that the hydrocracking abilities of the different Fe-based catalysts for coal liquefaction can be quantified by the free radical density ratio R and that the conclusions drawn from the ratio R are in good agreement with those obtained from direct liquefaction experiments (e.g., both experiments show that geothite-based catalysts are less effective in coal liquefaction than oxide-based catalysts). In-situ x-ray diffraction experiments are needed to determine any chemical changes that the catalysts might undergo under liquefaction condition and ESR experiments under high pressure of hydrogen are needed to investigate the hydrogenation process. Both sets of these experiments are planned for the near future.

(iii) Investigation of the coprocessing of coal with waste tires by ESR spectroscopy and thermogravimetry:

We have investigated the coprocessing of coal with waste tire rubber employing thermogravimetry and in-situ ESR spectroscopy of free radicals. The tire polymer used in these experiments was chipped from a used tire (Goodyear Vector) and it was mixed with the coal in

1:1 ratio with mortar and pestle. Samples were cut from the center and rim portions of the tire and in separate TG and ESR experiments we did not find significant differences in the results between them. For the ESR experiments, samples were either vacuum sealed in the ESR tube at room temperature followed by measurements at elevated temperatures or measurements were done in flowing H_2 gas [2,3]. We also measured the weight loss in thermogravimetry in flowing H_2 gas using Mettler TA3000 system.

Fig. 5 shows the remaining weight (%) as a function of temperature for the Blind Canyon coal, the tire and the tire coal mixture in a flowing H_2 experiment. Most of the weight loss due to release of volatiles occurs between 300 and 500°C and it is clearly evident that the coal-tire mixture has the highest weight loss. If we use the weight loss due to volatiles as the percentage conversion, then at 500°C, the percentage conversions for coal, tire and coal-tire respectively are 32%, 48% and 66%. The presence of tire polymers has clearly enhanced the percentage conversion of coal.

In ESR spectroscopy, only a single line is observed from the coal sample and no ESR signal was observed from the tire as determined in a separate experiment up to 500°C. In Fig. 6, we show the temperature variation of the free radical density N for the coal and the coal-tire mixture in flowing H_2 gas. It is clearly evident that the tire has considerable effect on the coal free radicals. The following points are noteworthy.

At the lower temperatures of around 100°C, there is a slight increase in N due to the effect of tire. Above 400°C, the N values in the presence of tire polymer are suppressed by a factor of two to three. This rapid decrease in the free radical density at the higher temperatures (Fig. 6) is most likely due to hydrogenation facilitated by the transfer of hydrogen from tire polymers to coal fragments [8]. The liquefaction experiments of Farcasiu and Smith [11] carried out 425°C and those of Liu et al [12] at 400°C with waste tires also showed higher conversion of coal coprocessed with tires. Thus our results show that waste tires coprocessed with coal lower the free radical densities above 400°C, and increase the evolution of volatiles and that the tires act as excellent hydrogen donors.

Similar experiments in coprocessing coal with polyethylene and polystyrene indicated rapid hydrocracking of coal. These findings are positive indicators for improved liquefaction of coals in the presence of tires and polymers. These results on coprocessing coal with waste tires

and polyethylene and polystyrene have been communicated for publication in the forthcoming ACS preprints.

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Fig. 1. Remaining weight(%) plotted as a function of temperature for coal, coal loaded with $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$, and coal loaded with $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$ and S. (The loadings were in the ratios, $\text{Fe}/\text{coal} \approx 1\%$, $\text{Fe}/\text{S} = 1/2$ and $\text{coal}/\text{DHP} = 1/2$.) The inset shows rapid boiling of DHP by 280°C in hydrogen flow.

Fig. 2. Variation of free radical density, N for unloaded blind canyon coal, coal loaded with $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$ and S, and coal loaded with $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$, S and DHP.

Fig. 3. Variation of N versus temperature for coal and coal loaded with $\text{Fe}_2\text{O}_3/\text{SO}_4(1)$, $\text{Fe}_2\text{O}_3/\text{MoO}_4$, and FeOOH/SO_4 .

Fig. 4. The experimental ratio $R = N_c/N_{\text{coal}}$ at 400°C for different catalysts (N_c is the free radical density of a catalyst loaded coal).

Fig 5. Remaining weight as a function of temperature for coal and coal tire mixtures (1:1 by weight). Tire(C) and tire(R) are cut from the central and rim portions of the tire. All measurements were done in flowing hydrogen.

Fig. 6. Variation of free radical densities with temperature for coal and coal-tire mixtures (1:1 by weight). Measurements were done under hydrogen flow. Free radical densities are corrected for changes in mass.

TASK II

Project II.4

ESR and ENDOR INVESTIGATION FOR COAL LIQUEFACTION UNDER MILD CONDITIONS

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INTRODUCTION

This annual report summarizes our research activities and accomplishments during May 1, 1992 through April 30, 1993. This period constituted the concluding year of our project, wherein our goal has been to obtain an enhanced understanding of the fundamental steps in the chemistry of coal liquefaction under mild conditions---low reaction temperature and pressure. Our working hypothesis has been that free organic free radicals (i.e., chemical entities bearing unshared electrons, therefore high chemical reactivity) play a key role in the mechanism of coal liquefaction, especially under homogeneous catalysis conditions. A strong support for our hypothesis has been provided by the pioneering studies of Farcasiu and coworkers¹. From their results on model compounds such as 1,2-di-1-naphthylethane (DNM), compound I here, these authors have suggested that radical cation species play the key roles in the mechanism of intramolecular bonds in such compounds¹. However, Farcasiu's evidence in support of this hypothesis was only indirect, since no direct spectroscopic data were cited¹. Since ESR and ENDOR spectroscopies are known to be the most direct techniques for characterizing free radical species, we proposed that such studies be carried out on compounds such as DNM, and related model compounds.

II. Experimental Techniques

A. ESR/ENDOR Measurements

All ESR and ENDOR measurements were made at the X-band (9.5 GHz) microwave frequencies utilizing the modified Bruker ER300D ESR/ENDOR spectrometer system. Over the years we have developed accessories for carrying out in-situ ESR investigations at

temperatures up to 800 °C, and ENDOR measurements up to 250 °C. In our system, the microwave frequency is measured with a Hewlett-Packard digital frequency counter, model 5430A, whereas the magnetic field is calibrated with an NMR gaussmeter. For liquid samples, the radicals are produced via reaction with triflic acid or a sodium/potassium reduction procedure. A methodology was developed for radical generation and ESR/ENDOR measurements under various gaseous atmospheres, including under a vacuum or an argon atmosphere.

B. Photochemical / Product Analysis Measurements

Photochemical reactions were carried out utilizing a mercury lamp-based reactor developed in our laboratory. Excitation was obtained at preselected wavelengths utilizing various cut-off filters. Product identification was carried out by gas chromatography, NMR, and mass spectrometry, utilizing laboratory-synthesized model compounds.

III. RESULTS AND DISCUSSION

During the past few months, we have investigated the bond cleavage mechanisms of polycyclic aromatic model compounds in order to better understand catalyst functions. Our approach towards understanding the bond cleavage mechanisms of polycyclic aromatic compounds has involved a dual pathway to elaborate the desired information. In the first pathway, independent generation of important reactive intermediates has been attempted in order to accurately assess their reactivity. A second approach has been to characterize the proposed radical intermediates by ESR techniques.

The mechanistic problem arises from the products isolated from a series of naphthylated model compounds which were subjected to coal liquefaction conditions with various catalysts which have been prepared elsewhere in the Consortium. Model compound I (i.e., 1,2-di-1-naphthylethane (DNM)) is shown in Figure 1 and is representative of the reactivity of this set of model compounds in that bond A cleavage is always observed. Bond A is the bond connecting the naphthyl group to the alkyl side chain. The bond A cleavage has been rationalized as originating from a radical cation, based on the observation of catalytic activity, the appearance of a surface charge on the catalyst at the same temperature as the onset of catalytic activity,¹ and theoretical calculations which indicate the least electron density in

Figure (1)

catalytic conditions. 1,2-di-1-naphthylethane is representative in that bond A is the predominate bond being cleaved under catalytic conditions. This result is shown in Figure (1). While the radical cation explanation of catalyst reactivity is attractive, the results of these naphthylated compounds are in apparent contradiction to the known reactivity of monoaryl systems. We report here results from the bond cleavage reactions of the radical cation of 1,2-di-1-naphthylethane (DNM) which appear to contradict the reactivity pattern postulated above.

Independent generation of the radical cation of DNM has been attempted by several routes. The first method for generating the radical cation utilized a well-known and accepted photochemical procedure in which an oxidant is created by photochemical excitation. This reactivity has been included in previous reports from this group and shows conclusively that the radical cation of 1,1,2,2-tetraphenylethane (TPE) cleaves only bond B. Following the same procedure that was used for TPE, 9,10-dicyanoanthracene was irradiated in a solution containing DNM. In analogy to reactions of 1,2-diphenylethane, no bond cleavage was observed which could be attributed exclusively to the radical cation of DNM, indicating that the bond dissociation energy of the radical cation must be somewhat high. An alternative method of generating the radical cation of DNM utilized the reaction of ferroin (i.e., $\text{Fe(III)(1,10-phenanthroline)}_3^{+3}$) with DNM in acetonitrile at 130°C. Only preliminary data are available on mass balance at the current time. Gas Chromatography results of the reaction shown in Figure (2) have been presented at the 1993 Annual Technical Meeting.

Since 74% of the reaction mixture resulting in two products which can only arise via Bond B cleavage were quantified, we conclude that a minimum of 37% of the radical cation reactivity at 130°C proceeds via bond B cleavage. Extensive efforts have been made to obtain an HPLC separation of the products, but so far our efforts have failed. A third method of examining the reactivity of the radical cation is to examine the mass spectral splitting pattern. From the ratio of the bond B cleavage products to the bond A products, a minimum ratio of 300:2 could be obtained for the reactivity of the gas phase radical cation of DNM.

Figure (2)

Since the quantification of the reaction did not proceed as desired, we have synthesized 1,1,2,2-tetranaphthylethane (TNE). Both photochemical and Fe based methods for radical cation generation proceed smoothly to yield products which can be easily characterized. The products are 1,1-dinaphthylmethane and 1,1-dinaphthyl-1-methoxy-methane, exactly analogous to those produced in corresponding reactions of TPE. Thus, there are no *a priori* differences in reactivity of the radical cations which lead us to believe that naphthyl containing polycyclic aromatic radical cations react differently than their phenyl counterparts. We are still attempting to get good mass balances from these reactions in order to make definitive statements.

Our second approach to understanding the reactions of radical cations is to identify them by ESR spectroscopy. In order to identify the radicals, appropriate methods of generation must be determined and the structures of easily identifiable intermediates must be conclusively identified. Representative of our efforts in this area is the spectrum of 1-methylnaphthalene shown below. It is apparent that sufficient fine structure exists to enable us to conclusively identify the radical when the resolution is optimized. However, the large number of nonequivalent hydrogens in this compound make an exact identity uncertain at the present time. (Other possible species in solution are the 1-methylnaphthalene radical or a dimeric radical cation species.) We have attempted to reduce the number of nonequivalent hydrogens by introducing symmetry into the molecule (e.g., 2,6-dimethylnaphthalene, 1,8-dimethylnaphthalene). However, producing spectra at this resolution has not yielded to our hands yet. Another approach for obtaining higher resolution was through ENDOR measurements. Strong ENDOR signals were easily obtained from radical cations and anions of the unsubstituted, symmetric model compounds naphthalene, anthracene and tetracene. However similar measurements were not successful on radicals obtained from compounds such as 4-(1-naphthylmethyl)-bibenzyl even in the powdered lattice, possibly because of the low ESR spectral intensity and/or fast electronic spin-lattice relaxation times. Efforts will be continued to complete these studies in the near future provided funding will be obtained.

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TASK II

Project II.5

XPS STUDIES OF RAW, CATION EXCHANGED AND LIQUEFIED CATION EXCHANGED LIGNITE COALS

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Introduction

X-ray photoelectron spectroscopy (XPS) has been used to investigate the surface characteristics of lignite coals and lignites that contain cation-exchanged iron. Cation exchanged lignite residues that have been processed in a coal liquefaction reactor have also been investigated. Beulah and Hagel lignite coals were used for this purpose. It has been reported that the liquefaction oil yield of lignites that undergo a cation-exchange process in which iron is exchanged primarily for calcium, was significantly increased.¹ The oil yield from the ion exchanged lignites was increased by 25% (for Beulah) and 10% (for Hagel) compared to the yield obtained by physically mixing 30Å ultrafine iron catalyst particles in the oxyhydroxide form with the coal samples. XPS studies of the two lignites confirm that the Fe and O concentration was generally increased after the ion exchange process. The increase of oxygen concentration in the ion-exchanged lignite is due to the majority of the iron particles being present in the oxyhydroxide form (FeOOH) after the ion exchange process. Sputtering with Ar⁺ ions followed by XPS depth profiling analysis has also been carried out to determine the distribution of the major elements in the surface and bulk regions of the coal particles. The elemental composition of each of the raw, cation-exchanged and liquefied lignite residues was found to change as the time of Ar⁺ sputtering increased. A systematic trend towards higher atomic concentrations of C and Fe was observed for the raw coals, the ion exchanged coals and the liquefied coal residues as the sputtering time increased. However, the surface concentrations of O and Si decreased consistently for all the coal samples as the sputtering time

increased.

Experimental

The two lignites used were Beulah (obtained from Department of Energy Coal Samples, DECS-11) and Hagel (obtained from Penn. State Office of Coal, PSOC-1482). These lignites were cation exchanged by stirring a slurry mixture of the lignite and ferric acetate $[\text{Fe}(\text{OOCCH}_3)_3]$ in a 10 liter fermenter wherein iron was exchanged mainly for calcium. The lignites were then subjected to liquefaction experiments. These liquefaction experiments were aimed at investigating the effect of ion exchanged iron catalysts on the total yield and product distribution in the liquefaction process.

Three samples each from Beulah and Hagel lignites were studied. They were raw Beulah and Hagel coal, ion exchanged coal and residue from liquefaction (for both Beulah and Hagel lignites). The particle sizes of the powdered samples were less than 200 mesh. The powdered samples were mounted on the spectrometer probe tip by means of a double sided adhesive tape. The samples were pressed with the help of a metallic spatula (cleaned thoroughly with acetone and distilled water) so that the coal powders stuck to the adhesive tape. The excess powder was carefully tapped off. To exclude the possibility of getting unwanted photoionization signals from the tape, a separate XPS analysis was carried out for the tape alone and it was found that the constituents of the tape were not detected by XPS. After heat treating at 65 °C for 10 hours in a pretreatment chamber to remove remaining volatile materials from the coal residues, the samples were inserted into an ultrahigh vacuum chamber for surface analysis.

The samples were examined by XPS using a Kratos XSAM 800 spectrometer. Mg $K\alpha$ (1253.6 eV) radiation was used and a fixed retarding ratio (FRR) mode at a pass energy of 12 kV and 13 mA was employed. Under these conditions, the full width at half maximum (FWHM) of the Ag ($3d_{5/2}$) peak is 1.1 eV. The system pressure was normally maintained below 3×10^{-8} torr using a 300 1/sec ion pump and Ti sublimators to minimize contributions from the vacuum contaminants.

To compensate for sample charging, carbon 1s at 285 eV were taken as a

reference. Elemental concentrations were obtained from peak areas and corrected for atomic sensitivity factors. Also radiation damage to the samples due to the long time exposure to the X-ray beam was not observed.

In situ Ar⁺ ion sputtering of the residue samples was carried out using a differentially pumped and computer controlled 3M mini-beam ion gun. The incident ion gun was operated at 3.5 keV and sample currents were kept around 3 μ A across a sample area of about 5x5 mm². The estimated etching rate of ca. 50 Å/min was determined from a SiO₂ standard film. The pressure in the main chamber was kept below 4x10⁻⁶ torr during ion sputtering. After ion sputtering, a consistent increase in the FWHM for all elements was found with increasing ion dose. No compensation was made for charging of the sample after Ar⁺ sputtering.

Results and Discussion

Surface Characterization of Hagel Lignites

The individual XPS surface scans were carried out on the raw, ion exchanged and liquefied Hagel residue coal samples. The surface XPS spectra showed a distinct peak for each of the major elements, carbon, oxygen, and silicon as well as the minor components, sulfur, iron and calcium in each sample. The binding energies of these elements showed the expected values for the most stable oxidation states. The raw and ion exchanged samples showed a S 2p peak split into two small background photolines at 170 eV and 164 eV, respectively. The higher binding energy photoline can be ascribed to the oxidized form of sulfur (sulfate) and the peak at 164 eV corresponds to the inorganic sulfide and other sulfidic forms. The surface of the Hagel samples seemed to be oxidized to a significant extent as the sulfate peak was more predominant. The iron concentration increased sharply in the ion exchanged sample (compared to the raw sample), indicating that iron has been exchanged primarily for calcium, whose concentration drops in the ion exchanged sample compared to the raw coal. It has been reported that the liquefaction oil yield of lignites that undergo a cation-exchange process in which iron is exchanged primarily for calcium, is significantly increased¹ and this was confirmed by XPS studies. Oxygen concentration also increased in the ion exchanged samples, due to the iron being present primarily

in the oxyhydroxide form ($\text{Fe}(\text{OOH})$). Silicon concentration dropped remarkably in the liquefied samples. Also noticeable was the decrease in iron concentration in the liquefied residue sample. This can be related to the fact that most of the iron becomes encapsulated by organic materials from the coal, as discussed in a later section of this report. The initial surface XPS elemental concentrations of the coal samples are given in Table 1. The Fe 2p peak shows the characteristic 13.6 ± 0.05 eV splitting between the $2p_{1/2}$ and $2p_{3/2}$ peaks in the ion exchanged sample. The observed splitting corresponds well with the Fe 2p peaks of Fe_2O_3 and/or FeOOH (Goethite) in model compound studies. The Fe compound on the surface of the catalyst samples can thus be ascribed to FeOOH .

Surface Characterization of Beulah Lignites

Similar surface XPS scans were carried out on the Beulah samples. The results were also quite similar to those of the Hagel samples. However the carbon concentration in the Beulah samples (except the liquefied residue sample) was higher than that of the Hagel samples. This is in accordance with the bulk analysis data. Also the surface concentration of iron in the Beulah ion exchanged sample was higher than that of the ion exchanged Hagel coal. Silicon also showed a higher surface elemental concentration for the raw and ion exchanged coal samples. A sharp drop in silicon concentration was observed in the case of the liquefied coal residue samples. This tendency corresponds well with the Fe element result. Further analysis is needed to characterize the mineral element effect on the oil yield. The initial surface XPS elemental concentrations of coal samples are given in Table 2.

Depth Profile Characterization of Hagel Lignites

In order to delineate the differences in the distribution of the elements and chemical changes between the surface and bulk, the samples were analyzed by combining Ar^+ ion sputtering with XPS measurement. For all the three Hagel samples, it was observed that a sharp drop in the oxygen concentration occurred, after the first sputtering, attributable to the air oxidation. The oxidized layer was estimated to be *approx.* 40-50 nm in thickness. An increase in Fe concentration was

observed with further Ar^+ sputtering time. This can be explained in terms of the surface iron particles being covered with an oxide layer. It can also be concluded that the iron particles are most likely encapsulated by organic materials from the coal. The silicon concentration also decreases with sputtering time. This is associated with silicon being preferentially etched over other elements. Figures 1, 2, 3 show depth elemental concentrations, as a function of etching time, of the Hagel raw, ion exchanged and liquefied coal residue samples, respectively. The Fe/S ratio was generally greater than 1 in the case of raw and ion exchanged coal but the ion exchanged coal showed much higher values than this as the time of Ar^+ ion sputtering was increased. The result is given in Figure 4. In coal liquefaction, the main role of the sulfate anion is to stabilize fine particles by retarding agglomeration and sintering of iron oxide particles. It has been reported that the oil yield from ion exchanged lignites is increased by 10 % for Hagel and 25 % for Beulah compared to the yield obtained by physically mixing 30 Å ultrafine iron catalyst particles in the oxyhydroxide form with the coal samples. This is due to lack of agglomeration during liquefaction and can be attributed to either S present in the liquefied samples (detected by XPS) or to the coal matrix, which appears to act as a substrate in preventing catalyst agglomeration.

Depth Profile Characterization of Beulah Coal

Most of the elements have the same trend in the Beulah samples as in the Hagel coal. With sputtering time, oxygen and silicon tended to decrease in concentration while carbon, iron, calcium and sulfur increased in concentration. The increase in calcium concentration was less in the beginning of the etching but with increased sputtering time (more than 30 minutes) the calcium concentration increased at a greater pace. Thus it can be said that the calcium distribution was less near the surface and was present in higher concentrations at a depth of 150nm (taking the sputtering rate to be 5 nm/min). There was a drop in oxygen concentration after the first sputtering period indicating that the surface oxides had been sputtered away. Figures 5, 6, 7 show depth elemental concentrations, as a function of etching time, of the Beulah raw, ion exchanged and liquefied coal residue

samples, respectively. The Fe/S ratio was always greater than 1 in the case of the ion exchanged coal as shown in Figure 8. EXAFS and Mossbauer studies have shown that under liquefaction conditions with dimethyl disulfide being added to catalyst/coal residue mixtures, the iron catalyst was converted to iron sulfide (pyrrhotite) within a few minutes of starting the reaction.²

Summary and Conclusion

It is apparent from this study that XPS and Depth Profiling can be used to delineate the elemental concentration distributions on a depth scale. XPS studies of the two lignites showed that the Fe and O concentrations generally increased after the ion exchange process. The increase of oxygen concentration in the ion exchanged lignites is due to the majority of the iron particles being present in the oxyhydroxide form (FeOOH) after the ion exchange process. With Ar⁺ sputtering a systematic trend towards higher atomic concentrations of C and Fe was observed for raw coals, ion exchanged coals and liquefied coal residues. However, the surface concentration of O and Si decreased consistently for all the coal samples as the sputtering time increased. The Fe/S (catalyst element) ratio was always greater than 1 in the case of ion exchanged coal samples but became less than 1 in the liquefied coal residue samples (after a sulfiding treatment).

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Table 1. XPS analysis (at. %) of Hagel coal samples

Sample	C	O	Fe	S	Ca	Si
Raw Coal	67.1	25.8	0.1	0.2	0.2	6.6
Ion Exchange Coal	64.1	27.8	1.1	0.2	-	6.8
Liquefied Coal	87.9	10.0	0.1	0.1	-	1.9

Table 2. XPS analysis of Beulah Coal Samples

Sample	C	O	Fe	S	Ca	Si
Raw Coal	76.9	18.6	-	-	0.2	4.3
Ion Exchange Coal	69.9	25.0	1.4	0.3	-	3.4
Liquefied Coal	85.8	11.3	0.2	-	-	2.7

Figure 1. Depth Profile of Element Concentrations of Hagel Raw Coal

Figure 2. Depth Profile of Element Concentrations of Hagel Ion Exchanged Coal

Figure 3. Depth Profile of Element Concentrations of Hagel Liquefied Coal Residue

Figure 4. Fe/S Ratio for Hagel Raw Coal, Ion Exchanged Coal and Liquefied Coal Residue.

Figure 5. Depth Profile of Element Concentrations of Beulah Raw Coal

Figure 6. Depth Profile of Element Concentrations of Beulah Ion Exchanged Coal

Figure 7. Depth Profile of Element Concentrations of Beulah Liquefied Coal Residue

Figure 8. Fe/S Ratio For Beulah Raw Coal, Ion Exchanged Coal and Liquefied Coal Residue

TASK II

Project II.6

COMPUTATIONAL CHEMISTRY OF MODEL COMPOUNDS AND DIRECT LIQUEFACTION CATALYSTS

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The two primary tasks undertaken during '92-93 were (i) the initiation of the microscopic study of iron-based direct liquefaction catalysts; and (ii) the completion of the study of radical hydrogen transfer (RHT) as a possible mechanism to explain selective bond cleavage in model compounds .

(i) Modeling of Iron-Based Catalysts

The development of effective, environmentally safe and economical catalysts is the key to making direct coal liquefaction a commercially viable goal. To this end, there has been a great deal of interest in sulfided iron catalysts for coal liquefaction.

Recent experimental results have lead to a greater understanding of the action of these iron-based catalysts. Pradhan, et al.¹ have shown that the presence of sulfur increases the liquefaction conversion and oil yields when starting with sulfated oxides and oxyhydroxides of iron. It is also known² that molybdenum is a more active catalyst for liquefaction than iron, that molybdenum produces a more highly hydrogenated product, and that the addition of molybdenum to the iron sulfided catalysts greatly increases the activity of the iron catalyst.³

Farcasiu, et al.⁴ have observed that the iron-sulfur systems formed in the reaction of many of the fine particle iron oxide catalysts lead to the selective hydrocracking of the bond between a condensed polyaromatic ring and an aliphatic carbon. To explain these results, Walter, et al.⁵ have proposed that in the presence of iron-carbonyl based catalyst precursors the iron dissociates hydrogen into atoms which can then insert into the naphthalene system, leading to either hydrogenation or bond cleavage. Also, from kinetic studies of the iron carbonyl catalysts Suzuki⁶ suggests that the role of the iron catalyst is to activate molecular hydrogen and transfer hydrogen to coal fragment radicals in a nonhydrogen donor solvent.

Through a charge distribution analysis study, Freund and Whang⁷ have observed that the surface of a magnetite catalyst becomes positively charged above 230°C. Between 275-410°C the surface is catalytically active toward dealkylation of 6-methyl-9-(1-methylethyl) dibenzothiophene-4-ol, suggesting that the active

magnetite surface acts as an electron acceptor. By contrast, the hematite surface remains negatively charged up to 450°C.

Microdiffraction patterns of several of the iron-sulfided catalysts suggest that the catalyst crystal is Fe_7S_8 in the $[001]_{\text{hcp}}$ orientation.⁸ Montano, et al.⁹ have proposed that the catalytic activity of pyrrhotites is the result of iron vacancies, and that hydrogen sulfide is necessary to maintain a surface with iron deficient sites.

We have investigated, through quantum chemical modeling, the possible action of an FeS catalyst toward a hydrogen molecule and other simple molecules such as toluene, as well as the influence of vacancies on such processes. Not many quantum chemical computational methods can handle large numbers of transition metal atoms. The ASED-MO method developed by A.B. Anderson,^{10,11} has been used by us in the study of the possible cleavage mechanisms of model compounds of interest to investigators in the field of direct coal liquefaction.¹²⁻¹⁵ Anderson has used the method to study ethylene hydrogenation mechanisms on Pt surfaces and ethylene and acetylene absorption on MoS_2 clusters.^{16,17} This method has also been used by Je and Companion¹⁸ to explain the Fischer-Tropsch catalytic properties of various Co surfaces. In the method one models a surface by a small number of atoms (i.e., such as the surface of a cluster of atoms). Thus, this method is ideal for the study of the small ultrafine particle catalysts and can possibly address whether the departure from bulk properties when the catalyst size approaches 10 nm is the cause of catalytic activity.¹⁹

The ASED-MO energy of adsorption of the species on the surface was calculated by computing the difference between the ASED-MO energy of the molecule adsorbed on the surface and the energy of the molecule and surface at infinite separation:

$$\text{Adsorption energy} = E_{\text{surface-adsorbate}} - (E_{\text{surface}} + E_{\text{adsorbate}}).$$

As defined here, a negative adsorption energy indicates an exothermic adsorption.

The bond dissociation energy (BDE) was found by computing the difference in the ASED-MO energies between the surface-adsorbate complex and the surface-radical complex and methyl-radical energies at infinite separation. As defined for the adsorption of toluene, the BDE expression would read

$$\text{BDE} = (E_{\text{CH}_3\cdot} + E_{\text{surface}\cdot\text{C}_6\text{H}_5\cdot}) - E_{\text{surface-adsorbate}}.$$

As can be seen, the bond dissociation energy will depend on the stability of the surface-radical complex as well as the bond strength as predicted by the overlap population of the adsorbed species. No optimization of either of the two free radical species formed upon bond cleavage was done, so these bond dissociation energies should be considered an upper bound to the 'true' value.

We have investigated the adsorption of simple aromatic ring compounds on three

different faces of an FeS cluster and on a pyrrhotite cluster. FeS has a hexagonal NiAs structure, with each Fe atom in an octahedral environment of S atoms.²⁰ The packing is a(Fe)-b(S)-a(Fe)-c(S). Pyrrhotite exhibits a similar structure with iron vacancies in alternate layers.²¹ Above 308°C pyrrhotite does not exist as a single crystal structure, but exhibits "a rather wide homogeneity range as a single solid solution Fe_{1-x}S with the NiAs structure, extending from the stoichiometric FeS to a composition of approximately $\text{Fe}_{0.81}\text{S}$."²² The Néel (antiferromagnetic ordering) temperature of FeS is 327°C. It should be noted that most of the liquefaction experiments are carried out above 350°C.²³ Thus, magnetic effects should not be relevant for the catalytic activity.

The first cluster we investigated is shown in Figure 1 and consists of 19 Fe atoms in the top layer, 12 sulfur atoms in the second layer and 19 iron atoms in the third layer for a total of 50 atoms. This face (0001) is hereafter referred to as the smooth face. This particular cluster was chosen in our initial studies because of its simplicity. The interatomic distances were chosen to correspond to those in an idealized pyrrhotite structure. The nearest neighbor distance between iron atoms in the same layer is 3.43 Å but 2.84 Å between layers. The Fe-S distance is 2.44 Å. This is to be compared with the nearest neighbor distance in bcc pure iron of 2.48 Å. While this cluster does not have the overall stoichiometry of FeS, it is representative of the correct stoichiometry in the immediate vicinity of the adsorption sites studied.

The adsorption of toluene was also investigated on a $(11\bar{2}0)$ surface. This two layer cluster, shown in Figure 2, consists of zig-zag chains of alternating Fe and S atoms and contains 28 S atoms and 20 Fe atoms for a total of 48 atoms. We have also investigated adsorption properties when the surface layer consists of sulfur atoms only. The surface of this FeS $(10\bar{1}0)$ cluster can be described as containing stepped layers of sulfur atoms. The cluster contains 27 Fe atoms and 25 S atoms for a total of 52 atoms. We have modeled the pyrrhotite structure by creating Fe vacancies in the smooth FeS cluster, as described below.

We have investigated the adsorption of toluene and 1-methylnaphthalene on the smooth FeS surface. A typical minimized geometry of the adsorbate with respect to the surface is shown in Figure 3. In this calculation the ring carbon atom of the $\text{C}_{\text{aromatic}}\text{-C}_{\text{aliphatic}}$ linkage was initially placed directly above the Fe atom in the center of the cluster. In all of the calculations the methyl group is oriented with one hydrogen down towards the surface and the other two up, as is shown in Figure 3.

Our computed results for the adsorption energy, BDE, and charge transfer for the smooth surface are summarized in Table 1. The adsorption energy of toluene to the surface is exothermic by 3.05 eV and that of 1-methylnaphthalene by 5.47 eV. With the parameters used, we observe the transfer of electron charge from the adsorbed molecules to the FeS cluster with a resultant decrease in the $\text{C}_{\text{ring}}\text{-CH}_3$ overlap population and bond breaking energy as compared to unabsorbed toluene and 1-methylnaphthalene. The transfer of charge for 1-methylnaphthalene was greater than that for toluene. The bond dissociation energy for toluene decreases upon

chemisorption from 4.25 to 2.99 eV and for 1-methylnaphthalene from 4.20 to 2.89 eV. Using unadsorbed toluene and 1-methylnaphthalene as reference points, it is observed that electron density is removed from the p_z (π) orbitals of the ring system and from the σ bond of the $C_{\text{ring}}-C_{\text{aliphatic}}$ linkage, thereby weakening the affected bond.

The adsorption of toluene was also investigated on a $(11\bar{2}0)$ surface. No stable adsorption site for toluene was found when the ring carbon of the $C_{\text{ring}}-\text{CH}_3$ linkage was initially placed above an Fe atom of this surface. However, a very weak adsorption was observed when the center of the aromatic ring was placed above an iron atom of the surface. The adsorption occurs at a distance 3.0 Å above the surface, and the adsorption energy is 0.09 eV. No charge transfer from toluene to or from the surface is observed and the charge density on the atoms in the toluene molecule resemble that of free toluene. No stable adsorption site for toluene was found on the stepped $(10\bar{1}0)$ surface with sulfur exposed when the ring carbon atom of the $C_{\text{ring}}-\text{CH}_3$ was placed directly above a surface sulfur atom.

In order to simulate the pyrrhotite iron deficient structure, the Fe atom under the ring carbon of the $C_{\text{ring}}-\text{CH}_3$ linkage was removed, thereby creating a vacancy. Toluene is not as strongly adsorbed in this case as in the pristine cluster; the energy of adsorption decreases to 1.95 eV. Also, the bond dissociation energy increases to 3.23 eV. As in the centered case, electron density is removed from the π orbitals of the aromatic system but not from the σ bond linkage.

Transition metal sulfides are used extensively as hydrotreating catalysts. To investigate the effect of FeS in such processes, we have studied the adsorption of H_2 on FeS clusters. When a hydrogen molecule is placed parallel to the stepped surface, one hydrogen atom directly above a sulfur atom and at a distance of 2.4 Å from the surface we find that the hydrogen molecule escapes from the vicinity of the surface as a hydrogen molecule. However, when the hydrogen molecule was pushed down to 1.4 Å above an exposed sulfur atom, as might occur under pressure, the hydrogen molecule dissociates and forms a pseudo- H_2S species on the surface of the stepped surface. The optimized geometry after dissociation has a H-S-H bond angle of 106° and a H-S bond distance of 1.4 Å.

We find that a hydrogen molecule (with the molecular axis parallel to the surface) is weakly physisorbed above an Fe atom on the smooth surface. No tendency for dissociation of the hydrogen molecule into hydrogen atoms is found.

Rodriguez and Baker²⁴ have recently undertaken a systematic study of the interaction of iron sulfides with hydrogen in the presence of graphite. Through an *in situ* diffraction analysis they observed the formation of pits on the graphite surface already at room temperature, even when the iron sulfide particles were not directly in contact with it. Our preliminary results suggest that reactive species are formed by the chemisorption of H_2 on certain FeS surfaces. Further work is needed to investigate whether the species so formed are released easily from the surface.

We observe that molecules with aromatic ring systems are strongly chemisorbed by Fe atoms of the FeS (0001) catalyst surface only, suggesting that there is a critical number of exposed Fe atoms necessary in order for stable adsorption to occur. Polycondensed aromatic ring compounds are more strongly adsorbed than monocyclic ring compounds. With the parameters used in the calculations, a transfer of charge from the molecule to the catalyst is observed, creating a radical cation-substrate complex and leading to a decrease in bond dissociation energies of bonds between aromatic rings and aliphatic carbons. This appears to be similar to the mechanism proposed by Farcasiu, et al.²⁵ in the context of the catalytic decomposition of 4-(1-naphthylmethyl)bibenzyl in the presence of carbon black.

(ii) Radical Hydrogen Transfer Mechanism

We had previously investigated radical hydrogen transfer (RHT) as a possible mechanism to explain the selective cleavage of C-C bonds in model compounds. In RHT a hydrogen atom is transferred from a solvent derived radical to the ipso position of an aryl-alkyl linkage of the substrate, followed by elimination of the substituent. Free hydrogen transfer may also compete with the RHT process.

In our earlier modeling RHT was studied by the addition of atomic hydrogen directly to various sites in Model I. During the current year, we extended these studies to include the transfer of hydrogen from a $C_6H_7\cdot$ radical (modeling a solvent derived radical) to the various aromatic sites in Model I. The three stages in our modeling are shown in Figure 5. The AM1 semiempirical method (within RHF with half-electron correction for radicals) was used as before.

Potential energy curves were calculated for the transfer of the hydrogen atom from the $C_6H_7\cdot$ radical in two different ways. In one series of calculations (referred to as series A below) the $C_6H_7\cdot$ radical was allowed to approach Model I until the energy started becoming repulsive. At this point the distance between the radical and Model I was held constant, and the transfer of H between the two components allowed to occur. In the other (referred to as series B) the $C_6H_7\cdot$ radical was allowed to approach Model I with no constraints along the transfer path. From the potential energy curves the barrier height for H atom transfer at positions 1-4 on Model I as labeled in Figure 6 were determined. Also, the bond dissociation energies for the dissociation of the corresponding (Model I - H) $\cdot$ radical was computed. Then, assuming that the hydrogen transfer is the rate determining step, the expected end product distributions were calculated and compared with the experimental results of Farcasiu, et al.²⁵ The results for the barrier for addition or transfer of hydrogen are compared in Table 2. It is seen that the barrier heights do not predict the preferential cleavage of the polycyclic aromatic-aliphatic linkage to be kinetically favored. The RHT mechanism as modeled in our study does not appear to explain the selective cleavage of Model I.

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Figure Captions

Figure 1. Top and side views of FeS (0001) cluster studied. The smaller spheres are the sulfur atoms and the larger spheres are iron atoms. The sphere sizes are not meant to represent the actual sizes of the atoms.

Figure 2. The zig-zag (1120) FeS cluster studied. The zig-zag chains on the top layer are marked.

Figure 3. Top and side views of toluene adsorbed on the smooth FeS (0001) surface.

Figure 4. Dissociation of the H₂ molecule on the stepped FeS (1010) surface.

Figure 5. The modeling of hydrogen transfer from the C₆H₇• radical to Model I.

Figure 6. The site labels for Model I used in Table 2.

(a) Top View

(b) Side View

FIGURE 1

FIGURE 2

(a) Top View

(b) Side View

Figure 4

Figure 5

Site	Free		Over Fe		Centered	Over Vacancy
Species	Toluene	1-methyl N	Toluene	1-methyl N	Toluene	Toluene
$-E_{\text{adsb.}}$			3.05	5.47	3.89	1.95
BDE	4.25	4.20	2.99	2.89	3.23	3.23
ΔQ to surface			$0.87e^-$	$1.68e^-$	$0.75e^-$	$0.55e^-$
$\Delta\rho_e$ from C_{aromatic}			0.1587	0.2036	0.1406	0.0875
$\Delta\rho_e$ from $C_{\text{aliphatic}}$			0.0663	0.0520	0.0005	-0.0006

Table 1 Summary of results of adsorption of toluene and 1-methylnaphthalene (1-methyl N) on FeS (0001) surface. Results for free (unadsorbed) species are included for comparison. ΔQ is the charge transfer to the surface; the last two rows give the total electron density removed from the aromatic carbon and the aliphatic carbon of the $C_{\text{aromatic}}-C_{\text{aliphatic}}$ linkage, respectively.

Barrier Heights (eV)

Pos.	H addition	H transfer	
		A	B
1	0.53	1.88	1.98
2	0.44	1.89	1.76
3	0.44	1.88	1.74
4	0.55	1.88	1.72
d _{M1-H} at highest energy		1.78Å	1.75Å 1.38Å

Table 2. Barrier heights for hydrogen addition (column 2), and hydrogen transfer in method A (column 3) and method B (column 4) (see text). The position labels are given in Figure 6.

TASK II

Project II.7

CHEMICAL CHARACTERIZATION AND HYDROGENATION REACTIONS OF SINGLE COAL PARTICLES

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No report was submitted.

TASK II

Project II.8

DEUTERIUM TRACER STUDIES OF THE MECHANISM OF THERMAL AND CATALYTIC REACTION OF 1-[4-(2-PHENYLETHYL)BENZYL] NAPHTHALENE

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INTRODUCTION

In previous reports we have described the thermolysis of 1,2-diphenylethane (DPE) and 1,2,3,4-tetraphenylbutane under D_2 (1,2). We have also described the results with 2,3-diphenyl-2,3-dimethylbutane (3). The patterns of deuterium incorporation into the reaction products and recovered starting materials in these studies were interpreted in terms of a mechanism where benzylic radicals react with D_2 to produce D atoms. These atoms then reacted in pathways that are the reverse of the processes involved in their formation and also to add to unsaturated centers in the molecules.

This mechanism suggests that a role for a catalyst in promoting cleavage of Ar-R bonds during coal liquefaction and in studies of model compounds could be simply to facilitate hydrogenation of species which might otherwise trap H atoms. For example, a catalyst may function to insure hydrogenation of the stilbene produced during pyrolysis in the diphenylethane system. In this case, cleavage of the Ar-R bonds might be promoted because H atoms produced during the reaction would have no alternative except to add with the aromatic rings or to recombine to form hydrogen.

In order to mimic the coal liquefaction process, a more complicated organic compound 1-[4-(2-phenylethyl)benzyl] naphthalene (NMBB) has been proposed and studied in some detail (4). The experiments conducted by Farcasiu and Smith (4) utilized a sealed sample tube. The results showed that under thermal reaction

conditions, 56% of the products result from breaking the d-bond in the reactant (Figure 1); under catalytic conditions, about 80-90% of the products are a result of breaking the a-bond.

It is interesting to know what kind of behaviors this model compound will have under coal liquefaction condition; that is, in the presence of H_2 , solvent and catalyst. A conventional coal liquefaction catalyst (sulfided cobalt-molybdenum-alumina) as well as some other catalyst have been used in this study. To eliminate the uncertainty regarding the catalytic properties of the metal reactor, we have used a glass reactor as was described previously (1,5).

RESULTS AND DISCUSSION

Thermolysis of NMBB under D_2

NMBB was synthesized by the procedure outlined in Scheme 1. The synthetic procedure is given in detail in the Experimental Section.

Scheme 1: Synthesis of NMBB

NMBB underwent thermolytic reaction at $400^\circ C$ to give benzene 1, ethylbenzyl naphthalene 2, toluene 3, methylbenzyl naphthalene 4, ethylbenzene 5, enzynaphthalene 6, bibenzyl 7, methylnaphthalene 8, methylbibenzyl 9, and naphthalene 10. These products derived from bond breaking as indicated in Figure 1. Even at temperatures as low as $400^\circ C$, significant amounts of p-xylene (11) was produced. This probably is due to the secondary cleavage of 4. The formation of

ethylmethylbenzene 12 can be explained by a secondary reaction, the cleavage of 2. Tetrahydro-NMBB 13 and naphthylmethylstilbene 14 are also present as major products. At 425°C and 450°C, the conversion was higher and the relative amount of each product changed, probably due to the secondary reactions. The product distribution for these runs are given in Table 1. Assuming a first order reaction for the thermolysis of NMBB under D₂, an Arrhenius plot yielded a straight line as indicated in Figure 2.

As can be seen from the data in Table 1, when N₂ was used rather than D₂, the conversion was similar, but the amount of 14 was increased. In addition, a significant amount of methylstilbene was produced in this run. This is understandable from our previous studies which showed that radicals formed from primary cleavage react with NMBB to produce 14. This is because NMBB is the only hydrogen source when nitrogen is used.

For the thermolysis of DPE, the formation of ethylbenzene and benzene can be explained by a reaction of DPE with a hydrogen atom, produced by the reaction of a benzylic radical with H₂; in the absence of H₂ (in the presence of N₂), those products were not formed. In the case of NMBB, the products derived from breaking a, b, c, d, and e-bonds are formed in the presence of N₂, but the amounts of them are smaller than that in presence of D₂.

The data in Table 2 summarize the selectivity for bond breaking of NMBB. To make these calculations, we take the amount of 1 as representative of e-bond breaking, simply because this compound is not subject to secondary cleavage. The same argument applies for 3, 5, 7 and 10. Secondary cleavage of 2 gives 10 and 12, which are present even at 400°C. A similar reaction can also occur in the case of 4, which generates 10 and 11. These reactions make a calculation of a-bond breaking more difficult because 10 can result from a-bond breaking as well as other secondary reactions, and 9 can be subject to secondary reactions. Here, the average of 9 and 10 is considered to be representative of a-bond breaking. The amounts shown in Table 2 may not have sufficient quantitative accuracy of the cleavage of each bond; however, for a qualitative discussion, the trend is clear: under thermal conditions, $d \gg a > c = e = b$.

The major compounds from the thermolysis of NMBB in the presence of D_2 are toluene, 3, methylbenzyl-naphthalene, 4 and unconverted NMBB. The deuterium incorporated into these compounds, summarized in Table 3, show that as the temperature increases from 400°C to 450°C, deuterium incorporation increases. However, the increase is much greater for NMBB than for toluene and 4. A similar amount of deuterium was observed in DPE in each case. For the 450°C runs, the D/mol in DPE at 30 minutes is about 7 times greater than at 8 minutes, while it is only 3 times greater for toluene (5).

Considering the 20 kcal/mol difference in the H-H bond and C-H bond in BDE (6), the benzylic radical formed in the first step of this reaction is more likely to react with the H atom from NMBB (eq. 1) than with D_2 .

The NMBB radical thus formed can react with D_2 gas as shown in equation 2 to generate a $D\cdot$ atom.

The active $D\cdot$ atom can then promote Ar-R bond cleavage as shown by equation 3.

Because the reverse of reaction (2) is energetically favorable, it seems likely that the NMBB radical will be formed again resulting in H/D exchange. The above mechanism can explain why under thermal conditions, NMBB exhibits more deuterium incorporation than toluene; it can also explain why the Ar-R bond is broken less frequently than the d-bond, simply because there is not enough D atoms present.

The Thermolysis of NMBB in the Presence of a Catalyst

Thermolysis of NMBB was undertaken using several catalysts in the presence or absence of a solvent. The reaction conditions and the conversions are summarized in Table 4, the selectivity for the bonds broken are summarized in Table 5 and the deuterium incorporation data are given in Table 6. From the data in these tables, several conclusions are possible:

1. As expected, when 10% of a catalyst was added, the conversion was increased. Based on just the conversion data, a conventional coal liquefaction catalyst, sulfided Co-Mo-alumina, is the best one. Unsulfided Co-Mo-alumina has a high catalytic activity but it is not as active as the sulfided catalyst. A 30% Co catalyst (G-67) was mistakenly used in one run and this catalyst also increased the conversion. It is difficult to determine whether the graphized carbon increased the conversion, but based on the selectivity of the bonds broken, it appears to be a catalyst.

2. In the presence of a catalyst, bond-breaking is very different from the runs without a catalyst. Under thermal reaction conditions, about 60-80% of the NMBB is converted by breaking the d-bond. However, under catalytic conditions, about 80-90% of the NMBB is converted by breaking the a-bond in the case of the sulfided Co-Mo-alumina catalyst, and about 60-80% for the unsulfided Co-Mo-alumina. When the Co catalyst was used, about 60% of the a-bonds and 30% of the b-bonds were broken. For graphized carbon, the bonds broken were: a-bond, 40%; b-bond, 20%; and d-bond, 30%.

3. The cleavage pattern of NMBB in the presence of dihydrophenanthrene (DHP) different from the ones obtained for runs in the absence of solvent and in the runs with a catalyst. If we take the ratio [d-bond broken/a-bond broken] as a measure of the catalytic activity, the value obtained for runs with DHP present but no catalysts falls in the middle of the range of values (Table 7). From the data in Table 7, it may be concluded that in the presence of DHP, whether the reaction was run under D_2 (or H_2) or in a sealed tube, the cleavage of NMBB differs from that of the thermal condition with neat reactant. It is believed that the breaking of the a-

bond in the presence of DHP is because of the radical mechanism shown in equation 4.

The radicals formed in the initial step of the thermolysis of NMBB can abstract an H atom from the DHP, a good H atom donor, and the DHP radical is formed. The DHP radical can abstract an H atom from another molecule of DHP; also it can abstract an H atom from either the aromatic or aliphatic groups of the unconverted NMBB. If the H atom was abstracted from the naphthalene ring of NMBB, the radical that was formed certainly can promote a-bond breaking by β -bond scission.

4. The data in Table 4 show that there is no difference in either conversion or the selectivity of bond breaking when DHP or phenanthrene is used as the solvent. These preliminary results also indicate that there is very little, if any, difference between the results using DHP/phenanthrene as solvent and those with neat NMBB. In the thermolysis of NMBB the solvent is not as important as in the coal liquefaction process, in which the conversion of coal in the absence of solvent was much lower. This raises a concern as to whether the results from NMBB can be used as a model for coal conversion since their behavior towards solvent are so different. Coal remains, to great extent, a solid under normal liquefaction conditions; however, the melting point of NMBB is only about 65°C. In the case of coal, a solvent is needed in order to increase the dispersion of at least the "soluble" fragments, but in the case of NMBB, this solvent action is not necessary because at the thermolysis condition it is a liquid.

5. Many roles have been proposed for the solvent in coal liquefaction. The most important one is hydrogen transfer. It is believed that the mechanism for hydrogen transfer is through the route as indicated in equations 4 and 5:

The DHP radical reacts with H_2 to generate the $H\cdot$ atom and DHP. If this is indeed the case, when the reaction is run using D_2 , we should see less deuterium incorporation into the product in the presence of DHP. As can be seen from the data

in Table 8, this is not the case. The H/D ratios of the major products, naphthalene and tetralin, are the same as the ratio of NMBB reactant and D₂ gases when the experiment was run without solvent. In the run with solvent, the H/D ratios of naphthalene and tetralin are the same as the ratio of the NMBB reactant plus DHP and D₂ gas, even at 9 minutes. These results indicate that DHP is providing another source of hydrogen; however, deuterium incorporation into the products may by-pass DHP and directly add to the products.

When DHP or phenanthrene was used as the solvent, four compounds were found in the final mixture. These compounds were identified by GC/MS to be DHP, OHP (octahydrophenanthrene), THP (tetrahydrophenanthrene), and phenanthrene. The relative ratio of these compounds in each run (Table 8) depends on temperature and reaction time. However under the same reaction conditions, whether DHP or phenanthrene is the initial solvent, the same ratio of compounds are obtained (Figure 3).

6. Under catalytic condition, deuterium was incorporated statistically into the products as well as unreacted NMBB. As can be seen from the data in Table 9, Figures 4 and 5, even at 9 minutes, the deuterium incorporation reached an equilibrium distributions. In comparing this result with the results from the thermal runs, we can see that there is a relationship between a-bond broken and deuterium incorporation. As more deuterium is incorporated into the products, the more a-bond breaking occurs during the thermolysis of NMBB. These results imply that the role of the catalyst in the thermolysis process is to activate the H-H bond rather than the Ar-R bond.

SUMMARY AND CONCLUSION

The mechanism for the reaction of NMBB with H₂ can be described as follows. The weaker d-bond is broken to generate the benzylic radical, this radical abstracts an H atom predominantly from unreacted NMBB as evidenced by the large amount of toluene-d₀ in the deuterium tracer studies. This radical may also react directly with D₂; this can explain why the small but significant amount of d₁ and d₀ toluene was also found in the products. The reaction of the benzylic radical with unreacted

NMBB produces the NMBB-radical. Just as in the DPE system, the NMBB-radical can react with D_2 to generate a D atom. The other products can be explained by the reaction of D atom with NMBB. Dehydrogenated NMBB and hydrogenated NMBB may also result from this kind of reaction. Evidence for the NMBB-radical reacting more readily with D_2 is provided by the GC/MS data in which the unreacted NMBB contain more deuterium than the toluene product does.

It is not surprising that the d-bond is broken during thermal conversions. However, under catalytic conditions the major products are produced by a-bond breaking. A hydrogenation catalyst operates in nearly, if not all, cases through a mechanism that involves homolytic dissociation of hydrogen. Thus, the catalyst becomes a source of hydrogen (or deuterium) atoms. In this case an adsorbed H (or D) atom can add to the most electron rich site, the naphthalene ring in NMBB, and thereby alter the reaction pathway from that of the thermal reaction. Thus, the rate limiting step in the thermal process is the breaking of the $-CH_2-CH_2-$ bond (the d-bond) whereas in the catalytic case the rate limiting step becomes that of bond breaking of a radical species which leads to breaking of the a-bond. Alternatively, it is possible that the catalyst functions first to hydrogenate NMBB as shown in equation 6:

The a-bond in the hydrogenated compound is expected to be broken much more readily than in NMBB.

Based on the d-bond breaking/a-bond breaking analysis, in the presence of DHP, the reaction should not be considered as a purely thermal reaction whether it is run under pressure, as in the present studies, or in sealed tube (4). In both of these cases, the cleavage pattern is significantly different from the purely thermal conditions conducted in this study using the neat compound.

The hydrogen transfer role of the solvent in coal liquefaction is elucidated to some extent by this study. The deuterium tracer data indicate that deuterium incorporation into the products and the unreacted NMBB may occur by a mechanism that by-passes the solvent.

EXPERIMENTAL SECTION

1. Preparation of naphthyl Bibenzyl Ketone

A 500 mL three-necked flask was fitted with a 250 mL addition funnel and a condenser protected by a drying tube connected to a NaOH trap. In it are placed 14.6 g (0.11 moles) of anhydrous aluminum chloride and 70 mL of dry carbon disulfide. The suspension was cooled to 10-15°C in an ice-water bath and 20.9 g (0.11 moles) of 1-naphthoyl chloride were added dropwise with stirring over a 30-minute period. After this addition was completed the reaction mixture was stirred for 15 minutes. A solution of 18.2 g (0.1 moles) of bibenzyl in 20 mL of dry carbon disulfide was added dropwise with stirring over a 1- hour period to the mixture, the temperature being maintained at 10-15°C.

After the addition was completed, the reaction mixture was refluxed for 1 hour and was then poured very cautiously with manual stirring onto a mixture of 200 g of crushed ice and 30 ml of 10% HCl in a 500 mL beaker. The mixture thus formed was extracted with carbon tetrachloride (3 X 50 mL). The combined organic extracts were washed with water (3 X 50 mL) and dried with MgSO₄.

The resulting solution was distilled and the residue was dissolved in 30 mL of CH₂Cl₂. The product was obtained by liquid chromatograph (silica gel: 250 g, 1 : 1 mixture of CH₂Cl₂ and hexane was used as the solvent system). The product was monitored by TLC (20% hexane in CH₂Cl₂; UV. R_f = 0.5). After the solvent was removed, 25 g of product was obtained. Yield: 74.4%.

¹H NMR 2.9 (m, CH₂), 7.2-8.1 9(m, aromatic).

M.P: 78-80°C (recrystallized from ethanol).

2. Preparation of 1-(4-(2-Phenylethyl)-Benzyl)-Naphthalene

A 500 mL three-necked flask was fitted with a condenser and a thermometer. In it are placed 34 g (0.1 moles) of 1-naphthyl bibenzyl ketone, 212 ml of ethylene

glycol and 43 mL of anhydrous hydrazine. The mixture was heated slowly with stirring to 80°C, it became a clear solution and then immediately the solution became milky, an indication of formation of the hydrazone. Then 15 g of potassium hydroxide was added slowly through the condenser and the mixture was refluxed overnight (140-160°C). After the ketone was no longer observed on the TLC plate, water and excess hydrazine were removed by a take-off condenser until the temperature rose to the boiling point of ethylene glycol (196-198°C). Refluxing was continued for at least 4 hours. (TLC was used to follow the formation of the product).

After the above mixture was cooled to room temperature, 100 mL of water was added. The mixture was acidified with 10% HCl to pH = 2, and then extracted with CH₂Cl₂ (4 X 100 mL). The combined organic layer was washed with water (3 X 50 mL) and dried over MgSO₄. After the solvent was removed, recrystallization from ethanol gave 28g of product. Yield: 87%.

M.P. 65-67°C (66-67°C).

Purity: > 99% (GC)

3. General Reaction Procedure

The reactions were conducted in a glass liner contained in a stainless steel reactor; the glass liner was sized to occupy most of the stainless steel value (Figure 6). Glass beads were added to the glass tube filled out one end with a capillary tube, and then the end of the tube with the larger diameter sealed off. A known amount of the solid reactant was added to the reactor through the capillary tube. The tube was placed in the stainless steel holder, using stainless steel wool to insulate the glass reactor from breaking while being shaken. The stainless steel reactor was connected to a glass handling system and pressurized with sufficient hydrogen to provide a pressure of about 2000 psig at reaction temperature. The reactor was placed in a preheated sand-bath. The reactor attained reaction temperature in 2 minutes or less. At the end of a run the reactor was removed from the hot sand-bath and transferred to a cold sand-bath where it cooled to below 100°C in 1 to 2 minutes.

Carbon disulfide was added through the capillary and the products removed for analysis using a long syringe needle. Little or no material is lost from the interior

of the glass bulb. Control experiments in which a hydrogenation catalyst was added showed that complete saturation of an aromatic compound could be effected under the appropriate reaction conditions, showing that the amount of gas and its mixing during the reaction was adequate.

Gas chromatographic analysis were carried out on a Hewlett Packard Model 5880A gas chromatograph equipped with an DB-5 60-m column. GC/MS analysis was accomplished using a Hewlett Packard GC/MS model 5890 instrument operated using 70 eV impact voltage.

Identification of reaction products was accomplished by GC/MS analysis and, when possible, by GC comparison with an authentic chemical sample. Reported product yields and overall conversion of NMBB are based on GC measurements using the appropriate response factor. GC/MS analysis provided deuterium data that was corrected for M+1 and M+2 peaks; where required, M-1, M-2, M-3 and M-4 peaks were also taken into consideration.

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FIGURE LEGEND

- Figure 1. Products of bond cleavage reactions of NMBB.
- Figure 2. Arrhenius plot for the thermolysis of NMBB under D_2 .
- Figure 3. Hydrogenation/dehydrogenation product distribution of DHP/phenanthrene in the thermolysis of NMBB (Top: starting from DHP; bottom: starting from phenanthrene).
- Figure 4. Deuterium incorporation into tetralin in the thermolysis of NMBB under D_2 at 400°C, 30 min. over Co-Mo-S. (-●-, without DHP; -□-, in the presence of DHP).
- Figure 5. Deuterium incorporation into naphthalene in the thermolysis of NMBB under D_2 at 400°C, 30 min. over Co-Mo-S (-●-, without DHP; -□-, in the presence of DHP).
- Figure 6. Glass reaction vessel for thermolysis under D_2 .

Table 1

Product Distribution in the Thermolysis of NMBB

<u>Compound</u>	<u>mol%</u>			
	<u>400°C/D₂</u>	<u>425°C/D₂</u>	<u>450°C/D₂</u>	<u>425°C/N₂</u>
1	0.3	0.5	0.8	0.2
2	0	0.2	0.5	0.1
3	1.7	13.8	28.6	9.2
4	1.4	5.8	15.7	6.4
5	0.1	0.4	0.9	0.1
6	0.3	0.7	2.3	1.3
7	0.3	0.3	0.6	0.3
8	0.3	1.2	2.0	0.7
9	0.8	2.4	4.9	2.0
10	0	2.0	4.6	0.5
11	0.4	0	0	0
12	1.0	0	0.1	0
13	1.5	1.7	2.7	1.1
14	0.5	2.2	3.4	4.9
NMBB	91.4	68.3	28.9	72.7
conversion	7.3	20.6	59.7	22.0

Table 2

Selectivity of Bond Breaking in Thermolysis of NMBB at 60 min

<u>Bond Broken</u>	<u>D₂/400°C</u>	<u>D₂/425°C</u>	<u>D₂/450°C</u>	<u>N₂/425°C</u>
a	19	13	13	11
b	9	2	2	3
c	5	3	5	6
d	57	79	78	79
e	10	3	2	2

Table 3

Deuterium Incorporation into the Major Compounds
in the Thermolysis of NMBB under D₂

	<u>Toluene</u>			<u>MBN^a</u>			<u>NMBB</u>		
	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>
d ₀	89.9	78.8	78.2	75.6	63.8	52.0	95.4	81.1	55.7
d ₁	8.5	20.4	19.4	24.3	34.2	39.7	4.1	16.5	32.5
d ₂		0.8	2.2		1.3	6.3		2.0	9.5
d ₃			0.2			1.8		0.4	1.9
d ₄									0.3
D/mol	0.13	0.22	0.24	0.25	0.39	0.59	0.05	0.22	0.59

a. MBN: methylbenzyl naphthalene

Table 4

Thermolysis of NMBB^a in the Presence of Solvent/Catalyst

<u>Temp.(°C)</u>	<u>Time (min.)</u>	<u>Catalyst</u>	<u>Gas (800 psi)</u>	<u>Solvent</u>	<u>Conversion mol.%</u>
425	60	/	N ₂	DHP	31.9
400	15	Co-Mo-S	D ₂	/	99.7
400	30	Co-Mo-S	D ₂	/	99.9
400	60	Co-Mo-S	D ₂	/	100
400	9	Co-Mo-S	D ₂	DHP	42.9
400	30	Co-Mo-S	D ₂	DHP	84.0
400	60	Co-Mo-S	D ₂	DHP	96.0
400 ^a	60	Co-Mo-S	D ₂	DHP	98.4
400	60	Co-Mo-S	D ₂	Phen.	98.4
425	60	Co-Mo-S	D ₂	DHP	99.1
425	60	Co-Mo-S	D ₂	Phen.	99.7
425	60	Co-Mo	D ₂	/	90.0
425	60	Co-Mo	N ₂	DHP	34.7
425	60	Co-Mo	D ₂	DHP	44.2
425	60	Co-Mo	D ₂	Phen.	95.2
425	48	G-67	N ₂	DHP	87.7
425	60	Graph. Carbon	N ₂	DHP	30.5

a. In this run 600 mg of NMBB and 60 mg of Co-Mo-S were charged.

Table 5

Selectivity of Bond Broken in the Thermolysis of NMBB
in the Presence of Solvent/Catalyst

<u>Reaction Condition</u>	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>
425°C/N ₂ /DHP/60 min	2	34	3	28	34
400°C/Co-Mo-S/D ₂ /15 min	88	11	0.4	1	0.1
400°C/Co-Mo-S/D ₂ /30 min	85	12	1	2	0.3
400°C/Co-Mo-S/D ₂ /60 min	83	13	1	0	0
400°C/Co-Mo-S/D ₂ /DHP/9 min	93	7	0.1	1	0
400°C/Co-Mo-S/D ₂ /DHP/30 min	91	7	0.3	2	0.2
400°C/Co-Mo-S/D ₂ /DHP/60 min	90	6	0.4	3	0.3
400°C/Co-Mo-S/D ₂ /DHP/60 min ^a	90	7	1	2	0.3
400°C/Co-Mo-S/D ₂ /Phen/60 min	90	9	0.2	1	0
425°C/Co-Mo-S/D ₂ /Phen/60 min	82	10	1	7	1
425°C/Co-Mo-S/D ₂ /DHP/60 min	84	7	1	8	1
425°C/Co-Mo/D ₂ /60 min	75	11	2	11	1
425°C/Co-Mo/D ₂ /DHP/60 min	66	7	2	23	2
425°C/Co-Mo/N ₂ /DHP/60 min	63	6	2	28	2
425°C/G-67/N ₂ /DHP/48 min	58	35	0.3	7	0.3
425°C/G-67/N ₂ /Grap. c/48 min	43	23	2	30	2

a. In this run 600 mg of NMBB and 60 mg of Co-Mo-S were charged.

Table 6

Deuterium Incorporation in the Major Components in the Thermolysis of NMBB under Catalytic Conditions

<u>Reaction</u>	<u>Conv.</u>	<u>D/molecule</u>								
<u>Condition</u>	<u>mol%</u>	<u>Toluene</u>	<u>EB</u>	<u>p-xylene</u>	<u>Tetralin</u>	<u>NP</u>	<u>MNP</u>	<u>DPE</u>	<u>MBB</u>	<u>NMBB</u>
Co-Mo-S/400°C 15 min	99.7	3.5	5.7	4.1	8.2	6.1	6.5	6.3	7.3	/
Co-Mo-S/400°C 30 min	99.9	4.2	6.2	4.9	8.3	6.3	7.0	7.5	8.8	/
Co-Mo-S/400°C 60 min	100	4.5	6.5	5.2	8.1	6.2	6.8	8.2	9.5	/
Co-Mo-S/400°C DHP/9 min	42.9	0.5	/	/	3.6	2.2	2.3	1.2	1.3	2.4
Co-Mo-S/400°C DHP/30 min	84.0	0.9	1.3	1.2	4.0	2.5	2.7	1.7	1.9	3.8
Co-Mo-S/400°C DHP/60 min	96.0	1.1	1.5	1.5	3.7	2.6	2.9	2.3	2.4	4.6
Co-Mo-S/400°C DHP/60 min ^a	98.4	1.2	1.7	1.6	3.5	2.6	2.8	2.4	2.4	5.0
Co-Mo-S/400°C Phen/60 min	98.4	1.8	/	/	4.3	3.4	3.7	3.5	4.0	/
Co-Mo-S/425°C Phen/60 min	99.7	2.3	3.0	2.7	4.5	3.6	3.9	4.3	4.3	/
Co-Mo-S/425°C DHP/60 min	99.1	1.4	2.0	1.8	3.6	2.8	3.1	2.7	3.4	5.6
Co-Mo/425°C Phen/60 min	95.2	1.6	2.2	2.0	4.0	3.0	3.4	3.1	3.5	6.2
Co-Mo/425°C DHP/60 min	90.0	1.5	1.4	1.4	3.2	2.6	2.1	2.7	2.9	4.7
Co-Mo/425°C 60 min	90.0	4.1	5.0	4.7	7.1	5.8	6.2	7.1	8.8	/

a. In this run 600 mg of NMBB and 60 mg of Co-Mo-S was charged.

Table 7
Comparison in Selectivity of Bond Broken

<u>Reaction Condition</u>	<u>d-bond broken/a-bond broken</u>
425°C/D ₂ /60 min	6.12
425°C/N ₂ /60 min	7.15
425°C/N ₂ /60 min/DHP	1.02
419°C/60 min/sealed tube/DHP ^a	1.4
425°C/N ₂ /60 min/DHP/graph.c.	0.71
425°C/D ₂ /60 min/DHP/Co-Mo	0.36
425°C/D ₂ /60 min/DHP/Co-Mo-S	0.09
425°C/D ₂ /60 min/Phen./Co-Mo-S	0.08
419°C/60 min/sealed tube/black pearl 2000/DHP ^a	0.06

a. Data from reference 4.

Table 8

The H/D Ratio in the Major Products
in the Thermolysis of NMBB under D₂ (800 PSi)

<u>Reaction Condition</u>	<u>Conversion</u>	<u>H/D Tetralin</u>	<u>NP</u>	<u>MNP</u>	<u>H/D_{calculated}</u>
Co-Mo-S/400°C 15 min	99.7	0.46	0.31	0.54	0.4
Co-Mo-S/400°C 30 min	99.9	0.44	0.27	0.44	0.4
Co-Mo-S/400°C 60 min	100	0.48	0.30	0.47	0.4
Co-Mo-S/400°C DHP/9 min	42.9	2.30	2.69	3.29	2.0
Co-Mo-S/400°C DHP/30 min	84.0	2.03	2.21	2.66	2.0
Co-Mo-S/400°C DHP/60 min	96.0	2.25	2.08	2.51	2.0
Co-Mo-S/400°C DHP/60 min ^a	98.4	2.47	2.03	2.54	2.4
Co-Mo-S/425°C DHP/60 min	99.1	2.32	1.87	2.28	2.0
Co-Mo-S/400°C phen/60 min	98.4	1.77	1.32	1.74	1.7
Co-Mo-S/425°C phen/60 min	99.1	1.66	1.24	1.54	1.7
Co-Mo/425°C DHP/60 min	44.2	2.74	2.14	3.80	2.0
Co-Mo/425°C 60 min	90.0	0.69	0.38	0.61	0.4
Co-Mo/425°C phen/60 min	95.2	1.99	1.64	1.93	1.7

a: In this run 600 mg of NMBB and 60 mg of Co-Mo-S were charged.

Table 9

The Relative Amount of Hydrogenation/Dehydrogenation Products
of 9,10-Dihydrophenanthrene/Phenanthrene in the Thermolysis of NMBB

<u>Condition</u>	<u>mol%</u>			
	<u>DHP</u>	<u>OHP</u>	<u>THP</u>	<u>Phen.</u>
425°C/D ₂ /60 min DHP/Co-Mo-S	21.3	16.8	22.2	39.7
400°C/D ₂ /60 min Phen./Co-Mo-S	28.2	14.4	17.9	39.5
400°C/D ₂ /60 min DHP/Co-Mo-S a	26.1	18.8	18.9	36.0
400°C/D ₂ /60 min DHP/Co-Mo-S	28.7	12.6	17.3	41.4
400°C/D ₂ /30 min DHP/Co-Mo-S	32.5	5.2	11.6	50.6
400°C/D ₂ /9 min DHP/Co-Mo-S	63.1	4.0	0.3	32.7
425°C/D ₂ /60 min DHP/Co-Mo	48.6	1.1	7.9	45.4
425°C/D ₂ /60 min Phen/Co-Mo-S	18.7	19.6	24.0	37.7
425°C/D ₂ /60 min Phen/Co-Mo	23.0	5.7	18.3	52.9
425°C/N ₂ /60 min DHP	84.3	1.0	1.0	13.7
425°C/N ₂ /60 min DHP/graph.c	82.7	0.8	1.0	15.5
425°C/N ₂ /60 min DHP/Co-Mo	43.1	0.8	3.0	53.2

Figure 1. Products of bond cleavage reactions of NMBB.

Figure 2. Arrhenius plot for the thermolysis of NMBB under D_2 .

Figure 3. Hydrogenation/dehydrogenation product distribution of DHP/phenanthrene in the thermolysis of NMBB (Top: starting from DHP; bottom: starting from phenanthrene).

Figure 4. Deuterium incorporation into tetralin in the thermolysis of NMBB under D_2 at 400°C, 30 min. over Co-Mo-S. (—, without DHP; - - -, in the presence of DHP).

Figure 5. Deuterium incorporation into naphthalene in the thermolysis of NMBB under D_2 at 400°C, 30 min. over Co-Mo-S (—, without DHP; ···, in the presence of DHP).

Figure 6. Glass reaction vessel for thermolysis under D_2 .

TASK II

Project II.9

DEVELOPMENT OF ADVANCED METHODS OF COAL LIQUEFACTION PRODUCT ANALYSIS

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This research program has the goal of developing HPLC methods and techniques to rapidly analyze coal liquids. This involves quantitatively separating them into well defined fractions on the basis of molecular size or type. Developing these methods will reduce analysis times from days to hours and will provide information necessary to assess product quality and to understand coal liquefaction process chemistry.

ACCOMPLISHMENTS

Since the outset of this program in May 1991, workers at West Virginia University have concentrated on separating the oil fraction of coal liquids by molecular type. An HPLC method was developed using three solvents, three columns and a column switching valve to separate a single injection of oil into saturate, aromatic and polar molecules, and further separate the aromatic molecules by ring size (1). Separating these same fractions using ASTM open column methods (2) requires several days work. With this HPLC method, these separations were achieved in just over one hour.

Quantitation of complex mixtures by HPLC is often difficult. The standard uv detector is not proportional to concentration and only sees molecules which absorb uv light. It does not detect saturate molecules at all. This quantitation problem has been solved for low boiling liquids by collecting fractions from the HPLC, adding internal standards for calibration and analyzing them on a gas chromatograph with a flame ionization detector (3). The method works well for distillate samples with molecules smaller than 20 or 25 carbon atoms. The method does not work for undistillable hydrocarbons.

Our solution for analyzing higher boiling hydrocarbons has been to add a mass sensitive, evaporative light-scattering detector to the HPLC system for direct quantitation of product molecules. This detector functions by spraying sample and solvent into a heated tube purged with inert gas. The low boiling components evaporate whereas higher boiling compounds form a mist whose concentration is measured by laser light scattering. The concentration of mist is a function of operating conditions and sample boiling point.

We have found that by operating the evaporative light-scattering detector (ELSD) at 40 °C, molecules with normal boiling points above 280 °C (536 °F) can be detected. On a molecular basis, this includes saturates like hexadecane (B.P. 286 °C) and aromatic hydrocarbons with 3 or more rings (B.P. > 340 °C). On a fuel basis, we can detect components in the heavy diesel range and higher.

Figures 1 and 2 show how the output of the uv and ELSD detectors differ for a mixture of aromatic compounds. Figure 1 shows the uv detector output for a Supelco PAH Test Mix whose components are listed in Table 1. Toluene (peak 1) is the solvent; all of the other components are present at a concentration of 0.06%.

Table 1. Supelco PAH Test Mixture

<u>Peak</u>	<u>Name</u>	<u>Rings</u>	<u>B. P. (°C)</u>
1	Toluene	1	110
2	Phenanthrene	3	340
2	Anthracene	3	340
3	Fluoranthene	4	375
3	Pyrene	4	393
4	Triphenylene	4	425
4	Benzo(a)anthracene	4	---
4	Chrysene	4	448
5	Benzo(e)pyrene	5	495
5	Perylene	5	---
5	Benzo(a)pyrene	5	495

Figure 2 shows the ELSD output for this same sample. Notice that toluene (peak 1) is not detected because it evaporates with the solvent. Peaks 2,3,4 and 5 remain because they have substantially higher boiling points and form a mist whose concentration is measured.

Peaks 2 and 3 each contain 2 components whereas peaks 4 and 5 each contain 3 components. If the ELSD provided a linear response, the peak areas would be in the ratio of 2:2:3:3. Peaks 4 and 5 seem to have about the same area, but the other peaks are much too small. This is the effect of a non-linear detector. The ELSD response as a function of operating conditions is currently being studied.

Examples of separated oil fractions for a Wilsonville heavy diesel (4) are shown in Figures 3 and 4. Figure 3 shows the output from the uv detector set at 254 nm. Polar molecules elute first followed by 1 and 2-ring aromatics. Saturate molecules are not in the figure since they are not detected by uv light.

Figure 4 shows the ELSD response for the same Wilsonville heavy diesel. The polar molecules have been resolved into 4 peaks whereas the saturates and aromatics have been separated into 2 peaks. The identities of the polar molecules are unknown. The first peak in the nonpolar is saturates and 1-ring aromatics that have not been resolved. The last peak is 2-ring aromatics.

The evaporative light scattering detector provides a means of detecting all high boiling molecules eluting from the HPLC and is promising for the analysis of coal liquids. Its response is non-linear but can be corrected with calibration curves. This problem is currently being studied.

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Figure 1: Supelco PAH Test Mix
uv Detector at 254 nm

Figure 2: Supelco PAH Test Mix
Evaporative Light-Scattering Detector

Figure 3: Wilsonville Heavy Diesel
uv Detector at 254 nm

Figure 4: Wilsonville Heavy Diesel
Evaporative Light-Scattering Detector

Task III

Novel Coal Liquefaction Concepts

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TASK III

Project III.1

BIOPROCESSING OF COAL

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SUMMARY

The influence of gas pressure on metabolism of *Desulfovibrio desulfuricans* for biohydrogenation of fumarate was studied. In order to overcome the hydrogen limitation, high pressure (5-500 psig) hydrogen gas was applied in a multipurpose bioreactor which was constructed in our laboratory. The study with *D. desulfuricans* under (normal and high pressure) H₂ showed complete (~ 100%) reduction of fumarate within 24 hours. The hydrogenation of fumarate was observed only when hydrogen supply was continuous. The effect of organic solvents containing stilbene on *Desulfovibrio vulgaris* under hydrogen gas was also studied. Toluene containing stilbene was treated with the cells of *D. vulgaris* present in an aqueous medium under H₂ (5 psig) to dissolve the stilbene and to enhance the solute transport through bacterial cell wall. Net decrease in H₂ pressure was 2.0 psig over the controls at the end of 5 days. The results also show that the amount of stilbene present in toluene phase was decreased to 80%. When the concentration of the cells was increased five fold, a 50% decrease in stilbene content was achieved in two days with the utilization of 4 psig H₂. Hence, the decrease in the stilbene content was attributed to the biological process.

Variation in liquefaction temperature showed that the direct liquefaction yield of the coal (KCER #91182) treated with *Thiobacillus ferrooxidans* was increased with increase of liquefaction temperature over the raw coal. Mossbauer data showed that all coals containing different high pyrite, high sulfur Illinois coals (IBC #102,105), and pyrite free DECS coal with added pyrite, (with initial pH 2.5) completely removed pyrite in 21 days. In-situ catalyst formation studies with *Acidianus brierleyi* showed

the formation of FeOOH crystals (by Mossbauer analysis). Although the percentage of iron in FeOOH (on DECS #17) was less than that of the other coals, it was clearly evident from IS value (.37) that it is indeed FeOOH. It also showed an increase of the liquefaction conversion of 14% over the control which did not contain *A. brierleyi*.

I. Biohydrogenation Studies Using Sulfate Reducing Bacteria

Microbial activities have been employed as the basis for chemical transformations of various compounds. One promising application involves the use of bacteria containing hydrogen uptake hydrogenase enzyme to hydrogenate coal. We have used *Desulfovibrio desulfuricans*, *D. vulgaris* and conducted several experiments to investigate the biohydrogenation of several substrates, including the coal-related model compound *trans*-stilbene.

Since hydrogen will be utilized for bioprocessing, the pressure must be increased in order to enhance the solubility of the gas in a liquid medium (e.g., it is known that at 50°C, for a change in pressure from 1 to 34 atmospheres, the solubility of hydrogen in water increases approximately 60 times). This research is also looking at the effect of pressure on the bacterial culture and hydrogenation reaction. The solubility of coal-related model compounds is also a limiting factor for biohydrogenation. The solubility of coal-related model compounds can be enhanced using nonaqueous (e.g., toluene) media for biohydrogenation.

a) Effect of Pressure on *Desulfovibrio desulfuricans*

Experimental Setup

For each experiment, 1-2 grams (wet weight) of bacteria were needed. The bacteria were cultured in 15 liter glass batch fermenters. The solution medium contained the following compounds in amounts scaled to grams per 1 liter of solution: 0.5 K₂HPO₄; 1 NH₄Cl; 5 Na₂SO₄; 0.02 CaCl₂·2H₂O; 0.2 MgSO₄·7H₂O; 18 60%(w/w) DL-sodium lactate; 0.5 ferric ammonium citrate; 0.1 sodium thioglycollate; 0.1 ascorbic acid; and 0.05 yeast extract. After mixing up the chemical medium, the pH was adjusted to 7.7 for optimum growth. Then we sterilized the medium and fermenter and sparged nitrogen through the system overnight to attain sterile

anaerobic conditions. The next day, we inoculated the medium with 1-2 liters of solution from a previous batch. The incubation period for growth was about 1 week.

After the culture matured, it was centrifuged to collect the bacteria. Ferrous sulfide precipitate is also collected in the process. The generation of this precipitate is important since it removes sulfide from solution that would otherwise inhibit the reaction. The solid pellet of bacteria and sulfide precipitate was repeatedly washed and centrifuged to separate out and purify the bacterial culture. Once purified, the culture was ready to use. It was very important to keep the bacteria away from open air at all times and to maintain anaerobic conditions because the bacteria are very sensitive to oxygen.

We constructed a 350 ml stainless steel batch reactor system (Figure 1). The reactor was equipped with a magnetic stirrer control and an electric temperature control to maintain a homogeneous medium at the optimum growth temperature (36°C). A constant overhead pressure could be applied to the reactor system. This configuration was used for the first two experiments involving stilbene hydrogenation.

The reactor was then modified to allow a known, steady stream of hydrogen gas to be sparged through the system. Further modifications included the addition of a high pressure sample port and a low (atmospheric) pressure reactor in series with the high pressure reactor. This would allow atmospheric pressure experiments to be simultaneously conducted for a comparison (Figure 2).

Hydrogenation of *trans*-Stilbene

Two experiments were conducted to determine if granular stilbene could be hydrogenated to form bibenzyl in an aqueous medium containing bacteria in the presence of hydrogen gas. A GC/MS spectra of stilbene and bibenzyl is shown in Figure 3. The desired reaction is given as

A constant overhead pressure of 500 psig was maintained. The reactor medium contained only the nutrients that the bacteria needed for stabilization. One gram of stilbene was added to 220ml of this medium and placed in the reactor. One to two grams (wet weight) of cells were added and stirred in while sparging with hydrogen to maintain anaerobic conditions. The system was then pressurized to 500 psig and maintained for five days. After depressurization, the medium was analyzed according to procedures outlined in the analysis section. A GC/MS analysis of the first two reactor runs with constant hydrogen pressure has revealed that no significant hydrogenation was detected (Figure 4) with 80% of the stilbene recovered.

After the reactor had been modified for gas sparging and sample removal, we ran a third experiment with stilbene at low and high pressure simultaneously. Samples of the medium were taken every day. This medium contained two additional nutrients, lactate and sulfate, previously left out of the first two runs. In the earlier experiments, lactate was not added since it also acts as the source of hydrogen and we desired to utilize hydrogen gas. The addition of lactate was initiated to help drive the reaction to the right. A small amount of sulfate was also added to the medium. This was added with the idea of initiating the hydrogenation reaction, then observing a substrate transfer from sulfate to stilbene.

Upon analysis, it was found that both the low and high pressure samples contained no significant degree of hydrogenation with 90% and 95% of the stilbene recovered, respectively. The bacteria, however, did retain its viability for all runs even after five days of high pressure exposure to stilbene. It was decided that the low conversion might be due to the low solubility of stilbene in water. Steps to enhance solubility would include dissolving the stilbene in an organic solvent and contacting it in a two phase system with bacteria in an aqueous medium.

Reduction of Sulfate

In order to characterize the effect of pressure on sulfate reducing bacteria, it was desirable to run experiments using the bacteria's natural substrate. The bacteria reduces sulfate to sulfide by the following reaction.

Both the high and low pressure batch reactors were filled with 300 ml of medium containing sulfate (0.65 g/L), lactate (1.29 g/L), and other necessary nutrients. After inoculation with *D. desulfuricans*, the reactor was pressurized to 250 psig with inert nitrogen gas. Samples taken over a six day time period were analyzed for cell growth, reduction of sulfate, and reaction of lactic acid. The conversion of sulfate was 78% and 88% for the low and high pressure, respectively. Similarly, the lactate was consumed with conversions of 99.8%. Figure 5 shows the concentration profile of lactate for both low and high pressure with time. Figure 6 shows the change in absorbance as related to cell protein for low and high pressure. It is important to note that both the lactate and protein analysis indicate that the hydrogenation reaction was initiated in the high pressure reactor well before the low pressure system. Since the gas used was inert nitrogen, we concluded that the high pressure aided in maintaining anaerobic conditions. *D. desulfuricans*, under high pressure (250 psig of nitrogen), not only survived, but also increased the cell protein with concomitant utilization of lactate. This experiment indicates that *D. desulfuricans* may be used under high pressure of hydrogen for the hydrogenation studies of the organic compounds.

Hydrogenation of Fumarate

The bacteria used to hydrogenate sulfate in the previous section was found to be very active. We decided to use this bacteria in an experiment to investigate hydrogenation of a soluble organic under low and high pressure hydrogen gas. Fumaric acid (.636 g/L) was added to medium containing basic nutrients. After inoculation, samples were taken every twelve hours. The hydrogenation reaction of fumarate to succinate is

After one day, the conversion of fumarate was 97.5% in the low pressure reactor and 96.2% in the high pressure reactor (Figure 7). The reaction occurred quickly due to the high activity of the hydrogenase enzyme in the bacteria. Results from the protein analysis show that the bacteria did not grow during this period (Figure 8). An analysis of the succinate in the medium is also being done to verify hydrogenation.

b) Analysis of the Bioreaction Materials

Several analytical techniques have been researched and developed to analyze the various compounds being tested. For the solid stilbene experiments, the reaction mixture is separated into liquid and solid phases and treated as in Figure 9. After washing and cleaning as shown in the figure, an extraction is carried out for both phases to dissolve all of the stilbene in methylene chloride (Figure 10). The resulting solutions are analyzed in a GC/MS against known standards.

Bacterial growth rates are analyzed by determining the amount of protein in the medium as described by Lowry¹. The protein was correlated to a standard curve of bovine serum albumin. Lactate is an important hydrogen donor and carbon source for sulfate reducing bacteria. We are using an accurate colorimetric method used by Lawrence^{2,3} to determine lactate concentrations in our experiments. Sulfate concentrations are determined using the gravimetric method⁴. We might also employ a turbidimetric method⁵⁻⁷ to determine sulfate concentrations as a function of time in future experiments. Fumarate concentrations were analyzed using a spectrophotometer at 210nm. The analysis of succinate will be done using either enzyme colorimetry or HPLC analysis.

c) Influence of Organic Solvents on Biohydrogenation of Stilbene by *Desulfovibrio vulgaris*

In order to solubilize stilbene and to mediate transfer of hydrogen, toluene was used for biohydrogenation experiments. A new culture, *D. vulgaris*, was used based on the highest activity and stability of the hydrogenase. The hydrogenation of the stilbene was carried out by supplementing the nutrients (e.g., lactate and iron) in limited quantities. These nutrients are required for the growth of the organism and to improve the activity of the hydrogenase which contains iron, nickel, and sulfur. In order to determine the requirements of any of these nutrients, individual experiments with different nutrients were done along with suitable controls. At the beginning of the reaction, all the vials were pressurized to 4.5 psig with hydrogen. In the presence of toluene, the head-space pressure decreased significantly when compared to all the other set of controls (Figure 11). Total protein content of the test with toluene was increased from 101 µg/ml to 251 µg/ml by the end of 12 days (Table 1). The increase in protein content also indicates that *D. vulgaris* can tolerate the presence of a minimum of 35% toluene. Toluene is also known to permeate the bacterial cells, which might allow for the transport of larger molecules into the cells.

The GC-MS analysis of the reaction mixture was carried out to determine the transformation of stilbene. With the analysis of the toluene phase obtained so far, stilbene present in test (with bacteria) solution with toluene decreased from 25 ng/ml to 4.7 ng/ml. Whereas the control with initial 25 ng/ml was recovered up to 24.5 ng/ml at the end of the reaction (Table 2). The control reaction system was identical in every respect with the test solution composition with the exception of the bacterial cells. Although 80% of stilbene decreased from the test solution, we did not find significant formation of bibenzyl as an end product. This may indicate that bibenzyl might have been dispersed in the inter-phase or it was not an end product but acted as an intermediate. In the present analytical method of the toluene phase, first six minutes were not analyzed due to the solvent (toluene) delay operation. Moreover, the inter-phase and the aqueous phase analysis have to be analyzed in search of any product formation.

When the initial cell protein concentration was increased to 498 µg/ml (~5 fold), approximately 50% of the stilbene content in the toluene phase was decreased in two days under hydrogen gas and toluene. This rate of decrease of stilbene clearly shows that it is due to the metabolic activity of *D. vulgaris* in the presence of hydrogen. The presence of tetralin containing stilbene showed only 0.2 psig hydrogen utilization in 24 h. Tetralin is toxic for the cells of *D. vulgaris* since, the cells were lysed and lost the original grayish-black pigmentation within 6 h. of the reaction. The cells recovered from the medium treated with the tetralin did not produce sulfide in the sulfate reducing medium.

A two phase hydrogenation experiment (under high pressure) contacting a solution consisting of stilbene dissolved in toluene with an aqueous medium containing *D. desulfuricans* is under way.

II. Precipitation of Active Iron Catalyst on Coal Surface Under Aerobic/Anaerobic Conditions

This part of the work deals with the improvement on the formation of ultra-fine active iron particles and to substantially reduce the time required for the deposition of the fine FeOOH crystals on the surface of coal by using iron/pyrite utilizing microorganisms. We reported earlier that the archaebacterium *Acidianus brierleyi* can bring about significant changes in the iron forms of biotreated coals (KCER #91182) with enhanced liquefaction yield (25%).

a) Effect of Temperature on Direct Liquefaction yield of the *Thiobacillus Ferrooxidans* Treated Coal

Coal (KCER #91182) was treated with *T. ferrooxidans* in a fermenter maintaining at constant pH 2.8, temperature 30°C and sparged with CO₂ plus O₂ followed by H₂. The biotreated and raw coal were subjected to direct liquefaction using DMDS at different temperatures for 15 min. under hydrogen (initial pressure 800 psig). With the increase of temperature, the biotreated coal showed higher conversion than that of raw coal (Ref. Half yearly report 1992-93). Approximately 10% increase in liquefaction yield was observed at 385°C over the raw coal.

Therefore, the present study clearly indicates the increase in conversion was solely due to biological treatment but not due to any abiotic process.

b) Biological Reaction Variations During the Processing of IBC and DECS Coals in the presence of *Acidianus brierleyi* and Effect on Direct Liquefaction of the Biotreated Coals

Different coal samples (IBC #101, #102, #105 equivalent to Argon premium coal and DECS #17), with varying amounts of iron and sulfur, were used for the catalyst formation. IBC #101, #102, and #103, which have very high pyrite (1.2 to 2.4% dry basis) and total sulfur (3.4 to 4.4% dry basis) were subjected to biotreatment with *A. brierleyi* at pH 2.5 and 65°C under aerobic conditions. DECS #17 which has a negligible quantity of pyritic and non-pyritic iron, was mixed with pyrite (2500 ppm). This mixture was then subjected to biotreatment with *A. brierleyi* at pH 2.5 and 68°C. Of the four biotreated coals studied, IBC #105 (with 2.4% pyrite dry basis) showed significant release of iron (220 ppm, at the end of 15 days) into the aqueous phase and then started to decrease the liquid phase iron concentration. Whereas the control showed only increase of liquid phase iron (148 ppm, at the end of 21 days) (Figure 12).

The amount of sulfate released by the biotreated coals into the aqueous phase was measured by the gravimetric method. Biotreated IBC #105 showed complete utilization of the pyritic sulfur (2.4% dry basis) as sulfate in the aqueous phase (Figure 13). DECS coal with added pyrite showed only traces of liquid phase iron (Figure 14) and the sulfate was not detectable in liquid phase even at the end of 21 days. The biotreated coals were analyzed using Mossbauer spectroscopy (by Dr. Huffman's group) to further elucidate the effect of biotreatment particularly to determine the forms of iron. It showed that pyrite was completely oxidized in all coals which were treated with *A. brierleyi* (Table 3). This analysis also revealed that the formation of the percentage of iron (36) as FeOOH (of IBC #105) was higher than that of DECS #17 (12% Fe of FeOOH) with predominant formation of jarosite (88% Fe) (Table 3). However, the liquefaction conversion went up by 14% only in the case of DECS coal treated with *A. brierleyi* (Table 4). This might be due to the formation

of FeOOH, which showed an IS value of .37, exactly the same as pure FeOOH. Whereas in other coals the IS value was away from .37 and thus resulted as an inefficient catalyst to influence the liquefaction yield. It is also interesting to note that FeSO₄ was utilized in the presence of *A. brierleyi*. The implication of this property is yet to be determined.

Further work will be focussed on DECS #17 with the addition of pyrite and IBC #105 with controlled pH at 2.5. This will enable *A. brierleyi* to oxidize pyrite rapidly. Then the pH will be increased to 2.8 for the reprecipitation of the liquid phase iron.

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Table 1. Analysis of Protein Content of *D. vulgaris* Cells Present in Aqueous phase (initial H₂ pressure = 4.5 p.s.i., pH = 7.6)

Treatment	Initial protein μg/ml	Protein (12th day) μg/ml
Test* (no toluene)	92	215
Aqueous medium only	0	0
Cells alone (aqueous medium)	98	123
Test* (35% toluene)	101	251
Toluene only	0	0

* Test was treated with *D. vulgaris*

Table 2. Decrease of Stilbene content (determined by GC-MS) in Two-phase System Containing 35% Toluene (pH = 7.6, temp. = 37°C, time = 12 days)

Sample	Area count* (of stilbene)	Mass (of Stilbene) ng/μl
Standard	221 377 764	50
Control (no bacteria)	108 649 612	24.5
Test (with bacteria)	20 765 469	4.7

* Area count was obtained from an average of three concurrent values (injections). This observation was also replicated in three different experiments.

Table 3. Composition and Phases of Iron Determined by Mossbauer Analysis of Different Illinois and DECS #17 Coals (5%) Treated with and without *Acidianus brierleyi* with an Initial pH of 2.5 at 68°C Incubated in Flasks Kept on a Rotary Shaker for 21 Days.

Coal type	%Fe			
	Pyrite	FeOOH ^a	Jarosite	FeSO ₄
IBC #101T	-	36 (IS .38)	64	-
IBC #101C	11	-	89	-
IBC #105T	-	22 (IS .36)	77	1.0
IBC #105C	12	-	85	2.5
DECS #17 ^b T	-	12 (IS .37)	88	-
DECS #17 ^b C	80	-	14	5

T - Test or coal was treated with *A. brierleyi*

C - Control or coal was treated without *A. brierleyi*

- - Not detectable

^a - The IS value for FeOOH is .37

^b - Pyrite (2500 ppm) was added to the pyrite free coal

Table 4. Direct Liquefaction Conversion and Oil Content of Different Illinois and DECS #17 Coals (5%) Treated with and without *Acidianus brierleyi* with an Initial pH of 2.5 at 68°C Incubated in Flasks Kept on a Rotary Shaker for 21 Days.

Coal type	Total conversion	Oil yield
IBC #101T	50	17
IBC #101C	47	16
IBC #105T	52	20
IBC #105C	46	17
DECS #17*T	79	25
DECS #17*C	65	20

T - Test or coal was treated with *A. brierleyi*

C - Control or coal was treated without *A. brierleyi*

* - Pyrite (2500 ppm) was added to the pyrite free coal

Liquefaction Conditions:

Temp. 385°C

Time 15 min.

Pressure 800 p.s.i., H₂ gas (cold)

DMDS 20% in excess of iron in coal

Figure 1. Schematic Diagram of High Pressure Biological Hydrogenation Unit

Figure 2. Schematic Diagram of Low Pressure Biological Hydrogenation Unit

Figure 3. GC/MS Analysis of *trans*-stilbene (20.0 min.) and Bibenzyl (17.6 min.)

Figure 4. GC/MS Analysis of *trans*-stilbene Treated with *D. desulfuricans*, 34 atm, 36°C, (Stilbene Peak Masked)

**Figure 5. Lactate Concentration vs. Time
Sulfate and Lactate Treated with
D. desulfuricans at 1 and 34 atm, 36°C**

Figure 6. Protein Concentration vs. Time
Sulfate and Lactate Treated With
***D. desulfuricans* at 1 and 34 atm, 36°C**

Figure 7. Fumarate Concentration vs. Time
Fumarate Treated with *D. desulfuricans*
at 1 and 34 atm, 36°C

Figure 8. Protein Concentration vs. Time
Fumarate Treated With *D. desulfuricans*
at 1 and 34 atm, 36°C

Figure 9. Hydrogenation Analysis Flowsheet

Figure 10. Liquid Extraction Process

Solids Extraction

Figure 11. Measurement of Head-space Hydrogen Pressure of Vials Containing Stilbene Medium Treated with *Desulfovibrio vulgaris* at 37°C and pH7.6 (Initial H₂ pressure = 4.5 p.s.i., experiment was repeated 3 times)

Figure 12. Variation of Liquid Phase Iron Released from IBC # 105 (5% coal) When Treated with *A. brierleyi* with an Initial pH of 2.5 at 68°C Incubated on Flasks Kept on a Rotary Shaker

Figure 13. Sulfate Released from IBC #105 (5% coal) When Treated with *Acidianus brierleyi* with an Initial pH of 2.5 at 68°C Incubated in Flasks Kept on a Rotary Shaker

Figure 14. Variation of Liquid Phase Iron Released from DECS #17 Coal (plus 2500 ppm pyrite) When Treated with *A. brierleyi* with an Initial pH of 2.5 at 68°C Incubated in Flasks Kept on a Rotary Shaker

TASK III

Project III.2

BETTER HYDROGEN MASS TRANSFER IN COAL LIQUEFACTION

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I. Introduction

During the initial stages of coal liquefaction, it is hypothesized that free radical reactions occur rapidly and that reaction rates increase almost exponentially. These fast reactions involve the thermal disruption of the coal structure to produce free radical fragments. If the free radicals are not stabilized by either molecular hydrogen or by hydrogen donor solvents, retrogressive reactions and catalyst deactivation take place. Hydrogen starvation in the initial stages of coal liquefaction has a permanent negative impact on product yields.

In order to address these problems, a new coal liquefaction reactor system was constructed in our laboratory prior to this work year. This jet loop reactor system incorporates a novel gas-driven pumping system for use under severe operating conditions. The development of the pumping system was essential to avoid the prohibitive cost of a suitable mechanical pump.

During the year, the complete system became fully operational for coal liquefaction studies. Initial experiments, detailed later in this report, showed that the conversion of coal and selectivity for oils was very high. The reactor system incorporates reaction rate control by modifying two control parameters: (1) reaction zone temperature, and (2) the frequency of cyclic switching. The two parameters can be adjusted to regulate the gas-liquid mass transfer requirements per reaction cycle.

The pumping system consists of two modified autoclave reactors used as stirred tanks, air-operated valves, gas holding tanks, a gas booster, an air compressor and a programmable logic controller (PLC). Differential pressure between the two stirred tanks is the driving force for slurry flow through the reactor system which is placed

between the two tanks. The fluid flow rate can be changed simply by adjusting valve action and gas pressures, and the fluids can range from low viscosity liquids to high viscosity slurries. The complete reactor system is shown in Figure 1.

The new coal liquefaction reactor system was used in an initial study to coprocess coal with waste oil. Coprocessing coal with waste oil was also performed in conventional tubing bomb microreactors in the presence of an iron oxide precursor. Initial studies indicate the beneficial effects of coprocessing coal with waste oil, and show that the new reactor system gives better results than the tubing bomb reactor.

Coprocessing coal with waste materials such as used tires, waste plastic and waste oil, all of which have expensive disposal costs, has the potential to improve the economics of coal liquefaction. Almost 1.2 billion gallons of waste oil are generated in the United States each year, posing an environmental hazard due to its metal bearing compounds and high sulfur content. The used oil must be re-refined and hydrotreated before use as a fuel or as a lube base stock. The undissolved coal could act as a trap for the metals removed from the oil during coprocessing, while the sulfur present in the oil could produce the sulfided catalyst needed for liquefaction.

Waste oil is primarily paraffinic and is a poor hydrogen donor solvent. It does, however, contain surfactants which could be advantageous to liquefaction. Additives found in the waste oil, such as detergent/dispersant additives, oxidation inhibitors, etc., are mostly organic sulfur compounds¹. These additives could help effectively disperse the coal and catalyst precursors throughout the coal/oil slurry during coprocessing. In addition, these additives can serve as sulfur sources to convert the catalyst precursors to the more active form. The unconverted coal could serve to trap the metals removed from the oil. The removal of metallic impurities from the oil during coprocessing of coal with a heavy oil was found to be due to deposition on the coal residue or pitch². The demetallation of used oil during hydrotreatment was also found to be primarily due to the process of physical deposition on the solid catalyst bed³.

II. Coprocessing Coal With Waste Oil

The coal conversion to THF solubles during coprocessing with waste oil was defined as:

Conversion (Y) = 100 * (1-X) where,

$$X = \frac{W_R - W_C - W_{ash}}{W_{moisture\ ash\ free\ coal}}$$

and conversion to hexane solubles (H) was defined in a similar manner. The selectivity was defined as the ratio of conversion to hexane solubles and conversion to THF solubles i.e.,

Selectivity = 100 * S where,

$$S = \frac{H}{Y}$$

W_R = weight of residue remaining after THF wash,

W_C = weight of catalyst (it was assumed that all the iron oxide was converted to FeS)

W_{ash} = weight of ash in the coal

Conversion and Selectivity. The conversion of coal and the selectivity for the formation of oils was measured in our coprocessing studies. The selectivity as defined above is the fraction of total products from coal that are soluble in hexane. The waste oil is completely soluble in hexane before the reaction. It was assumed that the residue remaining after the solvent wash of the products was primarily unconverted coal, ash and catalyst (when used).

The catalyst precursor used in the coprocessing experiments was superfine iron oxide (SFIO) supplied by Military/Aerospace Chemicals (MACH I, INC). The amount of iron oxide used was the stoichiometric amount (2.5 wt. %) required to remove all the sulfur (1.0 wt. %) present in the waste oil before coprocessing.

Tubing Bomb Microreactor (TBMR). (i) Effect of tetralin and catalyst. The conversion of coal and selectivity for oils was found to be very high (85% and 70% respectively) without the addition of a donor solvent (tetralin) and catalyst precursor. This is attributed to efficient dispersion of coal fragments, due to the presence of dispersant additives in waste oil. The conversion increased slightly with the addition of either the catalyst precursor or tetralin, but the selectivity change was not significant (Figure 2).

FIGURE 2. CONVERSION AND SELECTIVITY OF COAL IN THE TUBIN BOMB REACTOR

FIGURE 3. EFFECT OF TIME ON COAL CONVERSION DURING COPROCESSING (TUBING BOMB REACTOR)

(ii) Effect of time. Coprocessing experiments were conducted in order to study the effect of time on yields. No donor solvents or catalyst precursors were used. The conversion at the end of five minutes was only 50%, but the selectivity was relatively higher. The results are shown in Figure 3. The figure shows that the conversion and selectivity do not change significantly after a reaction time of 30 minutes. The selectivity in all cases is consistently high (more than 75%), and remains fairly constant, indicating that the coal is primarily converted to oils during coprocessing.

(iii) Effect of dispersion. The role of a dispersant in coal liquefaction was evaluated using a mineral oil (paraffinic oil with no additives) as the solvent and with different concentrations of a commercial dispersant additive added to the reaction mixture. The conversions were higher in the presence of the additive and increased with the concentration of the additive, but the selectivity decreased. However, a relatively lower increase in the conversion to hexane solubles was observed with the additive concentration (Figure 4). We believe the dispersant additive's function is to increase coal dispersion and dissolution. This can be seen by the increased conversion with the additive concentration, but a relatively lower increase in the conversion to hexane solubles. The selectivity and the conversion to hexane solubles can be increased by enhancing the gas-liquid mass transfer rate and by better control of the free-radical propagation rate. The jet-loop reactor system was designed for this purpose. The coprocessing results from the loop reactor system are discussed in the next section.

The typical concentration of a dispersant additive in a waste oil is a maximum of 3-6%. The shaking speed (425 rpm) of the TBMR during coal liquefaction with mineral oil and the dispersant additive was lower than that used with waste oil (720 rpm). The gas-liquid mass transfer limitations are lowered as the shaking speed is increased. A lower speed was used during liquefaction with the mineral oil to study the effect of the dispersant under conditions which could be mass transfer limiting. The conversion of coal in the mineral oil with a dispersant additive is comparable to the conversion with waste oil. However, the conversion to hexane solubles and selectivity are higher with the waste oil. These results are attributed, in part, to the higher shaking speed used while evaluating coal coprocessing with waste oil. This

FIGURE 4. EFFECT OF DISPERSANT ON COAL CONVERSION
(TUBING BOMB REACTOR)

supports the hypothesis that the dispersant additives present in the waste oil can play a significant role in improving the coal conversion.

The results from this initial study with waste oil in the TBMR indicate the potential beneficial effects of coprocessing. The improved dispersion of the coal particles in the TBMR resulted in higher conversions ($> 80\%$). The ratio of coal to waste oil was limited to 10 wt. % for most of this study. A few runs with higher coal concentrations (20 and 25%) resulted in a relatively lower conversion (60%) and selectivity (50%).

Reactor System. The samples collected in the reactor system during heat-up were used to determine the conversion of coal and selectivity for oils. The results are shown in Figure 5. At relatively low temperatures (275°C), the conversion was lower, but the conversion to hexane solubles was negative as indicated by the negative selectivity. The reactant hydrogen was introduced in this run after the temperature of the slurry at the reactor outlet reached 240°C . This was attributed to significant solvent (waste oil) incorporation into the coal. Solvent incorporation at lower temperatures has been reported by a number of investigators⁴. However, when the temperature was increased to approximately 305°C , the coal conversion was 15%, but the conversion to hexane solubles was higher as indicated by the high selectivity (90%). As the temperature increased to 320°C , the conversion increased to nearly 50% with a selectivity of over 95%.

The conversion to THF and hexane solubles from another coprocessing experiment in the loop reactor system is shown in Figure 6. The reactant hydrogen in this run was introduced after the slurry temperature at the reactor outlet reached 255°C . The results from this run confirm significant solvent incorporation into the coal at lower temperatures, which results in negative conversions. The conversion to THF solubles decreased in this run as the temperature increased from 275 to 335°C . This is believed to be due to increased solvent incorporation and the effect is evident with a further decrease in the conversion to hexane solubles for the same temperature range. The effect of solvent incorporation into coal was reduced as the temperature increased above 335°C . The conversions to THF and hexane solubles are very close at 360°C , indicating high selectivity for the formation of oils from coal.

FIGURE 5. CONVERSION AND SELECTIVITY DURING COPROCESSING

FIGURE 6. CONVERSION OF COAL DURING COPROCESSING IN THE REACTOR SYSTEM

In one coprocessing experiment, the temperature of the slurry coming out of the reactor was increased to 390°C and resulted in coal conversion of 83%, with a selectivity of 95%.

The conversion of coal and the high selectivity in the loop reactor system at relatively lower temperatures ($< 350^{\circ}\text{C}$) is significant. Shaw and co-workers^{5, 6} have reported recently that coal particle disintegration is characterized by mass transfer limited erosive breakage where molecular hydrogen is the principal reacting species. They found that the dissolution of coal was initiated at a lower temperature in the presence of molecular hydrogen and that the initiation temperature decreased with increased hydrogen pressure. Higher gas-liquid mass transfer rates were observed in model reactions using the loop reactor system^{7, 8}. Coal conversion and high selectivity at relatively lower temperatures in the loop reactor system is attributed, in part, to the high mass transfer rates.

The results from the TBMR and jet-loop reactor system indicate very high conversions of coal in the presence of a paraffinic waste oil. The dispersion of coal fragments by the additives present in the waste oil is believed to be the primary reason for this behavior in a very poor hydrogen donor solvent. Earlier results have shown that at lower agitation rates, the undissolved coal particles adhere to one another, preventing dispersion and fragmentation of the particles⁹. The presence of a dispersant reduces agglomeration and enhances dispersion which could result in increased coal dissolution and conversion.

The selectivity was higher in the jet-loop reactor system compared to the TBMR. The loop reactor system was designed to provide enhanced gas-liquid mass transfer rates, better control of free-radical propagation, and improved dispersion characteristics as reported in the model reaction studies^{7, 8}. The high selectivity in the loop reactor system is believed to be due to a combination of better control of free-radical propagation and improved mass transfer characteristics.

Sulfur and Ash Removal. The hexane soluble (oils) fraction was analyzed for sulfur and ash content. The reduction in the sulfur content (compared to the original waste oil) was higher (over 40%) when tetralin was present in the reaction system. This is probably due to the increased availability of hydrogen in the liquid

phase when tetralin is present, leading to increased removal of sulfur by forming hydrogen sulfide. The reduction in the ash content was greater than 70% in most of the runs. The ash reduction is believed to be due primarily to the deposition of metals on unreacted coal and residue^{2,3}.

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TASK III

Project III.3

DIRECT LIQUEFACTION OF COAL TO CLEAN TRANSPORTATION FUELS; OPTIMIZATION OF PROCESS VARIABLES AND DETAILED CHARACTERIZATION OF PRODUCTS

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I. Catalytic Hydroliquefaction of Coal, Catalysts, and Liquid Product Quality

(Larry L. Anderson and Win-H. Yuen)

During the year a matrix of experiments were performed to optimize reaction variables for hydroliquefaction of coals to liquid fuels. Following our earlier work, which showed that catalysts that performed well were those able to penetrate the coal particles during the reaction. Water-soluble compounds containing molybdenum, tungsten, iron, cobalt, and nickel were used as catalyst precursors. Coals tested included Blind Canyon (Utah high volatile bituminous) from the Penn State sample bank and Wyodak (Wyoming, subbituminous). Previous studies showed that good conversion without high gas yields could be obtained at 400°C so that temperature was used for most of the hydroliquefaction runs.

In typical runs the coal sample was impregnated with catalyst to the required loading by using an aqueous solution of catalyst precursors. For the bituminous coal samples the loading required water in the amount of about fifty per cent of the weight of the coal. For the subbituminous coal the weight of water was only about thirty six per cent of the coal weight. After impregnation of the catalyst precursor the coal was dried at 55°C under a vacuum (-60 kPa) for six hours. The catalyst/coal mixture was then placed into a tubing reactor, sealed, pressurized with hydrogen, and immersed into the sand bath used to heat the reactor.

After the hydroliquefaction reaction tubing reactors were taken from the sand bath, quenched, gases were vented for analysis, and the liquids and solids were extracted with tetrahydrofuran (THF). THF was stripped from the liquids after which they were extracted with toluene. Toluene-solubles were further extracted with cyclohexane to determine oil and asphaltene yields.

Table II.1.1 gives analyses for the coals tested during the year and Table II.1.2 shows the catalyst precursors used, which included compounds of iron, cobalt, nickel, molybdenum, and tungsten. Previous reports have given the effects of pressure, temperature, demineralization, reaction time, and catalyst concentration [especially molybdenum] on the conversion and liquid yields.

Of the many catalyst precursors used the highest yields were obtained with nickel (II) hexahydrate and ammonium tetrathiomolybdate which both gave liquid yields near 80 per cent. Ammonium iron (II) sulfate hexahydrate and cobalt(II) nitrate hexahydrate gave similar results with liquids near 70 per cent. Results from runs with all of the catalyst combinations used are shown in Figures II.1.1-11. Further characterization of the liquids, especially the oil fractions, are being done using simulated distillation and chromatographic methods.

This work will be presented at the International Conference on Coal Science to be held in Canada September 12-17, 1993. The paper was accepted for oral presentation. A paper summarizing the earlier work was also presented at the American Chemical Society Meeting in Denver, Colorado on March 30, 1993. The paper was included in the Fuel Chemistry Division Preprints¹.

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II. Coliquefaction of Coal and Waste Polymers to Produce Clean Liquid Fuels.
(Larry L. Anderson and Wisanu Tuntawiroon)

Preliminary experiments have been done to determine the suitable conditions such as temperature, pressure, reaction time and other variables on the conversion of mixtures of coal and waste polymers such as polystyrene, polyethylene, tire rubber, and commingled waste plastics. Initial experiments were thermal runs done on pure polymers, polystyrene and polyethylene. Reactions were done using the same reactors as was used in the hydroliquefaction of coal. Runs were also done using coal and rubber and coal and commingled plastic, mostly polyethylene, which was obtained from a local recycling center. Results are shown in Figures II.12-15. Although good conversion was found for pure compounds the results were much less satisfactory for commingled plastic. More appropriate conditions and/or catalysts for the coliquefaction of coal/polymer feeds are being determined. A paper describing this work has been accepted for presentation at the American Chemical Society National Meeting in Chicago, August 22-27, 1993. The paper is titled, "Coliquefaction of Coal and Polymers To Liquid Fuels.

Table II.1.1
Properties of Coals from the Penn State Coal Sample Bank

Coal Sample	DECS-6 (PSOC-1543)	DECS-17 (PSOC-1554)	PSOC-1520
Seam	Blind Canyon	Blind Canyon	Smith-Roland (Wyodak)
County	Emery	Emery	Campbell
State	UTAH	UTAH	Wyoming
Province	Rocky Mountain	Rocky Mountain	Northern Great Plains
Apparent Rank	HVA	HVA	Subbit C
Moisture Content (wt%, as received)	4.73	3.74	26.74
Ultimate Analysis (wt% dry coal)			
Ash	5.84	6.57	12.61
C	76.53	76.25	64.68
H	5.88	5.80	4.24
N	1.46	1.29	0.95
S	0.40	0.44	1.21
09.89	9.65	16.31	

Table II.1.2
Catalysts Used in Hydroliquefaction of Coals

Fe (III) & Fe (II)	Ni (II)	Co (II)	Mo & W
1. Ammonium iron (III) sulfate dodecahydrate $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$			1. Ammonium tetrathio-molybdate $(\text{NH}_4)_2\text{MoS}_4$ F.W.=260.27
2. Iron (III) nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ F.W.=404.00	1. Nickel (II) nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ F.W.=290.81	1. Cobalt (II) nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ F.W.=291.03	2. Ammonium tetrathiotungstate $(\text{NH}_4)_2\text{WS}_4$ F.W.=348.18
3. Iron (III) sulfate pentahydrate $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ F.W.=489.76	2. Nickel (II) sulfate hexahydrate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ F.W.=262.86	2. Cobalt (II) sulfate hydrate $\text{CoSO}_4 \cdot X\text{H}_2\text{O}$ F.W.=155.00	
4. Ammonium iron (II) sulfate hexahydrate $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ F.W.=392.14	3. Ammonium nickel (II) sulfate hexahydrate $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ F.W.=395.00		

FIGURE CAPTIONS

Figure II.1.1. Total liquids, oils and gases from hydroliquefaction of -60 mesh Blind Canyon (DECS-17) coal at 400 C and 2000 psi for 1 hour with ammonium iron (III) sulfate dodecahydrate as catalyst precursor.

Figure II.1.2. Total liquids, oil and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C, 2000 psi for 1 hour. Catalyst used was iron (III) nitrate nonahydrate.

Figure II.1.3. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using iron (III) sulfate pentahydrate as catalyst.

Figure II.1.4. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using ammonium iron (II) sulfate hexahydrate as catalyst.

Figure II.1.5. Total liquids and gases from hydroliquefaction of -60 mesh Wyodak subbituminous coal (PSOC-1520) at 400 C for 1 hour at 2000 psi using ammonium iron (III) sulfate dodecahydrate as catalyst.

Figure II.1.6. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using cobalt (II) nitrate hexahydrate as catalyst.

Figure II.1.7. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using cobalt (II) sulfate hydrate as catalyst.

Figure II.1.8. Total liquids, gases and oil from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using nickel (II) nitrate hexahydrate as catalyst.

Figure II.1.9. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using nickel (II) sulfate hexahydrate as catalyst.

Figure II.1.10. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using ammonium tetrathiotungstate as catalyst.

Figure II.1.11. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using ammonium tetrathiomolybdate as catalyst.

Figure II.1.12. Conversion of mixtures of coal and polyethylene in hydroliquefaction weight percent (liquid + gases) of feed material.

Figure II.1.13. Conversion of mixtures of coal and polystyrene at 400 C in hydroliquid faction reactions. Value are weight percent (liquid + gases) of feed material.

Figure II.1.14. Conversion of mixtures of coal and polystyrene at different temperatures. Value are weight percent (liquid + gases) of feed material.

Figure II.1.15. Conversion of mixtures of coal commingled plastic. Values are weight percent (liquid + gases) of feed material.

Figure II.1.1. Total liquids, oils and gases from hydroliquefaction of -60 mesh Blind Canyon (DECS-17) coal at 400 C and 2000 psi for 1 hour with ammonium iron (III) sulfate dodecahydrate as catalyst precursor.

Figure II.1.2. Total liquids, oil and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C, 2000 psi for 1 hour. Catalyst used was iron (III) nitrate nonahydrate.

Figure II.1.3. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using iron (III) sulfate pentahydrate as catalyst.

Figure II.1.4. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using ammonium iron (II) sulfate hexahydrate as catalyst.

Figure II.1.5. Total liquids and gases from hydroliquefaction of -60 mesh Wyodak subbituminous coal (PSOC-1520) at 400 C for 1 hour at 2000 psi using ammonium iron (III) sulfate dodecahydrate as catalyst.

Figure II.1.6. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using cobalt (II) nitrate hexahydrate as catalyst.

Figure II.1.7. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using cobalt (II) sulfate hydrate as catalyst.

Figure II.1.8. Total liquids, gases and oil from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using nickel (II) nitrate hexahydrate as catalyst.

Figure II.1.9. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using nickel (II) sulfate hexahydrate as catalyst.

Figure II.1.10. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using ammonium tetrathiotungstate as catalyst.

Figure II.1.11. Total liquids and gases from hydroliquefaction of -60 mesh DECS-17 coal at 400 C for 1 hour at 2000 psi using ammonium tetrathiomolybdate as catalyst.

Figure II.1.12. Conversion of mixtures of coal and polyethylene in hydroliquefaction weight percent (liquid + gases) of feed material.

Figure II.1.13. Conversion of mixtures of coal and polystyrene at 400 C in hydroliquid faction reactions. Value are weight percent (liquid + gases) of feed material.

Figure II.1.14. Conversion of mixtures of coal and polystyrene at different temperatures. Value are weight percent (liquid + gases) of feed material.

Figure II.1.15. Conversion of mixtures of coal commingled plastic. Values are weight percent (liquid + gases) of feed material.

TASK III

Project III.4

DESIGN OF COST-EFFECTIVE WASTE-MANAGEMENT SYSTEMS FOR COAL-LIQUEFACTION PROCESSES

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I. INTRODUCTION

The overall goal of this research program is to systematically design cost-effective waste management systems for coal-liquefaction processes. In particular, two main applications have been targeted: recycle/reuse of gaseous as well as aqueous wastes. The recent strong emphasis on environmental issues provides an additional dimension to the economic viability of coal-liquefaction processes. During the past decade, a number of coal-liquefaction processes have been modified so as to comply with the regulations set for the control of hazardous substances. Unfortunately, these modifications have not followed a systematic approach in design. Hence, these endeavors have been disconnected and the gained insights and expertise have been difficult to transfer from one case to another. While many economic, technical and environmental benefits will significantly accrue as a result of these methodologies, practicing environmental engineers will also be able to transfer waste-recovery technologies systematically and smoothly. The abovementioned challenging tasks call for the development of a novel approach to the design of cost-effective separation networks. Owing to its potential impact on coal-liquefaction technology, such an approach can contribute significantly to the economic competitiveness of coal utilization.

II. SUMMARY OF ACCOMPLISHMENTS:

Since the outset of this project in May, 1992, major findings have been

accomplished in designing waste-management systems for the removal of gaseous and aqueous wastes from coal-liquefaction processes. In particular, the following three tasks have been addressed:

1. The removal of hydrogen sulfide from the gaseous emissions of coal-liquefaction processes: A recovery/recycle/reuse approach has been adopted. Hydrogen sulfide, when recovered in its original form or when converted, by reaction, to some other form (e.g. elemental sulfur) may yield products that are reusable or salable. The design of an optimal, cost effective H_2S recovery network is by no means a straightforward task. It requires the simultaneous assessment of various, potentially applicable technologies and separating agents. This realization has led to the recent introduction of the novel notion of synthesizing reactive mass-exchange networks "REAMEN's" (El-Halwagi and Srinivas, 1992). This useful design technique has been employed to screen various potentially applicable technologies and mass-separating agents (both physical and chemical) and to develop a cost effective waste-management system which can reduce the hydrogen sulfide emissions generated in various parts of coal-liquefaction processes to an environmentally regulated level. The optimum system for recovering hydrogen sulfide was found to be a two-stage absorption process in which water is used followed by hot potassium carbonate. The cost of this novel configuration is \$1.94/bbl. This cost is significantly less expensive than other desulfurization systems.

2. The removal of phenols from the aqueous wastes of the coal-liquefaction process: One of the most serious environmental problems of coal-liquefaction processes is the generation of phenols in the aqueous wastes. To tackle this problem, a membrane-hybrid system has been devised. This system involves the use of solvent extraction, adsorption and reverse osmosis. In order to identify the optimum configuration of this system, the problem has been formulated as an optimization task with the objective of minimizing the total annualized cost of the system while satisfying all environmental and technical constraints. The result was a membrane hybrid system whose cost is \$1.64/m³ of treated wastewater. This cost is much cheaper than alternate dephenolization schemes.

3. Removal of Carbon Dioxide from Gaseous Emissions: At present, carbon

dioxide is not environmentally regulated. Nonetheless, there is a growing trend to impose discharge limits on green-house gases and particularly carbon dioxide. Due to the enormous quantities of carbon dioxide generated within a coal-liquefaction process, efforts have been undertaken to investigate the influence of any future regulation of carbon dioxide on the economics of coal liquefaction. It was found that an environmental specification of 200 ppm will yield an additional cost of about \$0.2/bbl. On the other hand, a stringent discharge limit of 30 ppm will result in an additional cost of about \$25/bbl.

In the following sections, a more extensive discussion on the findings of this research will be provided.

III. TREATMENT OF AIR EMISSIONS

The major air pollutants from a coal-liquefaction plant are sulfur compounds (H_2S , COS, C_2S and mercaptants), oxides of nitrogen, and carbon dioxide. However, of these, the effects of sulfurous compounds are most deleterious to the environment. The major sulphur compound in the gaseous emissions is hydrogen sulfide. There are three major sources of H_2S from the liquid faction plant. These are the gaseous waste streams leaving the hydrogen generation stage, R_1 , that from the gas separation stage, R_2 , and from the fractionation stage, R_3 . Hydrogen sulfide is known to be toxic and can cause chronic effects in living organisms on long exposures. Therefore the emission levels for H_2S ought to be reduced to an environmentally acceptable level of 5 ppm ($=2.1 \times 10^{-7}$ kmols/ m^3). Hence before these waste gas streams are let to the atmosphere, they have to be treated to bring down the level of H_2S to the acceptable level.

Acid gas treatment technologies that are most commonly employed in industry (Kohl and Reisenfeld, 1985; Astarita et. al. 1983) are (i) absorption into a physical solvent (ii) conversion of acid gas impurities into other chemical forms by chemical solvents and (iii) adsorption on to solids. Based on these methods, several desulfurization processes have been commercially developed. Despite their technical feasibility, the cost of these processes may differ substantially from one case to another. Hence, one should screen all potential processes simultaneously and allow for the possibility of integrating more than one technology. For the design of a

desulfurization network to treat the acid gas emissions from the coal plant, eight potential mass-separating agents will be considered which include both physical absorption, chemical absorption and adsorption. These include monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), (all of which are chemical solvents employed in commercial alkanoamine processes), diisopropanolamine (DIAA) (a chemical solvent employed in the ADIP process), hot potassium carbonate (a chemical solvent employed in the Benefield process), physical solvents of water and chilled methanol (employed in the Rectisol process) and activated carbon.

The design of a recycle/reuse desulfurization system for coal-liquefaction plant is based on the procedure of synthesizing a reactive mass-exchange "REAMEN", network (El-Halwagi and Srinivas, 1992). The problem is formulated as an optimization program to minimize the total annualized cost for the given separation task, subject to economic and environmental constraints. The optimization is accomplished via a two stage approach. In the first stage, all potentially applicable technologies and mass-separating agents, are screened simultaneously. The solution of first stage identifies the optimal separation process(es) and the minimum cost of the MSA's involved in performing the specified waste minimization task in a thermodynamically feasible way. This minimum utility cost is solved prior to any commitment to a network structure. The second stage of the optimization strategy is directed toward minimizing the fixed cost of the waste reduction operation by identifying the minimum number of mass-exchange units required for the specified task. The solution of this stage results in identifying the optimal waste reduction loads, stream matches, and thus results in the optimal waste minimization network. Details of this optimization formulation can be found elsewhere (Srinivas and El-Halwagi, 1993; El-Halwagi and Srinivas, 1992).

Based on the aforementioned design methodology, the optimal desulfurization network that is required to perform the required separation task for a 50,000 bbl/day plant at minimum total annualized cost is shown in Fig.1. It involves a single mass-exchange technology, absorption, and employs two different kinds of absorbing agents - a physical solvent, water, and a chemical solvent, hot potassium carbonate. The

optimal desulfurization network requires a minimum of five mass-exchanger to satisfy the desired waste reduction duty; two involving water and three involving hot potassium carbonate. The total annualized cost of the optimal desulfurization network is estimated to be $\$35.525 \times 10^6$.

Having solved the problem, it is interesting to compare the optimal solution with other solutions. For instance, one can generate other solutions by using a single MSA only in the network. Hence, the total annualized utility cost for the proposed optimal desulfurization network by using hot potassium carbonate, chilled methanol, DEA, MDEA and activated carbon are 8.41, 46.29, 55.98, 65.71 and 87.90 \$/bbl, respectively. These figures take into consideration the revenue from producing elemental sulfur in the Claus unit, from the stripped acid gases. As indicated by these figures, the optimal solution indeed offers significant cost savings compared to all other configurations.

IV. DEPHENOLIZATION OF AQUEOUS WASTES

One of the most serious pollutants produced by coal-liquefaction processes are phenols. Several technologies may be used to affect the separation of phenols from the aqueous waste streams. These include solvent extraction, adsorption and reverse osmosis. The task of identifying the optimum configuration of this system is quite challenging. One has to simultaneously screen all potential alternatives and identify the minimum-cost system. The problem was formulated as an optimal-synthesis task whose objective is to minimize the waste-reduction cost while satisfying all environmental regulations and technical constraints. The solution has yielded the optimal system shown in Fig. 2. It features a membrane-hybrid system involving solvent extraction, adsorption and reverse osmosis. The cost of this system is $\$1.64/\text{m}^3$ of treated wastewater. This is much cheaper than alternate dephenolization schemes such as aerobic coupling (Chin et al., 1985), solvent extraction (Greminger et al., 1982), and bio-oxidation (Goldstein and Yung, 1977) whose costs are 4.31, 6.42 and $6.47 \text{ } \$/\text{m}^3$ of treated wastewater, respectively. These results suggest that the devised membrane-hybrid system can indeed be technically and economically effective in tackling dephenolization problems in coal liquefaction.

V. ECONOMIC IMPLICATIONS OF REGULATING PROCESS CO₂ EMISSIONS

Over the past decade there has been a growing public awareness and concern about the consequences of global warming and the release of "green-house" gases into the environment. Though most of these gases are regulated by the USEPA, there still exists no regulation for the release of CO₂, one of the most dominant green-house gases. However, in light of the mounting public pressures, environmental regulations on the discharge of carbon dioxide may be enacted in the near future. In this regard, it is worth predicting the future of coal liquefaction facilities in the US with respect to the economic implications that may arise as a result of regulating the CO₂ emissions from various parts of the liquefaction plant.

The major source of CO₂ emission from a coal liquefaction facility is from the Claus unit. The acid gas streams entering the Claus unit are rich primarily in hydrogen sulfide and carbon dioxide. While hydrogen sulfide is converted into elemental sulfur in the Claus unit, the tail gases are vented into the atmosphere. This tail gas stream is the single major source of CO₂ process emissions from a coal liquefaction plant. The concentration of CO₂ in this stream can be as high as 600,000 ppm (Noyes Data Corporation, 1980).

As mentioned earlier, there exists several technologies and mass separating agents that can treat gaseous streams containing acid gases. In order to project the economics of reducing process CO₂ emissions to different specifications, five mass separating agents have been considered. These are monoethanolamine (MEA), water, chilled methanol, activated carbon and potassium carbonate solution (30 wt.%).

Based the systematic design procedure discussed earlier, it is now possible to design a reactive mass-exchange network to reduce the CO₂ content in the tail gas stream to different emission specifications. In this work five different emission specifications were selected; 500 ppm, 200 ppm, 100 ppm, 50 ppm and 10 ppm. The results of the optimal operating cost (\$/bbl.) required to reduce the CO₂ content in the tail gas stream to these levels is summarized in Fig. 3. It can be seen that while the cost to reduce the carbon dioxide content to 500 ppm is essentially negligible (\$ 0.10 - 0.20/bbl.), the operating cost increases exponentially as the emission specification is

reduced and finally becomes asymptotic as the level drops to 10 ppm. A similar trend is observed for treating tail gas streams of different flowrates (Fig. 4).

VI. CONCLUSIONS

Several systematic procedures for designing optimal waste management systems for coal-liquefaction processes have been developed. These procedures were used to identify cost effective solutions for two major environmental problems associated with coal liquefaction; desulfurization of gaseous emissions and dephenolization of aqueous wastes. The generated solutions enjoy noticeable technical and economic merits over alternate configurations proposed in literature. In addition, these techniques were used to assess the impact of any future regulations of carbon dioxide on the economics of coal liquefaction.

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Fig. 1. Optimal Desulfurization Network

Fig. 2. Optimal Dephenolization Network

Fig. 3. Economic Implications of Regulating Carbon Dioxide

Task IV

Novel Catalysts for Coal Liquefaction

Program Coordinators: Christine Curtis and Dady Dadyburjor

TASK IV

Project IV.1

CATALYTIC DEHYDROGENATION OF MODEL COMPOUNDS IN RELATION TO COAL LIQUEFACTION

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Introduction

Hydrogen donor and transfer reactions are of major importance in the direct liquefaction of coal (DCL). Studies of the catalytic dehydrogenation of coal and recycle solvents can provide valuable information on the ease of hydrogen transfer from hydroaromatic entities and from solvents to coal; the objective is to achieve insights into the chemistry of DCL. Catalytic dehydrogenation can be coupled with ^1H -NMR analysis to obtain information on possible structural properties of coal and recycle solvents during conversion to oils. The quality of recycle solvents, in terms of hydrogen donor ability, are related to their behavior in DCL.

The rate of evolution of hydrogen and the amount of H_2 evolved from coal by catalytic dehydrogenation could be an indication of the activity of the catalyst in DCL, suggesting that catalytic dehydrogenation may be developed as a rapid way to assess the activities of DCL catalysts. We hope to relate the rate of hydrogen removal from hydroaromatics to their reactivities in DCL as well as to the activities of DCL catalysts. Research on catalytic dehydrogenation may help us select good recycle solvents and catalysts for DCL.

The objectives of the present work are (i) to determine the fate of hydroaromatic hydrogen during catalytic dehydrogenation and donor abilities of recycle solvents, (ii) to search for possible mechanistic pathways in catalytic dehydrogenation, (iii) to explore the possibility that catalytic dehydrogenation can be used as an analytic method for determination of the activity of DCL catalysts and (iv)

to obtain information on the fate of hydrogen atoms attached to various polynuclear hydroaromatics during the liquefaction of coal.

Results and Conclusions

On the Nature of Hydrogen Transfer in Catalytic Dehydrogenation and Coal Liquefaction

Researchers have shown that coal conversion is influenced by the amount, and especially the quality, of donor solvents^[1]. It has also been suggested that catalytic dehydrogenation of hydroaromatics of coal may be a useful method to gain insight into catalysis of coal liquefaction^[2]. In the latter case, no direct evidence has been obtained to correlate catalytic dehydrogenation and coal liquefaction. The following discussion is based on comparing the rate of hydrogen removal from 9,10-dihydroanthracene (9,10-DHA) and from 9,10-dihydrophenanthrene (9,10-DHP), two commonly used hydrogen donor solvents; this work may contribute to our understanding of hydrogen transfer during coal liquefaction.

We have previously found that 9,10-DHA evolves hydroaromatic hydrogen to the gas phase more readily than 9,10-DHP, with either Pd/C or with MoS₂, a good DCL catalyst. Can this finding be related to different hydrogen donor abilities of the two isomeric hydrocarbons? Care must be taken to distinguish between hydrogen evolution to the gas phase and actual hydrogen transfer to an acceptor. The transfer of hydrogen from donor solvent to coal is an effective step in coal conversion to form lighter molecular entities; however, hydrogen evolution as molecular hydrogen may be a wasteful use of hydrogen in coal conversion. A crucial step in DCL is to stabilize radicals by providing hydrogen from donor solvents. It was thought informative to investigate the catalytic dehydrogenation activity of a mixture of 9,10-DHA and 9,10-DHP in the presence of a hydrogen acceptor such as stilbene.

When 9,10-DHA and 9,10-DHP were dehydrogenated individually in the absence of hydrogen acceptor, 9,10-DHA tended to lose molecular hydrogen more rapidly than 9,10-DHP. A series of catalytic dehydrogenation experiments were run with equal weight fractions of 9,10-DHA and of 9,10-DHP in the presence of only a half equivalent of stilbene. The curves shown in Figure 1 are revealing. The

decrease in weight fraction of 9,10-DHP and stilbene follows a similar trend; the two curves overlap almost during the whole run. The amount of molecular hydrogen increases proportionally with the increase in the anthracene weight fraction, implying that 9,10-DHA may be responsible for most of the hydrogen evolved to the gas phase. It is clear that 9,10-DHP tends to transfer more hydrogen to an acceptor whereas 9,10-DHA is more likely to lose molecular hydrogen to the gas phase.

The performance of the two hydroaromatic structures under coal liquefaction conditions was examined in experiments in which the concentration of the hydrogen donor compounds was carefully controlled. A 2:1 solvent to coal ratio was employed in the liquefaction of Illinois No. 6 coal to provide enough hydrogen to avoid recondensation of thermally produced radicals. A comparison of the values reported in Table 1 indicates that the loss of hydrogen to the gas phase from 9,10-DHA is significant; higher conversion and oil yields are obtained with 9,10-DHP as donor solvent. The better liquefaction performance of 9,10-DHP suggests that the reaction involves more hydrogenation and hydrogenolysis as compared with the use of 9,10-DHA. The higher liquefaction reactivity of 9,10-DHP can be explained by its ability to function as a good hydrogen transfer agent that can transfer hydrogen to coal at the right conditions of temperature and pressure.

Characterization of Hydrogen Donor Ability of Coal, Recycle Solvents and Heavy Oils

On the basis of the above findings, the hydroaromatic hydrogen content and hydrogen donor ability of DCL resids furnished by Consol Inc. were compared by catalytic dehydrogenation using quinaldine as the vehicle in the presence of a hydrogen acceptor. The samples listed in Table 2 consists of THF-soluble 850°F+ distillation resids. The samples were produced at the Wilsonville pilot plant and the HRI, Inc. bench unit and were chosen to represent variations in processing conditions. As shown in Table 3, the total amounts of hydrogen removed from samples 5 and 7 exceed that obtained from the others, but the amount of hydrogen transferred to a hydrogen acceptor is less, indicating that these two samples may not be effective in hydrogen utilization for DCL. It is noteworthy that the amount of hydrogen transferred from samples 3 and 4 to the hydrogen acceptor (stilbene) is

significantly higher although the total hydrogen removed is less. This is probably because samples 3 and 4 have higher contents of hydroaromatics. The ^1H -NMR analysis shows considerable increase in aromatic content in keeping with the amount of hydrogen transferred. It is reasonable to predict that the hydrogen donating efficiencies of samples 3 and 4 are better than the other resids. As far as DCL behavior is concerned, we predict that samples 3, 4 and 8 will be the best recycle solvents.

Catalytic dehydrogenation of Illinois No. 6 coal and characterization of the dehydrogenation residues by ^1H -NMR were conducted to identify structural changes in relation to DCL. Both phenanthridine (b.p. 350°C) and quinaldine (b.p. 248°C) were used as solvents and the reactions were interrupted at different time intervals to obtain partially or completely dehydrogenated residues for NMR analysis. Interestingly, as shown in Figure 2, the total hydrogen transferred to the hydrogen acceptor with quinaldine as solvent is comparable to the amount of H_2 gas evolved when phenanthridine is used as the solvent. All the residues were then characterized by ^1H -NMR to ascertain structural changes after dehydrogenation. Table 4 shows that the aromaticity of the coal residue increases proportionally to the amount of H_2 evolved. It appears that selective removal of hydroaromatic hydrogen occurred under the conditions employed.

When a heavy oil (North slope $725^\circ\text{F}+$) was dehydrogenated, the amount of hydrogen transferred to the acceptor at 248°C was always less than the amount of H_2 gas evolved at 350°C . Heavy oils contain saturated naphthenic polycyclic structures which are probably difficult to dehydrogenate. Other structures in heavy oils may be responsible for the excess of hydrogen evolved at higher temperatures. Three model compounds--cholestane, cholesterol and cholesterol stearate--whose molecular arrangement is believed to resemble some of the structures present in the heavy oil, were dehydrogenated with quinaldine and with phenanthridine as vehicles, respectively. No hydrogen was evolved from the fully saturated polycyclic compound, cholestane, even at 350°C . However, the other two substrates readily gave off hydrogen at 350°C , but none was evolved at 248°C . It was confirmed by GC-MS and ^1H -NMR that compounds containing an aliphatic hydroxyl or a single double bond in

a polynaphthenic structure could play a role in the release of hydrogen at high temperature. It is possible that compounds with structures resembling cholesterol, with isolated double bonds in one or more rings, are present in heavy oil. This could account for the difference in hydrogen yield when heavy oil was catalytically dehydrogenated by the different vehicles.

These results show promise that catalytic dehydrogenation, coupled with ^1H -NMR analysis, may be a valuable analytical technique to assess the amount and the nature of hydroaromatic hydrogen in coal, recycle solvents and petroleum residues.

Assessment of Activity of Coal Liquefaction Catalysts by Means of Dehydrogenation

Procedures employed for determining the activity of coal liquefaction catalysts (under DCL conditions) are complex and time consuming. A relation between the activity of Mo or Fe catalysts for DCL and that for catalytic dehydrogenation of model compounds has not been previously addressed. We found we could predict the activity of some DCL catalysts by measuring the rate of hydrogen removal from hydroaromatic compounds in catalytic dehydrogenation with phenanthridine as solvent.

Essentially no hydrogen was transferred to stilbene when DCL catalysts (Mo and Fe sulfide) were used in dehydrogenation of 9,10-DHA; evidently stilbene is not adsorbed on the Mo and Fe catalysts. The activities of Mo and Fe sulfides were compared by measuring the amounts of hydrogen evolved as H_2 gas. The percentages of theoretical hydrogen evolution from 9,10-DHA observed using several DCL catalysts are plotted against time in Figure 3. Initial experiments with pyrite (FeS_2) as catalyst showed a slow hydrogen evolution rate; reduction of FeS_2 with hydrogen improved the activity of these catalysts. The amount of hydrogen evolved greatly increased on pretreatment of FeS_2 with hydrogen. The hydrogen evolution rate is significantly enhanced with pyrrhotite, Fe_7S_8 , as catalyst.

Molybdenum and iron sulfides are good coal liquefaction catalysts, with molybdenum more effective than iron. In catalytic dehydrogenation, MoS_2 exhibits excellent activity in the dehydrogenation of model compounds. A quantitative comparison was conducted with a mixture of 20% MoS_2 and 80% Fe_7S_8 as

dehydrogenation catalysts. All the hydroaromatic hydrogen was evolved as hydrogen gas, suggesting that a small amount of molybdenum is active enough to catalyze dehydrogenation. To substantiate this, only 0.1 gram of MoS_2 was used in the dehydrogenation of 9,10-DHA. Comparison of the hydrogen yield from using MoS_2 , Fe_7S_8 , and a mixture of MoS_2 and Fe_7S_8 catalysts shows that 0.1 g of molybdenum sulfide is about as active a dehydrogenation catalyst as 0.5g of pyrrhotite. If the activities of iron and molybdenum for dehydrogenation reactions on a metal loading basis are compared, it is found that molybdenum is about six times more active than iron as a catalyst for dehydrogenation. This activity ratio of Mo to Fe correlates well with that obtained from activity comparisons of molybdenum and iron sulfide in direct coal liquefaction.

Of course, the ratio of the activity of the two catalysts would undoubtedly vary somewhat with the use of other model hydroaromatic compounds as substrates and different solvents in catalytic dehydrogenation. Indeed, when 9,10-DHP, an isomer of 9,10-DHA, was used as the substrate in catalytic dehydrogenation, it was found that, as with 9,10-DHA, molybdenum sulfide was more active than iron sulfide (Figure 4). It is also interesting to find that the rate of hydrogen evolution with 0.2g of MoS_2 and 0.6g of Fe_7S_8 are nearly identical. In this experiment, Mo is about four times as active as iron, corresponding well with the result from dehydrogenation of 9,10-DHA. Catalysts such as MoS_2 and Fe_7S_8 , which are active for direct coal liquefaction, have similar relative activities for catalytic dehydrogenation of the model compounds studied. It appears that there is a relationship between the activities of Mo and Fe in catalytic dehydrogenation to their activities in DCL.

Future Work

Different ranks of coal, recycle solvents and heavy oils will be dehydrogenated in the presence of a hydrogen acceptor, stilbene, and the products will be analyzed by NMR to help in understanding the chemistry involved in coal liquefaction. The hydroaromatic content and donor abilities of the asphaltenes obtained from DCL and from the pretreatment of heavy oils will be examined by catalytic dehydrogenation coupled with ^1H -NMR analysis with the objective of establishing a quantitative

measure of donatable hydrogen in various substrates.

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Table 1. Effect of Donor Solvents on Liquefaction of Illinois No. 6 Coal

Donor solvent	Total Conversion of Coal*	Oil yield	Donor solvent converted to aromatics (wt%)
9,10-dihydrophenanthrene	77.6	23.7	66.0
9,10-dihydroanthracene	70.2	21.2	84.6

* Reaction conditions: 400°C, 1000 psig of He, Solvent/Coal=2:1, and 60 minutes in a microreactor.

Table 2. Description of DCL Resids Obtained from Consol Inc.

Ref. No.	Seam	Mine	Source	Designation	Comments
3	Pittsburgh	Ireland	W; Run 259	V-131B	Resid Composite
4	Pittsburgh	Ireland	W; Run 259	V-131B	THF-Soluble Resid Composite
5	Wyodak and Anderson	Black Thunder	W; Run 262B	V-131B	Resid
6	Wyodak and Anderson	Black Thunder	W; Run 262B	V-131B	THF-Soluble Resid
7	Wyodak and Anderson	Black Thunder	H;Run CC-2-14	PFL	THF-Soluble Resid
8	Wyodak and Anderson	Black Thunder	H;Run CC-15-9ABC	PFL	THF-Soluble Resid

Note: W=Wilsonville; H=HRI; all Wilsonville samples are from vessel V-131B (recycle stream); all HRI samples are pressure filter liquids (PFL).

Table 3. Comparison of Hydrogen Donor Abilities of Recycle Solvents with Quinaldine as Vehicle in the Presence of Stilbene.

Sample ^a	H content (wt%)	Hydroaromatic H by ¹ H NMR (wt%)	Total H removed (cc/gram)	H-transferred to stilbene (cc/gram)	H ₂ evolved as H ₂ (cc/gram)	% hydrogen transferred to stilbene
3	6.5	24.3	138.2	68.9	69.3	49.9
4	6.74	24.3	139.3	70.0	69.3	50.2
5	7.6	21.6	190.6	49.3	141.3	25.9
6	8.19	22.4	159.0	61.7	97.3	38.8
7	8.16	19.7	200.7	48.7	152.0	24.3
8	7.46	18.4	174.0	71.3	102.7	41.0

a. Samples are the distillation residu from DCL furnished by Consol Inc.

The volume of hydrogen was measured at 25°C, 740 mm Hg.

Table 4. Characterization of Residues from Catalytic Dehydrogenation of Illinois No. 6 Coal

Run Time(min)	Aromatic/Hydroaromatic Hydrogen by ¹ H-NMR	Amount of Hydrogen evolved (ml/g)*
60	42.9	112.5
120	68.6	161.5
180	88.9	212.0
210	96.1	227.5

* Reaction conditions: Pd/CaCO₃ as catalyst, phenanthridine as solvent, H₂ was measured at 25°C, 744 mmHg.

Figure 1. Dehydrogenation of a mixture of 9,10-DHA and 9,10-DHP in presence of half an equivalent of hydrogen acceptor with Pd/C as catalyst, quinaldine as vehicle.

Figure 2. Determination of the hydroaromatic content in Illinois no.6 coal using different vehicles.

Figure 3. Evolution of molecular hydrogen from 9,10-DHA in presence of DCL catalysts, phenanthridine as vehicle.

Figure 4. Evolution of molecular hydrogen from 9,10-DHP in presence of DCL catalysts, phenanthridine as vehicle.

TASK IV

Project IV.2

IMPROVED CATALYSTS FOR COAL LIQUEFACTION AND CO-PROCESSING: NEW INITIATIVE IN DISPERSED SLURRY PHASE CATALYSIS

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INTRODUCTION

During the past year, we have studied the catalytic activity of a nanoscale dispersed iron oxyhydroxide catalyst using four coals and several model compounds in a tubing bomb microreactor. Several forms of iron catalyst were examined including the original 3 nm iron oxyhydroxide, H₂ pre-reduced and in-situ sulfided forms. The objective of our research was to examine the effectiveness the dispersed iron catalyst in coal liquefaction and model compound reactions. A variety of coals and process conditions was examined. Model compound reactions were performed using the same catalyst to provide additional insight regarding catalyst performance.

EXPERIMENTAL SECTION

The original catalyst employed in our experiments was a commercial superfine iron oxyhydroxide obtained from Mach-I Inc. Analysis showed the catalyst to be 64 wt% Fe (FeOOH = 63%), with a N₂ BET surface area of 215 m²/g and particle size of 3 nm. Except as noted, the catalyst was used as received without drying, or other pretreatment. Coal liquefaction runs were performed using HVA bituminous Blind Canyon (BC) DECS-17 coal and three Argonne coals, Illinois No. 6 (ILL), Pocahontas No. 3 (POC), and Wyodak (WY). Elemental sulfur was added

as an additional sulfur source for sulfidation of the catalyst. The detailed reaction conditions are shown in Table I. The pentane and tetrahydrofuran insoluble products were determined as an indication of catalyst activity and liquefaction reactivity. Equation 1 was used to calculate the pentane solubles (PS) (including gases) and tetrahydrofuran solubles (THFS) on an maf coal basis.

$$\% \text{ MAF SOLUBLES} = \frac{W_o(1-M)-(IS-W_c)}{W_o(1-A-M)} \cdot 100 \quad (1)$$

W_o : initial weight of coal as charged to TBMR.

A : fraction of ash in the coal as charged.

M : fraction of moisture in the coal as charged.

IS : weight of insolubles from fractionation procedure, including ash and catalyst.

W_c : weight of catalyst following reaction.

Model compound reactions chosen were the hydrogenation of naphthalene (NAPH) and biphenyl (BPH) and the hydrocracking of dibenzyl ether (DBE), benzaldehyde (BAH) and benzyl alcohol (BAL). Experiments were carried out in two different types of TBMR at the conditions in Table I. The catalyst reduction process was performed by placing the TBMR in a furnace for 24 hours with a H_2 flow rate of 100 cc/min measured at ambient conditions. For model aromatic ring hydrogenation reactions, an extent of hydrogenation A_H was defined as follows:

$$\text{or } A_H = \frac{2M_{TET} + 5M_{DEC}}{5(M_{NAPH} + M_{TET} + M_{DEC})} \quad A_H = \frac{3M_{CHB} + 6M_{DCH}}{6(M_{BPH} + M_{CHB} + M_{DCH})} \quad (2)$$

In equation (2), the M_i are the moles of compound i in the reaction products consisting of tetralin (TET) and decalin (DEC) for NAPH hydrogenation and cyclohexylbenzene (CHB) and dicyclohexyl (DCH) for BPH hydrogenation, respectively. For hydrocracking reactions, activity was expressed by the conversion of the original reactant.

Product samples collected were analyzed by gas chromatography using temperature programming to improve peak resolution and decane as an internal standard. Peak identification was made from previous literature results confirmed by standard addition of authentic compounds.

RESULTS AND DISCUSSION

Coal liquefaction experiments were performed in the presence and absence of dispersed iron catalyst using several coals under various reaction conditions including catalyst loading and initial surface area, solvent type, and reaction temperature. BC coal was the baseline coal used in our experiments.

Effect of Catalyst and Sulfur Addition on Blind Canyon Coal. Figure 1 shows the effect of catalyst and sulfur additions on product yields with BC coal at the baseline reaction conditions in Table I. Sulfur alone increased PS by 5% while the iron catalyst alone gave a 7% increase. Combination of sulfur and catalyst increased the PS yield by 11%. The THFS show corresponding although somewhat smaller relative increases in line with the behavior of the PS. It appears that the effect of sulfur and catalyst are approximately additive and that a large degree of synergism is not reflected in the increased yields. To some degree this lack of synergism argues against the necessity of having the iron in the sulfided form, FeS_x ($x \approx 1.05-1.15$), to function catalytically.

Catalyst Activity with Various Solvents. Figure 2 shows a comparison of the results obtained using different liquefaction solvents with BC coal at baseline reaction conditions. Tetralin was used as the baseline solvent. When mineral oil (an aliphatic non-donor) was used in place of tetralin, little difference was obtained between the PS and THFS yields with or without catalyst. The lack of effectiveness of the catalyst with this solvent emphasizes the fact

that a catalytic effect in coal liquefaction is a result of a combination of effects including the solvent, e.g. possibly hydrogen shuttling, in addition to its effect on the coal alone. The results with the aromatic solvent, 1-methylnaphthalene, showed a similar trend as tetralin with regard to the effectiveness of the catalyst. The PS yields with creosote oil were very low in that there was actually an increase in pentane *insolubles* formed during the liquefaction reaction. It is probable that creosote oil undergoes regressive combination reactions with coal radicals. In general, these results affirm that catalytic coal liquefaction must be viewed in light of the *overall* solvent-coal reaction system rather than simply as a catalyst-coal interaction.

Effects of Catalyst Loading and Surface Area. Variations in catalyst loading and surface area were examined using both BC coal and model compounds. As shown in Figure 3, increasing the catalyst loading increases the PS and THFS yields; however the incremental increase is not linear and additional catalytic benefit declines significantly as the loading is increased. Similar results were observed with the model hydrogenation reaction of NAPH in mineral oil as shown in Figure 4, where the extent of hydrogenation defined by equation (2) increased sharply in a very narrow range of catalyst loading to a constant level, corresponding to the complete conversion of NAPH to TET. Figure 5 shows the dependence of product yields on the initial surface area of the catalyst. There is a decrease of PS and THFS with the decrease in catalytic surface area. These results are believed to be caused by sintering of the original 3 nm catalyst particles or by a change in chemical structure.

Liquefaction of Argonne Premium Coals. Figure 6 shows the effect of catalyst addition on liquefaction of three different Argonne coals at both 400°C and 425°C. Also shown is the baseline DECS-17 BC coal. The WY and the ILL coals did not show as significant an increase in PS as did POC, which is a LVB coal. All Argonne coals showed significant increases in THF

solubles in the presence of the catalyst with POC again showing the greatest relative increase. The trend in liquefaction yields evidenced by the Argonne coals is in general agreement with other reported results using these same coals.

Effect of Reaction Temperature. Figure 6 also illustrates the effect of increasing reaction temperature from 400 to 425°C on catalytic liquefaction with the BC and Argonne coals. Generally all coals showed a significant increase in PS and THFS at 425°C as compared to 400°C, however, the coals showed rather different susceptibilities to catalytic vs. thermal action. The contrast in the response of POC as compared to WY and ILL with regard to catalytic vs. thermal actions is particularly striking. POC was greatly affected by catalyst and little influenced by temperature while ILL and WY were primarily responsive to the change in temperature and less affected by the catalyst. On the other hand, BC appears to be about equally affected by catalyst and temperature. The THFS yields of the coals are not quite as definitive as the PS yields regarding catalytic vs. thermal activity, although increases with both temperature and catalyst for all coals are readily apparent.

Model Compound Hydrogenation Reactions. Several forms of dispersed iron catalyst were employed including the original iron oxyhydroxide, H_2 pre-reduced iron and FeS_x . For some experiments the original iron oxyhydroxide was pre-reduced with H_2 . To establish a proper pre-reduction procedure, the hydrogenation of NAPH was studied using iron which had been pre-reduced for 24 hours at temperatures of 200 to 600°C. The results in Figure 7 show that reduction temperatures above 250°C are detrimental to the catalyst activity, presumably due to sintering of the catalyst during reduction. Therefore, a reduction temperature of 200°C was chosen for further experiments. Figure 8 shows that, for the hydrogenation of both NAPH and BPH, the pre-reduced iron catalyst gives higher extents of hydrogenation (eq. (2)) than the original oxide form, while

CS₂ addition almost completely poisons both catalysts, whether in the original form or pre-reduced form. These results show that the sulfided form is a *much less active* aromatic ring hydrogenation catalyst than the reduced form. A notable phenomenon observed is that, in both NAPH and BPH reaction systems, significant secondary hydrogenation reactions, i.e., the conversion from tetralin to decalin and from cyclohexylbenzene to dicyclohexyl, took place *only* when the catalyst had been pre-reduced, even when the catalyst loading was increased almost ten times as shown for NAPH hydrogenation in Figure 4. This observation suggests that the greater aromatic ring hydrogenation activity of reduced iron is due to largely catalytic sites of greater activity rather than merely an increase in number of sites. Moreover, it is likely that when the original oxyhydroxide catalyst is used in the complete absence of sulfur, a partial in-situ reduction occurs and the active sites are a reduced iron phase.

Model Compound Hydrocracking Reactions. DBE and the related model compounds, benzaldehyde (BAH) and benzyl alcohol (BAL) were used as initial reactants to examine the activity and selectivity of the dispersed iron catalyst in this work. Figure 9 shows the conversions of DBE, BAH and BAL with and without catalyst at 300°C. All of the iron catalysts catalyzed the cracking of DBE, particularly the reduced iron and iron sulfide which had approximately the same activities. This is in marked contrast to the NAPH and BPH aromatic hydrogenation reactions where the reduced iron had much greater activity. In the presence of catalyst, toluene was always the dominant cracking product of DBE, while BAH and BAL were detected only in trace level. When BAH was used as initial reactant in the absence of any catalyst, benzoic acid (BZA) was found to be the major product. When the catalyst was employed, however, primary products were TOL and BAL with the concentration of BZA being greatly reduced. The evidence that TOL was found to be always the dominant cracking product in all of the three reaction

systems in the presence of catalyst implies that the iron catalysts generally promote the complete cleavage of the C=O bond in BAH and the C-O bond in BAL and DBE. Reduced iron and iron sulfide had almost the same activities for the cracking of DBE and BAL, while reduced iron showed superior activity to iron sulfide for the cracking of BAH. In additional model compound reactions carried out in this work, no significant catalytic cracking was observed when applying the same catalysts to the reaction systems of biphenyl, diphenylmethane and isopropylnaphthalene at 400°C and 7.9 MPa H₂ (cold) where the cracking of C_{ar}-C_{ar} or C_{ar}-C_{alk} bonds was required.

Table I. Baseline Reaction Conditions for Coal and Model Compound Experiments

TBMR Type ^a	A	A (B)	A (B)	A (B)
Reactant wt., g	Coal 3	NAPH 0.12 (0.24)	BPH 0.12 (0.24)	DBE,BAH & BAL 0.12 (0.24)
Catalyst wt., g	0.06	0.03 (0.06)	0.03 (0.06)	0.03 (0.06)
Solvent wt., g	Tetralin 10	Mineral Oil 6 (12)	Hexadecane 6 (12)	Cyclohexane 6 (12)
Sulfur Source wt., g	Elementary Sulfur 0.1	CS ₂ 0.012 (0.024)	CS ₂ 0.012 (0.024)	CS ₂ 0.012 (0.024)
Temp., °C	400	350	300	300
H ₂ Pressure ^b , MPa	8.6	7.9	7.9	7.9
Time, h	1	1	1	1

^a The volume of Type A was 45 cc for coal runs and 17 cc for model compound runs. Type B is the same as Type A (45cc) except modified to have both inlet and outlet ports. This type TBMR was used for catalyst pre-reduction with H₂.

^b Measured at ambient temperature.

Figure 1 Effect of catalyst and sulfur addition on pentane and tetrahydrofuran soluble yields with Blind Canyon coal

Figure 2. Catalyst performance using Blind Canyon coal with different types of liquefaction solvents.

Figure 3. Variation in pentane and tetrahydrofuran soluble yields with catalyst loading

Figure 4. Effect of catalyst loading on extent of naphthalene hydrogenation at 350°C.

Figure 5. Variation in pentane and tetrahydrofuran soluble yields as a function of initial catalyst surface area at constant loading of 2 wt% of coal.

Figure 6. Comparison of catalytic and non-catalytic liquefaction yields with BC and Argonne coals at 400°C and 425°C.

Figure 7. Effect of reduction temperature of catalyst on extent of naphthalene hydrogenation.

Figure 8. Effect of catalyst on extent of naphthalene and biphenyl hydrogenation at 350°C and 300°C, respectively.

Figure 9. Effect of catalyst on hydrocracking of dibenzyl ether, benzaldehyde and benzyl alcohol at 300°C.