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Cooperative Research in Coal Liquefaction

**Final Report on DOE Contract
No. DE-FC22-90PC90029
Period: May 1, 1990 to April 30, 1991**

**Submitted to
U.S. Department of Energy**

**On Behalf of the
Consortium for Fossil Fuel Liquefaction Science**

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

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**Submitted by the University of Kentucky
On Behalf of the**

Consortium for Fossil Fuel Liquefaction Science

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

**Overview of Research Conducted by the
Consortium for Fossil Fuel Liquefaction Science**

on DOE Contract #DE-FC22-90PC90029

Period: May 1, 1990 - April 30, 1991

G. P. Huffman, Director

Consortium for Fossil Fuel Liquefaction Science

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SUMMARY

Introduction

The Consortium for Fossil Fuel Liquefaction Science (CFFLS) is currently engaged in a three year contract with the U.S. Department of Energy investigating a range of research topics dealing with direct coal liquefaction. This report summarizes the results of this program in its second year, from May 1, 1990 to April 30, 1991. A brief overview of the principal results obtained this year is given below.

Iron-Based Catalysts

A systematic study has been made of the preparation, characterization, and catalytic activity for direct coal liquefaction of the sulfated metal oxides based on iron, tin, and molybdenum. The catalysts studied included: $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{FeOOH}/\text{SO}_4^{2-}$, $\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$, $\text{SnO}_2/\text{SO}_4^{2-}$, and $\text{SnO}_2/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$. The physicochemical properties of these catalysts were also determined. The sulfated oxides of iron, with a particulate size of 30-80 Å, formed finely dispersed pyrrhotites with particle sizes of 20-30 nm under coal liquefaction conditions in the presence of sufficient sulfur. For both Illinois No. 6 and Wyodak coals, conversions on the order of 90%+ were obtained with the sulfated iron oxides as catalysts; oil yields exceeded 70%. All experiments used 3500 ppm iron with respect to coal. Further improvement in selectivity to lighter oils was obtained by adding 50 ppm of molybdenum to the $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst. The following order of catalyst activity for direct coal liquefaction was observed: $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{SnO}_2/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$, $\text{SnO}_2/\text{SO}_4^{2-}$, $\text{FeOOH}/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3$ and $\text{Fe}(\text{CO})_5$ in the

presence of sulfur. At 400°C under 1000 psig (cold) of H₂, use of 3500 ppm of Fe in the form of sulfated iron oxide resulted in higher yield of oils than did 500 ppm of Mo added as Mo(CO)₆. The sulfated iron and tin oxides were also found active for coal-heavy oil coprocessing reactions.

Systematic development studies have continued on the low-temperature depolymerization-liquefaction (HT-BCD-HPR) treatment of premium U.S. coals. Two additional coals, Wyodak and Lewiston-Stockton were investigated. Structural analyses of the products were carried out by GC/MS and elution chromatography. Chemical trends illustrate the effect of different treatment steps: during the initial mild HT, the H/C ratio increases but there is little change in the O/C ratio; then, during BCD, the O/C ratio decreases with little change in the H/C ratio; finally, during HPR, the H/C ratio increases significantly while the O/C ratio continues to decrease somewhat. On the basis of boiling point distributions, the final HPR product is a light hydrocarbon oil primarily (>70%) in the gasoline, kerosene, and light gas oil range.

Hiawatha coal macerals (vitrinite and resinite) have been impregnated with iron chloride catalyst and hydrotreated (HT) at 290 C. Electron microprobe analyses indicate dissociation of the Fe and Cl ions and separate migration in the coal macerals, with significantly better penetration into the vitrinite macerals than the resinite macerals. Following the HT, diffuse reflectance FTIR reveals an increase in intensity of the CH stretching bands of methyl groups in the vitrinite sample that is not observed in the resinite sample. Additionally, the HT vitrinite experiences 8% weight loss, while the HT resinite experiences 40% weight loss. These observations are consistent with the model of the impregnated iron ions catalytically promoting cleavage of methylenic linkages.

A new chemical method of producing fine particle iron sulfides is being explored. The method consists of reacting sodium sulfide with iron chloride to produce Fe₂S₃ and NaCl. The Fe₂S₃ then disproportionates to a mixture of Fe_(1-x)S and FeS₂. The relative amounts of the two iron sulfides can be controlled by varying annealing temperature and

time. Tests are underway to establish the optimum annealing conditions for maximum activity using a newly designed and constructed continuous flow-through liquefaction reactor.

^{57}Fe Mössbauer spectroscopy and x-ray absorption fine structure (XAFS) spectroscopy were used to characterize a wide variety of iron-based catalysts, including sulfated Fe_2O_3 and FeOOH catalysts, iron incorporated into coal by the Shabtai treatment, iron cation-exchanged into lignite, iron carbides prepared by laser pyrolysis, ultrafine (3 nanometer) Fe_2O_3 particles, and iron sulfides and other species produced during liquefaction or hydrotreatment. Good progress was made in developing an improved theoretical model for analyzing the superparamagnetic Mössbauer spectra exhibited by such catalysts. It was confirmed by a quantum relaxation model that size distributions derived earlier using a much simpler model were essentially correct. Typical particle sizes observed range from 2 to 10 nanometers. Fe_3C and Fe_7C_3 were identified as the principal phases in ultra fine iron carbide particles formed by a laser pyrolysis process. In samples subjected to liquefaction or hydrotreatment, the ultrafine ferric oxide particles are normally converted to pyrrhotite if sufficient sulfur is present.

In related work, SQUID magnetometry was used to examine an $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst. Assuming a log normal particle size distribution, the M vs. H data were analyzed to determine the parameters of the distribution. The results were a mean particle size of 6.5 nanometers, with a particle size range of 3.5 to 11.5 nanometers, in reasonable agreement with the results of the Mössbauer analysis of the same catalyst.

Radial distribution functions derived from the XAFS spectra show that the iron atoms in fine ferric oxide catalyst particles have on average less iron atoms in shells located at second through fourth nearest neighbor distances than the corresponding bulk compounds (Fe_2O_3 and FeOOH). This is because such fine particles have a significant percentage of their iron atoms located on or near the surface of the particle. A model is being developed to determine particle size from iron shell coordination numbers. High

temperature in situ XAFS studies of iron-based catalyst reactions have also been initiated.

A unique in situ sampling probe has been developed to extract samples directly from a one liter stirred autoclave reactor under hydrogen or nitrogen into sealed sample containers for Mössbauer, XAFS, or other types of analyses. The first successful test of this system was run this year using a Wyodak coal and a sulfated Fe_2O_3 catalyst with fairly standard liquefaction conditions. This system will be used in the future to study the kinetics of catalyst reactions.

XPS studies were carried out on a variety of sulfated oxide catalysts prepared at the University of Pittsburgh, containing Fe, Sn, and Mo oxides. For the sulfated catalysts, the surface S concentration was usually about double the bulk sulfur concentration. A detailed peak deconvolution was made of the oxygen band for a $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4$ catalyst, giving the following results; 47% oxygen as Fe_2O_3 , 41% as SO_4^{2-} , and 12% as MoO_3 . Oxygen peak deconvolution appears to be a fairly sensitive method of analyzing the surface structure of such catalysts.

Other Types of Catalysts

In work on supported Ni-Mo catalysts, it was demonstrated that calcium impregnation was effective in extending the lifetime of a unimodal catalyst, but was not effective for a bimodal catalyst. The diffusivity of aged catalysts was generally reduced by an order of magnitude relative to fresh catalysts, but could be completely restored by oxidative regeneration.

Boron nitride shows better catalytic activity for HDN than a commercial Co-Mo catalyst, based on surface area of the catalysts. Pretreatment with H_2S improves the activity but decreases the HDN. Pretreatment with NH_3 improves the activity less than H_2S does, but HDN is decreased less for NH_3 than for H_2S . The BN is not very active at 300 and 350°C. The presence of H_2O deactivates BN.

A study of catalytic dehydrogenation is aimed at improving our basic understanding

of hydrogen transfer and at determining if the activity of a catalyst for dehydrogenation is a good measure of its potential activity in coal liquefaction. Experiments have been carried out using Pd/CaCO₃, Pd/C and Fe₂O₃/SO₄ catalysts and model compounds. Both Pd catalysts are good dehydrogenation catalysts but no hydrogen was evolved using the iron catalyst, surprisingly. It was determined that the Fe₂O₃ was being reduced to Fe₃O₄ and the hydrogen was being evolved as H₂O. The rate of hydrogen evolution in catalytic dehydrogenation is observed to vary with the nature of the vehicle, increasing as the reduction potential of the vehicle decreases.

Exploratory Research on Coal Conversion

In the continuing effort to determine carbon skeletal structures, a significant effort was made in the measurement and interpretation of ¹³C chemical shift tensor data on model polycyclic aromatic hydrocarbon compounds. Additionally, ¹H relaxation data was obtained for Pittsburgh #8 coal and chars prepared from it at various temperatures. Generally, the relaxation time becomes shorter for higher temperature chars.

Excellent progress was made in the program to develop a GC/MS + vacuum thermogravimetry(TG) method of measuring molecular weights(MW) of coal liquids. An approximately linear relationship was observed between MW and GC elution temperature using a short (40 cm) column operating at high carrier gas velocities for 103 model compounds. It was also established that there was close agreement between vacuum TG and short column GC/MS profiles. This results indicate that the combined GC/MS/vacuum TG technique can be empirically calibrated for the proposed MW determination method. An on-line mass spectrometry interface for high pressure reactor environments is also being developed. Initially, it has been used to study several model compound reactions.

A high pressure-high temperature ESR cavity system for in situ studies to 500 C and pressures to 750 psi has been successfully fabricated and tested. This system will be

extended to 1000 psi and used to carry out cracking/hydrogenation experiments using Mo an Fe sulfide catalysts.

Quantum chemical computational methods are being applied to model compounds and molecular fragments of relevance to coal liquefaction. In the past year, the following investigations were completed:

- (1) A comparative study of bond dissociation energies, in the presence and absence of a catalyst;

- (2) Calculations of the heats of reaction for hydrogenation of a model compound in the presence and absence of a catalyst.

Other investigations initiated this year included theoretical treatment of the effect of an electron-removing catalyst on bond cleavage in model compounds, development of a molecular dynamics method suitable for large complex molecules, and exploration of methods for the study of the surface electronic structure of Fe-S alloys.

A new approach being applied to the investigation of coal conversion and catalyst reactions utilizes an electrodynamic balance to suspend single particles. The suspended particles are then irradiated with laser beams and both their size and structure can be determined. In the current year, the apparatus has been modified to allow suspension of single coal particles 5 to 20 microns in size by a combination of aerodynamic and electrodynamic forces, and it has been demonstrated that adsorption isotherms can be measured in selected gases or vapors. Additionally, a significant improvement in the signal to noise ratio of Raman spectra obtained from such suspended particles has been made.

Some coals utilize gaseous hydrogen very efficiently so that conversion during the early period of liquefaction is greater in 1-methylnaphthalene, a non-donor solvent, than it is in tetralin, a good hydrogen donor solvent. This enhanced conversion could be viewed to be due to hydrogen shuttling by the formation of di- or tetra-hydro methylnaphthalene. If the methyl group is to be effective in adding hydrogen, we could

visualize 1,2 deuterium addition as:

If deuterium shuttles by a 1,2-dihydro-1-methylnaphthalene intermediate [reaction 1], exchange should occur predominantly in the ring-2 position. If the shuttling occurred through reaction [2] exchange at the ring 3 and 4 position should occur in equal amounts.

The data clearly eliminate the participation of reaction [2] since the 4- (para) position exchanges to a much greater extent than the 3- (meta) position. Likewise the ring α position in the unsubstituted ring exchanges more rapidly than the β position. We likewise eliminate reaction [2] because (1) the exchange in the 4-ring position is greater than in the 3-position and (2) the exchange in the unsubstituted α -ring position is greater than exchange in the 2-ring position. Dihydrogen intermediates, if they are responsible for shuttling, must be the result of 1,4 hydrogen addition, and this is considered unlikely.

Exchange appears to be different in coal structures and the 1-methyl-naphthalene solvent molecules since the alkyl hydrogens in coal fragments exchange at 385°C but do not do so in the solvent. Furthermore, coal solubilization appears to occur more rapidly than deuterium exchange. In addition the extent of deuterium incorporation into solvent molecules appears to be about the same extent in the presence or the absence of coal. Thus, the results of the deuterium studies appears to eliminate the shuttling of hydrogen

by solvent molecules as being responsible for the apparent superior conversion in the non-hydrogen donor 1-methylnaphthalene.

Novel Coal Liquefaction Concepts

In order to study biological hydrogenation of coal for enhanced liquefaction, experiments were conducted with different bacteria on various coals and model compounds. Our results obtained using Warburg apparatus showed hydrogen uptake by a number of coals and model compounds resulting from biotreatment with *Sulfolobus brierleyi* and *Desulfovibrio desulfuricans*, the hydrogen uptake of a pretreated KY #9 coal and an asphaltene sample were 2370 and 1793 ($\mu\text{mol/g}$) of coal respectively. The effect of *S. brierleyi*, *D. desulfuricans* and Oil-2 isolate on DPM and coal (KCER#91182) were observed in the presence of an organic solvent, benzene. Although maximum bacterial growth was observed in the absence of benzene, the experiment showed that the bacteria did grow even in the presence of 80% benzene in the medium. *Sulfolobus brierleyi* has been used to study the formation of in-situ mixed metal catalysts (Mo and Ni) containing active iron derived from coal.

During the past year, we have completed our evaluation of 1,4-dihydroquinone (DHQ) as a coal hydrogenation source. DHQ yields larger amounts of THF-extractables with several given coals than standard hydrogen sources. The enhancement of THF-solubility occurs at very low temperatures (ca. 200°C). Model compound studies show that DHQ functions by providing a source of hydrogen to quench radical chain processes.

A new set of hydrogen donors known as cyclic olefins (CLO's) has been evaluated to determine their effectiveness as hydrogen donors to coal. These CLO's, as well as their conventional donor analogues TET, OHA, and DHA, were reacted with the coals from the Argonne Premium Coal Sample Program under equivalent reaction conditions. The CLO's and their analogues were also reacted with Pittsburgh No. 8 coal at reaction times of 5, 15, 30 and 60 minutes under equivalent conditions. Reactions with a combined

HHA / DHA (1:1 ratio by weight) system were also performed. Reactions were also performed with process solvents derived from Pittsburgh No. 8 and Illinois No. 6 coals supplied from the liquefaction experiments of the Wilsonville coal liquefaction pilot plant.

Several results need to be emphasized for the Argonne coals. In all of the liquefaction reactions the cyclic olefin ISO always produced greater coal conversion to THF solubles and released more hydrogen than its conventional hydrogen donor analogue TET. The cyclic olefin HHA always produced greater coal conversion and released more hydrogen than its conventional donor analogue OHA. In the liquefaction reactions performed, ISO always produced more coal conversion than OHA, except for those reactions with Western Kentucky No. 9 coal. The conventional donor compound TET produced lower conversions to THF solubles than the reactions of Upper Freeport, Blind Canyon, or Beulah-Zap coals with no added donor. In all of the liquefaction DHA produced more coal conversion than HHA. For all the added donors in the liquefaction reactions, Illinois No. 6, Western Kentucky No. 9, and Pittsburgh No. 8 coals were reactive; Pocahontas No. 3 coal was completely unreactive in the reaction system used, regardless of the donor present. As was shown by the GC analysis of the reaction products, the cyclic olefins were completely converted in all of the liquefaction reactions that were performed. By contrast, their conventional hydrogen donor analogues all remained partially unreacted in every reaction system. For all of the liquefaction with DHA, there was a net incorporation of hydrogen through its formation of OHA, which is a much poorer hydrogen donor compound for coal conversion.

For the reactions with Pittsburgh No. 8 coal, the 1:1 combined HHA / DHA system was the most effective at producing the highest coal conversion in the least amount of time. The cyclic olefin's release their hydrogen rapidly to produce an initial increase in coal conversion to THF solubles and the rate of hydrogen lost from HHA in the combined HHA / DHA reactions was nearly the same as in the 100% HHA reaction system. In general, coal conversion increased with increasing reaction time for all the reactions with

a given hydrogen donor compound. In the liquefaction reactions, the cyclic olefin ISO always produced higher coal conversion than its conventional donor analogue TET; ISO also produced higher, or equivalent, conversion as the conventional hydrogen donor compound OHA. In the liquefaction reactions, the cyclic olefin HHA always produced higher coal conversion than its conventional donor analogue OHA.

Coal liquefaction is similar to other catalytic gas-liquid slurry-type reactions that are free-radical driven. A simple kinetic model has been used to demonstrate the important role that hydrogen mass transfer plays during the initial stages of coal liquefaction. The model was shown to predict observed profiles for the H:C ratio of liquefaction products versus reaction time curves.

The experimental phase of the work involved the development of more effective gas-liquid contactors. Two basic parameters were identified as important to effective mass transfer: initial bubble-size distribution and effective bubble pathlength. Gas-liquid mass transfer coefficients were experimentally determined for different combinations of gas-liquid contactors and columns by utilizing a catalyzed sodium sulfite reaction system. It was found that the most critical factor in the gas-liquid contactors studied was the shear stress at the point of gas introduction.

Two model reactions, known to be mass transfer limited, were used to test equipment designs for their potential use in coal liquefaction. The model reactions studied were naphthalene hydrogenation and tetralin oxidation. Injector nozzles were fabricated, tested, and installed in a pilot reactor system. Also, different packing sizes and pumps were evaluated in the pilot reactor system using the naphthalene hydrogenation reaction. Optimization of this reaction was carried out to the point where the free radical generation rate, not gas-liquid mass transfer, was limiting the reaction.

The tetralin oxidation (TO) reaction was studied to gain experience with a more complex reaction mechanism. A kinetic study was conducted in the reactor system and a novel reaction mechanism, based on this study, is proposed. Data analysis showed that

the pilot reactor system was gas-liquid mass transfer limited at catalyst concentrations greater than 0.0769 M. Small concentrations of acetic acid and N,N-dimethylacetamide were added in the reaction as catalyst dispersants and found to significantly improve conversion. Based on experimental observations, the active state of the catalyst is an organometallic complex formed during the reaction. One role of these dispersants was thought to be in facilitating the formation of this highly catalytic organometallic complex.

The TO reaction was observed to model coal liquefaction in that inhibitors were observed to terminate free-radical generation and completely halt reaction once they were present above a certain threshold concentration. This aspect of the TO reaction, as with coal liquefaction, represents a challenge that must be further addressed in future research.

Another phase of the work had to do with developing means of applying techniques observed to be effective for improving mass transfer in commercial-scale systems and to microreactor methods used in exploratory laboratory studies. As has been discussed in past reports, one technique observed to improve mass transfer is to control the free-radical generation rate by switching temperature from a high to a low level at a sufficiently high frequency. By cyclic switching temperature, the rate of free-radical generation, and thus reactant (H_2 or O_2) demand, will also shift between high and low levels. Because of this switching, reactant demand (kinetics) can be kept in balance with reactant supply (mass transfer capabilities). This concept was tested using the pilot reactor system and the TO reaction. A doubling of the frequency via a simple design alteration appears to have improved the mass transfer rate significantly.

In preparation for doing exploratory coal liquefaction studies, attempts were made to develop a methodology for evaluating the effect of switching frequency on liquefaction product distribution. To this end: a series of microreactor studies were performed using the model naphthalene hydrogenation reaction. Reaction conditions were identified at which mass transfer was controlling (i.e. reaction rate was limited by hydrogen supply). Responses in the rate of conversion and loss of catalyst activity in relation to changes in

switching frequency were measured. It was observed that a high switching frequency, of the order of less than one switch every ten seconds, was required. The necessity of using this high of a frequency made it very difficult to use a standard microreactor to study the effect of this parameter.

Catalytic hydrothermal liquefaction has been shown to be a viable way to produce liquids from coal. With the proper catalyst, only a small amount of coal was unconverted or crosslinked to form insoluble products. Ammonium iron (III) sulfate showed high activity for this reaction. Although molybdenum is moderately expensive (per unit mass), molybdenum sulfide from ammonium tetrathiomolybdate exhibited extremely high activity even at low concentration (0.2%). Hence, molybdenum might prove to be a justified catalyst for coal hydrothermal liquefaction. Co-catalysts of iron and molybdenum sulfide were shown to be very active and was better than iron or molybdenum alone. Future study will be concentrated on finding the best catalyst for catalytic hydrothermal liquefaction of coal. This includes searching for a new catalyst, trying to reduce the amount of molybdenum, and exploring the promoter/synergistic effect of molybdenum and iron.

Laboratory experiments were performed to investigate the effect of ultrasound on coal liquefaction in different solvent extraction conditions. In this research project, ultrasonic waves were generated by a Fischer-Sonic Dismembrator with a titanium tip.

Experiments were done to reveal the relation between the coal liquid yield and other parameters such as: the tip intensity, reaction time, solvent and catalyst. From a series of experiments, the best ultrasonic tip intensity generated by this dismembrator for coal extraction was 88.6 W/Cm².

Coal samples used in this project were Blind Canyon Coal (PSOC-1503) and Argonne high-volatile bituminous coal (ID 601:00065). Solvents such as THF, THF-water and pyridine-methanol were used with catalysts such as FeCl₃, KOH, and TBAH.

It was shown that pyridine-methanol-water mixture with a small amount of tetrabutyl-n-ammonium hydroxide gave a high yield of coal liquid when applied on Blind

Canyon Coal (PSOC-1503). After 2 hours ultrasonic extraction, the yield was 30 to 44% higher than the THF Soxhlet extraction.

Task I

Iron-based Catalysts for Coal Liquefaction

Program Coordinators: Irving Wender and Gerald P. Huffman

Task I

Iron-based Catalysts for Coal Liquefaction

Program

Coordinators: Irving Wender and G. P. Huffman

Report Period: May 1, 1990 - April 30, 1991

Project I.1 Sulfate-Promoted Metal Oxides as Direct Liquefaction Catalysts (I. Wender and J.W. Tierney)

SUMMARY

We have made a systematic study of the preparation, characterization, and catalytic activity for direct coal liquefaction of the sulfated metal oxides based on iron, tin, and molybdenum. The catalysts studied included: $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, $\text{FeOOH}/\text{SO}_4^{2-}$, $\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$, $\text{SnO}_2/\text{SO}_4^{2-}$, and $\text{SnO}_2/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$. The physicochemical properties of these catalysts were also determined. The sulfated oxides of iron, with a particulate size of 30-80 Å, formed finely dispersed pyrrhotites with particle sizes of 20-30 nm under coal liquefaction conditions in the presence of sufficient sulfur. For both Illinois No. 6 and Wyodak coals, conversions on the order of 90%+ were obtained with the sulfated iron oxides as catalysts; oil yields exceeded 70%. All experiments used 3500 ppm iron with respect to coal. Further improvement in selectivity to lighter oils was obtained by adding 50 ppm of molybdenum to the $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst. The following order of catalyst activity for direct coal liquefaction was observed: $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{SnO}_2/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$, $\text{SnO}_2/\text{SO}_4^{2-}$, $\text{FeOOH}/\text{SO}_4^{2-} > \text{Fe}_2\text{O}_3$ and $\text{Fe}(\text{CO})_5$ in the presence of sulfur. At 400°C under 1000 psig (cold) of H_2 , use of 3500 ppm of Fe in the form of sulfated iron oxide resulted in higher yield of oils than did 500 ppm of Mo added as $\text{Mo}(\text{CO})_6$. The sulfated iron and tin oxides were also found active for coal-heavy oil coprocessing reactions.

INTRODUCTION

Liquid fuels obtained from coal by direct coal liquefaction processes are an alternative to petroleum-based fuels. The economic viability of these processes is, to a large extent, contingent upon development of effective catalysts¹ for the conversion of coal containing mineral matter and heteroatoms to distillable liquids. Direct liquefaction consists of a dissolution step in which solid coal is partially converted into liquids with removal of the mineral matter and some of the heteroatoms², followed by an upgrading step in which additional liquefaction and conversion to desired products is achieved. In each step, catalysts play a key role.

Highly dispersed solid catalysts are very active for conversion of coal to liquids via direct coal liquefaction³⁻⁵; supported metal catalysts such as Co-Mo/Al₂O₃ suffer from poor contact with the reactants and rapid deactivation⁶. Unsupported dispersed catalysts offer efficient contact of coal-solvent slurries with catalyst surfaces⁷. Catalysts with high specific surface area and fine particulate size can usually be utilized at low concentrations to achieve better performance in terms of overall coal conversion and selectivity to lighter products (oils). Highly dispersed catalysts can be obtained by impregnation⁸, use of water-soluble⁹ or oil-soluble¹⁰ precursors and use of finely divided powders¹¹. All these methods can be used to form finely dispersed active inorganic phases, which allows the use of catalyst concentrations well below 1.0 wt% with good performance. If catalyst consumption can be kept low, it may be possible to use them on a once-through or disposable basis.

A cheap, readily available, environmentally compatible, and disposable catalyst such as iron is highly desirable for coal liquefaction. We have studied the catalytic activities and physical properties of sulfate and molybdate anion-treated iron and tin oxides for this purpose. These oxides have been termed "superacids" as have the oxides of other transition metals in group IVB of the periodic table such as Ti, Zr, and Hf¹²⁻¹⁴. These sulfated oxides can catalyze a variety of hydrocarbon transformations at low temperatures. Tanabe et al.¹⁵ reported that a sulfated iron oxide (Fe₂O₃/SO₄²⁻), a solid superacid, was active for promoting C-C bond cleavage in coals and for hydrocracking of a bituminous Akabira coal (% C = 83.0) at 400°C, under 100 atm of H₂ (cold). A sulfated iron oxide with about 2 wt % sulfate was reported to be almost as active as a well-known supported hydroprocessing catalyst, CoO-MoO/Al₂O₃. Use of the iron oxide in its sulfated form gave about 75 wt% coal conversion (with 31% oils) as compared to only 60 wt% coal conversion with 20% oils obtained using the unsulfated iron oxide.

Kotanigawa et al.¹⁶ compared the catalytic activities of sulfate (S^{6+}) and sulfide (S^{2-}) in sulfur-promoted iron oxide catalysts used for coal liquefaction and for model compound reactions. They found that use of the sulfated iron oxide (Fe_2O_3/SO_4^{2-}) gave a very high coal conversion for bituminous coals and lignites, with a concomitant removal of heteroatoms. They concluded that sulfate-promoted iron oxide was an effective catalyst for dehydrogenation and cracking reactions, promoting the formation of radicals or radical ions.

It is pertinent to learn that both iron and tin oxides in their sulfated forms are of interest to material scientists because of their refractory nature and unique gas sensitivity. Nakatani et al.¹⁷ reported that small amounts of sulfate anion introduced in Fe_2O_3 resulted in a substantial increase in sensitivity for reducing and combustible gases. They attributed this effect to an increase in the oxide surface area by virtue of a decrease in the average crystalline diameter of the oxide. The effects of anionic dopants such as sulfate, chloride and phosphate on the physical properties of various transition metal oxides and hydrous oxides has been well addressed by Matijevic et al.¹⁸ Farcasiu et al.¹⁹ have also studied the catalytic activities of sulfated iron oxide and related iron-sulfur systems for cracking of a model compound, 4-(1-naphthylmethyl)bibenzyl, and have found them effective for the cracking reactions relevant to coal liquefaction.

We have synthesized and characterized a number of sulfate-promoted oxides of Fe, Zr, Ti, Hf, and Sn in our laboratory. We have also recently reported on the use of sulfate-promoted iron and tin oxides for the direct liquefaction of Argonne Illinois No.6 coal with tetralin²⁰. We have also investigated coprocessing of the same coal with Maya ATB heavy oil²¹.

We compared the catalytic properties of sulfated iron oxides synthesized using both homogeneous and the heterogeneous routes²². The activity of the sulfated oxides was compared with that of finely dispersed catalysts resulting from soluble precursors such as $Fe(CO)_5$ and $Mo(CO)_6$ for both direct liquefaction and coprocessing reactions. Work was done to characterize the composition and the extent of dispersion of the sulfided phases obtained during coal liquefaction reactions. This included the study of the rate at which the initial sulfated metal oxide is converted to pyrrhotite under liquefaction conditions and determination of the extent of catalyst particle agglomeration with time at reaction temperature.

EXPERIMENTAL

Catalyst Preparation and Characterization: The sulfated oxides of iron and tin were prepared from

their respective sulfate and chloride (or nitrate) salts precipitated with either ammonia water or urea, depending on whether a heterogeneous or homogeneous coprecipitation route was followed to prepare the intermediate oxyhydroxides of iron and tin. The catalysts were characterized by BET-surface area analysis, sulfur analysis, thermogravimetry (TGA), acidity measurement, thermal stability measurements, X-ray diffraction, and electron microscopy. Average crystallite sizes were calculated from line broadening of the diffraction peaks, corrected for instrumental broadening. A Cahn electrobalance was used for thermogravimetric analyses and acidity measurements of catalysts. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were carried out for structural investigation of the catalysts using JEOL 35 CX SEM and JEOL 200 CX TEM models. The residues of the coal liquefaction experiments were analyzed using X-ray diffraction and a JEOL 2000 FX STEM (100 kV beam) with an energy dispersive X-ray spectrometer (EDX) to determine composition and dispersion of the catalytic phases formed under liquefaction conditions.

Reaction Studies: Direct coal liquefaction and coal-oil coprocessing experiments were carried out in a 300 ml stainless steel autoclave (Autoclave Engineers) equipped with a turbine impeller (1500 rpm) and heated by a tube furnace. Elemental sulfur was used in excess for sulfiding the catalysts in situ. Soxhlet extraction with methylene chloride was used to determine coal conversion. Soluble products were recovered by rotary evaporation at 45°C under vacuum. Pentane solubles (oils) were determined by adding 40 volumes of n-pentane to the methylene chloride solubles followed by Soxhlet extraction with n-pentane. Pentane-insoluble but methylene chloride soluble material was designated as asphaltenes. Methylene chloride insolubles (residues) were recovered and stored for further characterization. Gaseous products of the reaction were analyzed on a gas chromatograph (Varian 3300 Series) using a flame ionization detector. These gases consisted of a mixture of hydrocarbons (C_1 to C_4).

RESULTS AND DISCUSSION

The sulfated iron and tin oxides studied are listed in Table 1.

Catalyst Characterization: For the sulfated and molybdated metal oxides used in this study, we measured catalyst dispersion, chemical composition before and after reaction, and catalyst acidity. The specific surface area of the catalyst and the particle or grain size of the catalyst are two important measures of dispersion. We employed X-ray diffraction, BET-surface area, electron

microscopy, light scattering, and porosimetry to determine structure and morphology-related properties of the catalysts. The results are shown in Table 2.

The specific surface areas, as determined by the BET method, of all the oxides and hydrous oxides increased significantly upon introduction of 2-4 wt% of SO_4^{2-} or MoO_4^{2-} . The primary particle or grain size was much smaller than that of the pure metal oxides themselves. The sulfate-promoted oxides were also found to have unusual surface morphologies. Elongated and extremely thin primary particles of sulfated iron oxide, as observed using TEM and SEM, are shown in Figure 1.

The pore size, pore distribution, and the formation of loosely held physical agglomerates (secondary particles) was studied by using laser-scattering and porosimetry. The agglomerate or the secondary particle sizes of the sulfated iron oxides synthesized using both the homogeneous and the heterogeneous routes were in the range of 0.1 to 10 microns. However, there was a notable difference in their pore size distribution. The porosity is, we think, due to open, irregular void spaces between the fine nanosize primary particles of the sulfated oxide catalyst. The sulfated iron oxide synthesized using a homogeneous coprecipitation route had a bimodal distribution of the pores with more than 90 % of the pores being meso- and macropores (pore diameters from 30 - 500 Å). The catalyst prepared by the heterogeneous route, on the other hand, had a unimodal pore distribution with most of the pores smaller than about 50 Å. For coal liquefaction reactions involving high molecular weight asphaltenes that range in diameter from about 100 to 250 Å, it is essential to have a more "open" pore structure (preferably, bimodal, to maintain a good balance between catalyst activity and stability). As shown in Figure 2, the iron catalyst synthesized using homogeneous coprecipitation has a bimodal pore-size distribution and, indeed, was more effective in converting coal/asphaltenes to oils than the catalyst prepared using a heterogeneous route, which had a unimodal distribution of pores.

Acidities of the sulfated oxides were measured by using pyridine adsorption-thermogravimetry. The nature of the acid sites and their variation with temperature was studied by using pyridine adsorption-FTIR spectroscopy. The relative acidities and the ratio of Lewis to Bronsted sites of unsulfated and sulfated iron and tin oxides are shown in Table 3.

It is clear that the sulfated iron oxide holds substantial amounts of pyridine at high temperatures under vacuum at 400°C and 1 mtorr. The ratio of Lewis to Bronsted acid sites increased with increase in temperature for all the sulfated oxides and hydroxides studied. The

IR absorption bands at 1449 cm^{-1} and 1540 cm^{-1} correspond to coordinatively bonded pyridine (Lewis acid sites) and the pyridinium ions (Bronsted acid sites). Complete decomposition of the sulfate and of the molybdate groups from the iron oxides, as determined using thermal methods, occurred above 550°C . The BET surface area of $\text{FeOOH}/\text{SO}_4^{2-}$ catalyst was higher than that of $\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$, yet the latter has a smaller grain size. The reason for this is probably the greater pore volume of the former (0.4 g/cc) with a wide distribution of meso- and macropores as compared to the essentially nonporous $\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$ catalyst (pore volume $< 0.1\text{ g/cc}$). The more open or porous surface morphology of the $\text{FeOOH}/\text{SO}_4^{2-}$ catalyst can be seen from the SEM micrograph of this catalyst shown in Figure 4. The surface of the sulfated iron oxyhydroxide catalyst resembles small-sized balls comprised of a number of nano-sized needles. A TEM micrograph showing the structure of the needles is shown in Figure 5. TEM shows that the $\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$ catalyst forms fine size particles, spherical in shape and about 10 nm in average dimension. Examination of the chemical composition of the surface of the sulfated or molybdated iron oxides by XPS revealed the presence of S^{6+} and Mo^{6+} species in the catalyst.

Catalyst Activity Evaluation by Reaction Studies:

Direct Coal Liquefaction :

(i). Sulfated Iron and Tin Oxides:

The sulfated iron and tin oxides were effective for converting Argonne Illinois No. 6 coal to asphaltenes and oils in the presence of sufficient sulfur for metal-sulfiding. The amounts of metals (iron, tin, and molybdenum) used in our catalytic systems (with respect to coal) were small (3500 ppm Fe , 4000 ppm Sn , 50 ppm Mo). The activity for direct liquefaction of Illinois No. 6 coal, expressed in terms of conversion of coal to n-pentane solubles (oils), is given in Figure 6. The sulfated oxides (of iron and tin) resulted in higher conversions of coal to oils than did their respective unsulfated oxides. It is also evident that the sulfated iron oxide, containing $3.4\text{ wt\%}$ sulfate and synthesized using the homogeneous coprecipitation route resulted in a higher conversion to oils ($60\text{ wt\%}$) than the one synthesized using the heterogeneous coprecipitation route and containing higher amounts of sulfate ($6.1\text{ wt\%}$), which resulted in about $50\text{ wt\%}$ oils. This was true even though the initial catalyst dispersion in terms of specific surface area and grain size of these two catalysts was almost the same. The total coal conversion (to asphaltenes, oils, and gases) due to these two catalysts was also almost equal (90 and $88\text{ wt \% maf}$). The

difference in their selectivities to lighter oil products is likely due to differences in their pore size distributions described earlier. The sulfated iron oxide, synthesized using the homogeneous route, had a bimodal pore distribution with more than 75 % of pores larger than 100 Å; this proved to be more effective for conversion of coal asphaltenes (average diameter = 120 Å).

(ii). *Activity of iron-based sulfated oxides and soluble precursors:*

To measure the effect of immobilizing the sulfate group on the iron oxide, the activity for coal conversion of different well-known precursors which form finely divided Fe-containing catalysts under reaction conditions was compared to that of the sulfated iron oxide systems. The results of these experiments expressed as wt% total coal conversion and wt% yield of oils are shown in Figure 7. A very finely divided iron oxide powder (grain size of about 3 nm), ferric sulfate, and iron pentacarbonyl were the iron-precursors compared with the sulfated iron oxide. The sulfated iron oxide containing 3.4 wt % was more active than any of the other finely divided precursors of iron. We believe that the sulfated iron oxides maintain their high initial dispersion for longer times at reaction temperature without undergoing observable sintering or agglomeration because of their ability to resist sintering.

(iii). *Activity of sulfated and molybdated oxides and hydrous oxides for liquefaction of Wyodak coal:*

The activities of some hitherto unknown sulfated oxyhydroxides of iron ($\text{FeOOH}/\text{SO}_4^{2-}$) and of molybdated iron oxide ($\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$) were compared with sulfated iron oxide, unsulfated (but fine grain size) iron oxide, and Fe_2O_3 + dilute H_2SO_4 (the amount of sulfuric acid used was essentially equivalent to the amount of sulfate anion present in the sulfated iron oxide). The last combination was used to determine whether a fine iron oxide with dilute sulfuric acid (separately) formed the same kind of catalytic species under liquefaction conditions as that resulting from the sulfated iron oxide. The results of these experiments are shown in Figure 8. Use of the $\text{FeOOH}/\text{SO}_4^{2-}$ and $\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$ catalysts resulted in comparable levels of coal conversion to n-pentane solubles as obtained with the sulfated iron oxide. It was also determined by thermal methods and by FTIR spectroscopy that the sulfated oxyhydroxide prepared using the homogeneous route transforms to a material quite similar to sulfated iron oxide at higher temperatures. From Figure 8 we see that the modifying effect of anions on the catalytic properties of transition metal oxides is not anion-specific so long as the modifying anion is held strongly by the oxide surface. The effect of separately adding sulfuric acid and unsulfated iron

oxide was not the same as that of using sulfated iron oxide. The combination of iron oxide and dilute sulfuric acid gave slightly higher coal conversion than did the iron oxide alone, but these conversions were lower than those obtained with presulfated iron oxide.

Coal-Oil Coprocessing:

A thermal run (no addition of external catalyst) was made to determine the catalytic activity of the mineral matter (especially pyrite) inherent to coal. This resulted in a 37 wt% (maf) coprocessing conversion, with about 57 wt% selectivity to oils. Conversions and selectivities are defined by the equations in Table 4.

(i). Activity of the Sulfated Oxides:

Sulfated iron and tin oxides were used in small concentrations for coprocessing of Illinois No. 6 with Maya ATB. Use of an $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst containing 3.4 wt% of sulfate group resulted in a coal conversion of 70 wt% with 72 wt% selectivity to oils at 400°C using 3500 ppm of iron with respect to the coal-oil mixture. When $\text{SnO}_2/\text{SO}_4^{2-}$ (3.9 wt% sulfate) was used as catalyst with 3500 ppm of tin at 400°C, a 62 wt% conversion was obtained with 76 wt% selectivity to oils. A reaction was carried out with a molybdenum containing catalyst precursor, $\text{Mo}(\text{CO})_6$, for comparison, using 100 ppm of Mo. This resulted in a 71 wt% coal conversion with 70 wt% selectivity to lighter oils. A bimetallic, bifunctional catalyst, $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, containing 50 ppm Mo and 3500 ppm Fe resulted in a coal conversion of 80 wt% with 80 wt% selectivity for lighter oils. The higher activity of this catalyst is attributed to the presence of dual sites (acidic and hydrogenative) in the catalyst. Activity comparison experiments are shown in Figure 9.

Results obtained in a coprocessing reaction employing a bimetallic sulfated oxide of iron and tin, $\text{SnO}_2/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, as a catalyst (with 1750 ppm of each iron and tin) are also shown in Figure 9. As expected, the increase in total conversion as well as the increase in conversion to oils obtained with sulfated oxides is attributed primarily to enhanced "dispersion" (surface area/gm) with possibly a small contribution from the high surface acidity of these oxides. Conversion of the oxides to active catalytic sulfide phases (pyrrhotites) is facilitated by the increase in the specific surface area and decrease in the average particle size of the oxides upon addition of small amounts of the sulfate group, . More of the active catalyst surface of these sulfides becomes available for reaction and catalyst agglomeration is decreased.

(ii). Activity of $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ Catalysts at 400 and 425°C:

Addition of small amounts of Mo (20-100 ppm) to the sulfated iron oxides resulted in a substantial improvement in selectivity to lighter products. A series of experiments was carried out to determine conversions of Illinois No. 6 when coprocessed with Maya ATB at 400 and 425°C using different molybdenum loadings on $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ (Figure 10). Total coal conversion as well as selectivity to lighter oils increased at both temperatures when the amount of Mo increased from 0 to 100 ppm with respect to the coal-oil mixture. Conversions as high as 84 wt% (maf coal) with selectivity higher than 80 wt% were obtained at about 100 ppm of Mo + 3500 ppm of Fe added in the form of $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$. Surprisingly, we obtained slightly lower values of both coal conversion and selectivity to oils in almost all reactions carried out at 425°C as compared to those at 400°C. This apparent decrease in coprocessing conversion may be attributable to increased coking due to the presence of an acidic functionality in the catalyst.

CONCLUSIONS

(i). Synthesis of iron and tin oxides in the presence of either a sulfate or a molybdate anion improves the initial catalytic dispersion in direct coal liquefaction reactions.

(ii). The sulfated iron oxides synthesized using a homogeneous coprecipitation method were more effective coal liquefaction catalysts than the ones prepared using a heterogeneous route, probably due to the more "open" pore structure provided by the former catalysts.

(iii). The sulfated iron and tin oxides were more active than their respective unsulfated counterparts for coal liquefaction. Sulfuric acid added separately to unsulfated iron oxide did not yield any significant improvement in conversion.

(iv). The finely dispersed sulfated iron oxides were more active than soluble precursors of iron and molybdenum used at comparable metal concentrations.

(v). Introduction of small amounts of molybdenum into sulfated iron oxide catalysts (20 to 100 ppm with respect to coal plus heavy oil) enhanced the hydrogenating ability of the catalyst, thereby resulting in higher selectivity to oils.

FUTURE WORK

(i). Catalyst concentration versus conversion studies will be carried out for the direct liquefaction of a bituminous and a subbituminous coal with tetralin as a solvent (2:1 solvent-to-coal) in the presence of sulfated oxide/hydrous oxide catalysts.

(ii). Model compounds reactions will be carried out to elucidate the mode of action of the sulfated metal oxide catalysts.

(iii). Analysis of the coal liquefaction reaction products will be carried out using GC-MS, NMR, and vacuum distillation.

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Table 1. Metal Oxide Catalysts and Method of Synthesis.

Cat. Designation	Catalyst Formula	Synthesis
I	Fe_2O_3	Heterogeneous
II	$\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$	Homogeneous
III	$\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$	Heterogeneous
IV	$\text{FeOOH}/\text{SO}_4^{2-}$	Homogeneous
V	$\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$	Heterogeneous
VI	SnO_2	Heterogeneous
VII	$\text{SnO}_2/\text{SO}_4^{2-}$	Heterogeneous

Table 2. Dispersion Related Properties of Iron and Tin Based Catalysts.

Catalyst	% SO_4^{2-}	Sur. Area (m^2/g)	D_{average} (by XRD)	D_{average} (by TEM)	PSD ¹
I	0.0	26.8	46 nm	65 nm	nd.
II	3.4	81.7	16 nm	20 nm	Bimodal
III	6.1	79.5	12 nm	20 nm	Unimodal
IV	10.2	127.0	12 nm	25 nm	Unimodal
V	-- ²	88.0	9 nm	15 nm	Unimodal
VI	0.0	60.5	19 nm	nd.	Unimodal
VII	3.9	146.3	5 nm	15 nm	Bimodal

¹ Characteristic pore size distribution of the catalyst.

² Catalyst V, the molybdated iron oxide, contained about 7.5 wt % MoO_4^{2-} anion.

Table 3. Acidity Related Properties of Metal Oxide Catalysts.

Catalyst	Acidity (TGA) ¹	(L/B) ²	Onset Temp. ³
I	0.131	-- ⁴	415°C
II	0.301	1.50	410°C
IV	nd	0.70	400°C
V	nd	1.21	400°C
VI	0.108	nd	410°C
VII	0.271	1.58	385°C

¹ The total acidity of the surface of the catalysts, expressed as mmols of pyridine adsorbed per gm of catalyst, was determined using the pyridine adsorption-thermogravimetry method.

² The ratio of Lewis to Bronsted acid sites was determined using pyridine adsorption-FTIR. Values were obtained at 400°C under vacuum.

³ The characteristic temperature of the onset of coal liquefaction determined by using a polarising optical microscope.

⁴ The unsulfated iron oxide did not retain any pyridine at high temperatures.

Table 4. Equations for Coprocessing Calculations.

$$\% \text{Coprocessing Conversion} = Y_c = [(1 - W_i - W_c) / W_a] * 100$$

$$\% \text{CH}_2\text{Cl}_2 \text{ Solubles} = Y_s = (W_s / (W_a + W_m)) * 100$$

$$\% \text{Yield Asphaltenes} = Y_p = (W_p / (W_a + W_m)) * 100$$

$$\% \text{Yield Oils} = Y_o = Y_s - Y_p$$

$$\% \text{Product Selectivity} = [(\% \text{Yield}) / (Y_c * K)] * 100$$

$$K = (W_a) / (W_a + W_m)$$

W_i = Weight of Ash-Free CH_2Cl_2 Insolubles

W_c = Weight of Catalyst

W_a = Weight of Ash-Free Coal

W_m = Weight of Resid

W_s = Weight of CH_2Cl_2 Solubles

W_p = Weight of Asphaltenes

$\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$
(SEM)

avg. size = $0.1\ \mu\text{m}$

Wt % SO_4^{2-} : 3.4

Figure 1. TEM and SEM images of Catalyst I: sulfated iron oxide.

$\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ (TEM)

average grain
size = 20 nm

Figure 2. Pore size distributions for sulfated iron oxides prepared using homogeneous and heterogeneous routes, catalysts II and III.

Figure 3. FTIR spectrum of pyridine adsorbed on Catalyst II, a sulfated iron oxide.

Figure 4. SEM micrograph of Catalyst IV, $\text{FeOOH}/\text{SO}_4^{2-}$

$\text{FeOOH}/\text{SO}_4^{2-}$:
(SEM)
avg. size = 0.1 μm
wt % SO_4^{2-} : 10.2

Figure 5. TEM micrograph of $\text{FeOOH}/\text{SO}_4^{2-}$ catalyst and an

$\text{Fe}_2\text{O}_3/\text{MoO}_4^{2-}$ catalyst.

Figure 6. Activity of metal oxide catalysts for direct liquefaction of Illinois No. 6 coal at 400°C and 1000 psig H₂ (cold).

Figure 7. Activity of soluble iron catalyst precursors for direct liquefaction of Illinois No. 6 coal at 400 °C and 1000 psig H₂.

Figure 8. Activity of new iron oxide-based catalysts for direct liquefaction of Argonne Wyodak coal at 400°C and 1000 psig H₂.

Figure 9. Activity of sulfated metal oxides for coprocessing of Illinois No. 6 with Maya ATB at 400°C and 1000 psig H_2 .

Project I.2 Low Temperature Depolymerization and Liquefaction of Premium U.S. Coal Samples

(Joseph Shabtai)

The main lines of research during the May 1990-April 1991 period were as follows:

1. Continuation of systematic process development studies on the low-temperature depolymerization-liquefaction (HT-BCD-HPR treatment) of premium U.S. coals. Specifically, the liquefaction behavior of two additional coals, i.e., those from Wyodak, WY and Lewiston-Stockton, WV, was examined.
2. Structural analysis of depolymerized coal products (in collaboration with M. Lee, H. L. C. Meuzelaar, H. Huai and R. J. Pugmire).
3. Model compound studies intended to clarify the reaction mechanisms involved in the FeCl_3 -catalyzed mild hydrotreatment (HT) and base-catalyzed depolymerization (BCD) of coals.
4. Design and development of a flow reactor system for the process feasibility study of the HT-BCD-HPR procedure.

Following is a short description of progress achieved along these lines.

A. Low-Temperature Depolymerization-Liquefaction Studies of Wyodak (WY) and Lewiston-Stockton (WV) Coals.

The effects of processing conditions, i.e., catalyst concentration, temperature, pressure and reaction time in the HT-BCD depolymerizing treatment of a Wyodak premium coal (Argonne) sample were systematically investigated. This allowed for a comparison of this representative subbituminous coal with previously studied HVB coals, e.g., those from Pittsburgh No. 8, Illinois No. 6 and Blind Canyon (see Final Report for the period May 1989-April 1990).

Figure I.2.1 summarizes the change in the yield of THF-soluble product from mild hydrotreatment (HT) of the Wyodak coal as a function of (impregnated) FeCl_3 catalyst concentration. As seen, the yield first increases with increase in FeCl_3 concentration but then levels off, as expected for a catalytic reaction. The yield increases also with increase in HT temperature from 275°C to 290°C. For all previously studied HVB coals, the optimal HT

temperature was $\sim 275^{\circ}\text{C}$; at this temperature the yield was usually very low, i.e., only 8-10 wt, but the yield in the subsequent BCD treatment, viz, the overall depolymerization yield from the combined HT-BCD processing, was optimal (>90 wt%). In comparison, the optimal HT temperature for the subbituminous Wyodak coal, viz, the temperature leading to maximal depolymerization yield in the combined HT-BCD treatment, was higher, i.e., $\sim 290^{\circ}\text{C}$. By applying this temperature in the HT step, it was found that a low concentration of FeCl_3 catalyst (3-7 wt%) is sufficient for effective overall HT-BCD reaction.

Table I.2.1 summarizes results on the yield and distribution of depolymerized, THF-soluble products from Wyodak coal as a function of BCD temperature (keeping the FeCl_3 concentration and the HT temperature constant at 7.0 wt% and 290°C , respectively). As seen, the total yield of THF-solubles reaches a maximum of 90-91 wt% (MAF basis; excluding ~ 5 wt% of pre-extract) at a temperature between 290 - 305°C . In this BCD temperature range the product contains 50.3 to 57.0 wt% of cyclohexane-solubles (oils) plus 20-21 wt% of benzene-solubles. The latter were found by GC/MS to be in a closely similar molecular weight range with the cyclohexane-soluble fraction, the main difference being a higher O content (and consequent lower solubility in cyclohexane) of the benzene-soluble components. It should be noted that the total yield of cyclohexane-soluble products from the subbituminous Wyodak coal (50-57 wt%) is lower than the typical yields (65-75 wt%) of such products found previously for HVB coals. However, the total yield of fully depolymerized products (cyclohexane- plus benzene-solubles) from the subbituminous coal reaches the high level of 70-78 wt% (Table I.2.1) at 290 - 305°C . As previously found for HVB coals this yield can be further improved by recycling the residual THF-solubles through the HT-BCD procedure.

Table I.2.2 summarizes the elemental composition of the starting Wyodak coal, the depolymerized coal (cyclohexane- and benzene soluble fractions) and the final hydroprocessed (HPR) product. The starting coal is characterized by high O content (18.02 wt%) and low H content (5.35 wt%). Depolymerization (HT-BCD treatment) resulted in a major reduction of O content (by means of base-catalyzed decarboxylation and dehydroxylation reactions) and some increase in H content by means of a limited extent of base-catalyzed hydrogen transfer from the methanol solvent used in the BCD step. The cyclohexane- and benzene-soluble products have similar elemental composition except for the moderately higher O content of the benzene-solubles apparently due to the presence of components having two oxygen atoms per molecule, e.g.,

diphenols and alkoxyphenols. Since the benzene-solubles formed by mild HT-BCD have low molecular weights (in the same range as the cyclohexane-solubles) they are not designated as asphaltenes. This is for the purpose of differentiation from high molecular weight asphaltenes formed in high temperature coal liquefaction processes. The final HPR product, obtained by hydroprocessing of the depolymerized coal (combined cyclohexane- and benzene solubles) with a 6Co8Mo/Al₂O₃ catalyst, at 365°C and 2700 psig H₂ pressure, consists of a hydrocarbon oil having a H/C ratio of 1.62 (Table I.2.2).

The overall direction of main chemical changes involved in the HT-BCD-HPR treatment of Wyodak coal can be elucidated by plotting the changes in H/C vs O/C ratios accompanying this sequential procedure. Such a plot is provided in Figure I.2.2. As seen, the transition from the starting coal to the mildly hydrotreated (HT) coal is accompanied by a significant increase in H/C ratio (due to hydrogenolysis of intercluster alkylene linkages) but no change in the O/C ratio, indicating preservation of oxygen-containing functional groups at this stage. BCD at gradually higher temperature (225°, 275° and 290°C) results in a gradual decrease in O/C ratio due to base-catalyzed decarboxylation and dehydroxylation reactions. The hydroprocessing (HPR) of the BCD product results in completion of the deoxygenation reaction (as reflected in the very low O/C ratio in the final product), and a major increase in H/C ratio resulting from ring hydrogenation and (additional) hydrogenolysis reactions.

The boiling point distributions of the depolymerized Wyodak coal and of the final HPR product are given in Table I.2.3. As seen, the oxygen-rich depolymerized coal consists mostly of high boiling fractions (mostly alkylated phenols; see below) in the heavy and vacuum gas oil range, with only 8.5 wt% appearing in the gasoline, kerosene and light gas oil range. In contrast, the final HPR product is a light hydrocarbon oil boiling primarily (71.3 wt%) in the gasoline, kerosene, and light gas oil range (b.p. up to 350°C/760 torr).

GC/MS analysis of depolymerized Wyodak coal products (performed by Dr. H. Huai) indicated that alkylsubstituted mono- and bicyclic phenols are predominant components. An example of the analysis of the oil (cyclohexane-soluble) fraction of such products is provided in Figure I.2.3. It is noteworthy that for the depolymerized subbituminous coal, alkylsubstituted monocyclic phenols are in higher concentration than alkylsubstituted bicyclic phenols. A similar trend was previously observed for the corresponding products from a Victoria, Australia brown coal. Further, alkylsubstituted phenol products are mostly polyalkylsubstituted and not single-

chain substituted as found by FTIR analysis of the (arom)C-H out-of-plane bending bands. Another important class of compounds found are polyalkylsubstituted arenes. Free paraffins are indicated in trace amounts only.

B. Structural Analysis of Depolymerized Coal Products

This part of the work was performed in collaboration with Prof. M. Lee and his co-workers. In order to facilitate an in-depth analysis of depolymerized coal products, the latter were first subjected to chemical class fractionation by elution chromatography on alumina (Lee, Shabtai, et al., Fuel, 1991, in press). Table I.2.4 summarizes the results of such a separation of three previously studied HVB coals and a lignite into four fractions, i.e., aliphatics, alkylarenes, and two polar fractions containing mostly phenols (accompanied by some N-containing heterocyclics). During the reporting period the detailed GC/MS analysis of the first two fractions was completed and results obtained are summarized in Figure I.2.4, providing compositional data on the aliphatic fraction, and Figure I.2.5, providing compositional data on the alkylarene fraction. The results illustrate the potential for structural analysis of mildly depolymerized coal products down to the molecular level. The analysis of the predominant polar fractions is continuing and results will be reported in the near future. Optimal conditions for high-yield (85-92 wt%) conversion of the Lewiston-Stockton coal into depolymerized, THF-soluble products, consisting mostly (65-70 wt%) of cyclohexane-solubles (oils), were also developed.

C. Catalytic Studies with Coal-Simulating Model Compounds

FeCl_3 catalysts, both unsupported and supported on various oxides, were used in model compound studies for the purpose of (1) clarifying their mode of catalytic action, and (2) developing optimal conditions for their application in hydrogenolysis reactions. This was of importance both for the current project on low-temperature coal depolymerization-liquefaction, as well as for other projects in the Department requiring the use of acidic hydrogenolysis catalysts.

Model compounds studied included diphenylmethane (1), 1-benzyl-naphthalene (2) and dinaphthylethane (3), which contain alkylene linkages between two aromatic ring systems. The important observation was made that in all cases $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (both unsupported or supported on SiO_2 , $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{TiO}_2\text{-Al}_2\text{O}_3$) exhibited sharply higher hydrogenolysis activity than

corresponding catalyst systems based on anhydrous FeCl_3 .

D. Design and Development of a Flow Reactor System for the HT-BCD-HPR Procedure.

Figure I.2.6 provides a schematic view of a flow reactor system which is being designed and constructed through the joint effort of the University of Utah research group. This reactor in series will allow for testing of the HT-BCD depolymerization stage (Stage I) of the procedure as a single operation. The reactor consists of (1) a newly-acquired, continuous stirred tank reactor (Autoclave Engineers) for the mild hydrotreatment (HT) of the coal feed and (2) a coiled tubular reactor for the immediately following BCD treatment. The hydroprocessing (HPR) stage (Stage II) of the procedure is being studied in a separate flow microclave reactor (Autoclave Engineers), equipped with a Robinson-Mahoney catalyst basket.

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Table I.2.1

Yield and Distribution of Depolymerized (HT-BCD)
Products from Wyodak (WY) Coal

Run No.	W-36	W-32	W-37	W-38
HT Temperature, °C ^a	290	290	290	290
BCD Temperature, °C ^b	255	275	290	305
Yield of THF-solubles, wt% ^c	85.1	90.2	90.5	90.3
Distribution of THF-solubles, wt%				
Oils (cyclohexane-solubles)	33.0	43.4	50.3	57.0
Oils (benzene-solubles)	6.7	11.1	19.8	20.6
THF-solubles (benzene-insolubles)	60.3	45.5	29.9	22.4

^a The HT step in all runs was performed using 7.0 wt% of FeCl₃ catalyst; 1500 psig H₂ pressure.

^b The BCD step in all runs was performed under 1000 psig N₂ pressure.

^c MAF basis; excluding ~ 5%wt of THF pre-extract.

Table I.2.2

Elemental Composition of Wyodak Coal Products, wt% (MAF)

Element	Starting Coal (Argonne)	Depolymerized Coal ^a		HPR ^b product
		A ^c	B ^d	
Carbon	75.01	82.47	80.34	87.57
Hydrogen	5.35	8.23	7.40	11.80
Nitrogen	1.12	0.60	0.95	0.14
Sulfur ^e	0.47	0.21	0.24	<0.01
Oxygen	18.02	8.49	11.07	0.48
H/C ratio	0.85	1.19	1.10	1.62

^a HT at 290 °C and BCD at 290 °C

^b HPR at 365 °C (2500 psig H₂)

^c Cyclohexane - solubles

^d Benzene-solubles

^e Organic S

Table I.2.3
Boiling Point Distribution of Depolymerized (W(W) Coal and of Hydrocarbon
Products Derived from It by Hydroprocessing (HPR^a)

Fraction (b.p., C), wt%	Depolymerized Coal		Hydroprocessed (HPR) product	
Gasoline (<200°)	2.6		29.8	
Kerosene (200-275°)	2.7	8.5	33.2	71.3
Gas Oil (275-325°)	3.2		8.3	
Heavy Gas Oil (325-400°)	10.9		14.7	
Vacuum Gas Oil (400-538°)	44.8		12.0	
Total Distillable (<538°)	64.2		98.0	
Atmospheric Residue (>350°)	89.8		23.2	
Vacuum Residue (>538°)	32.6		2.0	

^a Boiling point distributions were determined by simulated distillation.

Table I.2.4
Fractionation of Depolymerized Coals into Chemical Classes
by Elution Chromatography

Fraction, wt% ^a	Beulah-Zap	Illinois No. 6	Blind Canyon	Pocahontas No. 3
Aliphatics ^b	3.2	2.7	8.3	2.2
Alkylarenes	11.5	13.0	18.2	19.5
Polar-1 ^c	28.6	2.5	3.4	24.0
	56.7	54.4	48.0	32.1
Polar-2 ^c	28.1	51.9	44.6	8.1
TOTAL	71.4	70.1	72.5	51.8

^a Wt% of the MAF coal

^b Paraffins, isoparaffins and naphthenes

^c Mostly phenols

Figure I.2.1. Yield of THF Solubles from HT of Wyodak Coal as a Function of FeCl_3 Concentration (1500 psig H_2)

Figure I.2.2. Change in H/C vs O/C Ratios Involved in the HT-BCD-HPR Treatment of Wyodak Coal

Figure I.2.4. Aliphatic Fractions of Depolymerized Coals

Figure I.2.5. Alkylarene Fractions of Depolymerized Coals

Figure I.2.6. Diagram of an Unified Low-Temperature Coal Depolymerization (HT-BCD) Flow Reactor System

Projects I.3.1 and Task I.3.2 Construction of Continuous Gas Flow-Through Reactor for Liquefaction Investigations; An Examination of Ferric Sulfide as a Liquefaction Catalyst; and the Use of NaFeS₂ as a Potential Liquefaction Catalyst

(John Zondlo, Alfred Stiller, Peter Stansberry, and Dady Dadyburjor)

INTRODUCTION

The beneficial effects obtained from the use of metal compounds as catalysts for the direct conversion of coal to liquid products have been known for decades.^{1,2} The use of catalysts results in reduced operation severity,^{3,4} improved hydrogen utilization,⁵ and increased distillate conversion.⁶

The sulfides of metals such as iron, molybdenum, and tungsten have demonstrated good coal hydrogenation and depolymerization activity. Iron sulfides, while not quite as active as the molybdenum or tungsten counterparts, remain attractive because of their availability and low cost.

Pyrite (FeS₂) and the non-stoichiometric iron sulfides collectively termed pyrrhotite (FeS_x) have received the greatest attention from the coal community for use as disposable or once-through catalysts. The literature is replete with evidence about the efficacy that iron catalysts have on increasing coal conversion and improving product distribution.⁷⁻¹⁸ However, there is as yet, even after years of effort, considerable uncertainty and debate in the literature on the exact nature and role that iron catalysts play, as well as on their chemical composition and active form under liquefaction conditions. Nevertheless, there is some general agreement among researchers that the activity of iron-based liquefaction catalysts is to a large extent determined by their particle size, crystalline morphology, and stoichiometric composition.

BACKGROUND

We have been investigating two iron sulfides, ferric sulfide (Fe₂S₃) and sodium ferric sulfide (NaFeS₂), as potential coal liquefaction catalysts. For the former, it was suggested several years ago that fine-particle-sized iron sulfides of known composition and crystallinity could be synthesized from aqueous solutions of ferric chloride and sodium sulfide.¹⁹ By varying annealing

time, pressure, and temperature, Fe_2S_3 can be disproportionated into different mixtures of pyrite and pyrrhotite that are in intimate association. This pathway is different from that by which pyrrhotite and pyrite mixtures are obtained during coal liquefaction, viz., the reduction of indigenous pyrite at high hydrogen pressure.

The synthesis of NaFeS_2 was conducted using a procedure published by Bronger.²⁰ This material is a sulfide anion with iron in the +3 valence state. Thus it is anticipated that the ferric ion would exhibit some depolymerization activity. Also, unlike most other iron sulfides, NaFeS_2 is completely water soluble. This feature should make it possible to disperse the catalyst easily throughout the pore system of the coal or on the coal surface.

In conjunction with the synthesis and development of iron-based catalysts, WVU will evaluate catalytic materials under liquefaction conditions through the use of high-pressure and high-temperature reactors. The overall objectives of this three-year program will involve the design, construction, and debugging of the reactor apparatus and its subsequent use as a test facility for the Consortium. Initially, the system will function in the batch mode and will later incorporate a continuous flow of hydrogen gas at constant pressure. Hydrogen consumption can be accurately monitored by the incorporation of mass flow meters and controllers on the hydrogen feed and effluent streams. The use of high-pressure traps in the effluent for the collection of light distillate products will make mass balances possible. Finally, a continuous coal slurry feed and product withdrawal system will be incorporated so that liquefaction processes can be followed in a more realistic fashion.

EXPERIMENTAL

The synthesis of Fe_2S_3 was conducted using a procedure described by Stiller et al.¹⁹ Equal volumes of 0.2 M ferric chloride and 0.3 M sodium sulfide in deoxygenated, distilled water were placed into a nitrogen-purged glove box. The glove box is situated in a cold room that is maintained at about 5°C. The synthesis must be carried out at such a low temperature because, at temperatures above about 10°C, Fe_2S_3 disproportionates into pyrite, pyrrhotite, and sulfur. The crystallite size and morphology of the iron containing products are very sensitive to heating rate and annealing time.²¹ Equal volume aliquots of each solution were placed into 10 mL hand-blown Pyrex glass ampules and shaken vigorously to ensure complete mixing. The ampules were then sealed with Teflon tape so that air could not enter when the glove box was opened.

After the samples were removed from the glove box, the glass ampules were permanently sealed with a torch while the contents were still at 5°C. The disproportionation of Fe_2S_3 was performed by transferring the ampules into hydrothermal bombs of nominal volume of 25 mL. The bombs were sealed and immersed into a preheated fluidized sandbath set at the desired temperature and reacted for predetermined periods of time. At the end of the experiment, the bombs were quickly quenched to room temperature by immersion in cool water.

Two analytical methods were used to determine the reaction products of disproportionation. These are x-ray diffraction (XRD) and atomic absorption spectrophotometry (AA). XRD was performed in the laboratory of Professor M. Seehra, Department of Physics, WVU on whole reaction products to determine crystal structure development. Before the atomic absorption determination of pyrite and pyrrhotite formed after disproportionation could be performed, the two iron sulfides were first separated based on their solubility in mineral acids: pyrrhotite is soluble in 6 M hydrochloric acid (HCl) while pyrite is soluble in 6 M nitric acid (HNO_3). After the separation of pyrite and pyrrhotite, AA yielded the amounts of Fe present in both solids. This procedure allowed the complete mass balance for iron to be determined. Sulfur was determined by difference. This allowed the composition of pyrrhotite and pyrite to be determined.

The synthesis of NaFeS_2 is essentially a two-step process, first involving the formation of sodium tetrasulfide (Na_2S_4) followed by its reaction with elemental iron. Sodium tetrasulfide was made by dissolving sodium sulfide (Na_2S) in hot distilled water, adding a stoichiometric amount of elemental sulfur and mixing until the sulfur was dissolved. The water was removed from the sodium tetrasulfide by vacuum drying at about 110°C for 1 day. Using a mortar and pestle, powdered iron and sodium tetrasulfide were mixed in stoichiometric amounts, placed into a ceramic boat, and the boat inserted into a quartz tube. The tube was sealed at both ends with stoppers and purged with dry nitrogen. The quartz tube with its contents were placed into a high temperature furnace and heated to 800°C for about 2 hours. The tube was then removed from the furnace and cooled to room temperature. The sodium ferric sulfide thus formed was a black, brittle solid.

Several modes of catalyst addition to coal were examined. For Fe_2S_3 , two methods were used. The first method involved physically mixing prepared catalyst with coal using a blender designed for solids. The other method involved the precipitation of Fe_2S_3 onto partially swollen

coal. In this method, coal was mixed with a solution of ferric chloride which had 10 vol% N-methyl pyrrolidone (NMP) added. NMP was chosen because it is one of the best of the common organic solvents used to swell coal.²² To this slurry was then added a solution of sodium sulfide and mixing continued for about an hour. The aqueous phase was then removed by simple filtration, the coal washed with distilled water, and then the impregnated coal dried in vacuum at 100°C for about 24 hours. For the sodium ferric sulfide, simple physical addition was used with the blender as described above. Also, since sodium ferric sulfide is water soluble, coal was impregnated with an aqueous solution of the salt by simple slurrying for about an hour. The excess water was removed by vacuum drying at 100°C until the coal was dry. All catalysts were calculated to give a loading level of 1 wt% based on dry coal.

Liquefaction experiments were conducted in 450 mL stirred Parr pressure reactors. The results will be used as a control data base so that comparisons with the new reactor system can be made. The coal used was a Pittsburgh seam coal (Humphrey Mine, WV) with the following characteristics: ash, 7.66%; sulfur, 2.54%; VM, 36.27; Fixed C, 56.06.

The reactor was charged with 20 grams of coal+catalyst and operated with or without 80 mL of tetralin. All liquefactions used 1000 psig hydrogen (initial cold pressure) and were conducted at either 350 or 450°C for 1 hour. Following reaction, the reactors were vented and the contents washed out with tetrahydrofuran (THF) into a tared extraction thimble. The thimble was placed into a Soxhlet apparatus and extraction carried out under a blanket of nitrogen for 2 days. The THF solubles were then partitioned into various products defined here as: asphaltols, THF soluble and benzene insoluble; asphaltenes, benzene soluble and hexane insoluble; oil + gas, hexane soluble. Total conversion was determined as the difference between the weight of dry starting coal and weight of recovered dry residue, asphaltols and asphaltenes as recovered, and oil + gas by difference. All products are expressed on a dry-and-ash-free coal basis.

RESULTS

Figure 1 shows the amounts of pyrite and pyrrhotite formed from the disproportionation of ferric sulfide as a function of temperature. At 100°C, it can be seen that pyrrhotite formation is initially more favorable than pyrite. With increasing treatment time, however, pyrrhotite is slowly transformed to pyrite. Raising the temperature to 200°C

alters the kinetics such that the amount and rate of pyrite formation is greatly increased. However, at 300°C the proportion of pyrrhotite and pyrite is nearly the same initially but changes slowly with time. The effect of time and temperature on the pyrrhotite and pyrite formation can be more clearly seen in Figure 2. Moreover, the iron mass balance closure was typically +/- 2%. These data are very useful since they provide a basis by which mixed iron sulfides of known composition can be synthesized.

We are working on a mathematical model to quantify the transformation between pyrite and pyrrhotite with time and temperature by the simple reversible reaction:

When this is complete, we expect to be able to model the more complicated net reaction:

In Figure 3 are typical x-ray diffraction spectra of the mixed iron sulfides as a function of time for the 100°C preparations. It can be seen that initially the material is almost amorphous but that pyrite bands appear as the annealing time increases. Pyrrhotite bands are not present or are only weakly visible at the longer time periods.

The effects of added catalyst on coal conversion and product distribution are listed in Table 1. For the runs done at 350°C without liquefaction solvent, we see that NaFeS_2 lowers the overall conversion somewhat (compared to the thermal case) but that Fe_2S_3 is moderately active, producing considerably more oil than any of the other samples. With tetralin present at 350°C, all the catalytic runs generally produce more soluble products, but again the product slate and total conversion do not significantly differ from the purely non-catalytic case.

Raising the reaction temperature to 400°C in the absence of tetralin produces total conversions similar to those obtained at 350°C in the presence of tetralin, except that the yield of oils is much higher. Undoubtedly at the higher temperature, the heavier molecules crack to oils. The 400°C experiments with tetralin produce the highest total conversion as would be expected. The product distribution also changes in that the catalytic runs produces more asphaltols.

The Fe_2S_3 used for these experiments was stored at room temperature for a period of time before conducting the liquefaction experiments. It was felt that storage might change the sample.

Therefore, three fresh samples of Fe_2S_3 were prepared and then immediately disproportionated to give pyrrhotite-to-pyrite ratios of 0.3, 1.0, and 6.5 respectively. The iron sulfides were then physically blended with coal and liquefied in tetralin at 350°C . The results tabulated in Table 2 clearly show that these catalysts are much more effective than for the results presented in Table 1. Not only are the total conversions greater than for the thermal liquefactions, but also the yield of oils increases. The product slate and overall conversion are particularly sensitive to the pyrrhotite/pyrite ratio. No attempt has yet been made to identify the iron sulfide species present at the end of the reaction.

A few experiments were conducted to determine if better dispersion of the Fe_2S_3 catalyst can improve liquefaction performance. The results in Table 3 indicate that preswelling the coal with NMP has a dramatic effect on coal conversion at 350°C with no tetralin. Total conversion is nearly as great as that obtained at higher temperature, with most of the products being asphaltols.

CONCLUSIONS

Thus far the work has produced several interesting and significant results:

- 1) The synthesis of various iron sulfides via the disproportionation of Fe_2S_3 is a function of time and temperature, and the product ratio can be controlled to yield any desired composition.
- 2) Some catalytic activity has been noted, especially with respect to the oil yield. The catalyst composition and nature of its introduction onto the system are key variables. The use of the swelling solvent, NMP, as an aid in catalyst impregnation is significant.
- 3) The Parr-type reactor used here will serve as a base-line for on-going reactor development.

FUTURE WORK

Work will continue on the kinetic study of the disproportionation reaction. As more data are obtained, the kinetic model will be used as a tool to predict conditions for any desired pyrrhotite-to-pyrite ratio. Novel magnetic techniques developed by M. Seehra will be applied for the particle size determination of the various iron sulfide catalysts. Further, synthesis of very fine catalyst particles will be attempted using a novel aerosol reactor. Particular emphasis will

be placed on closing the sulfur mass balance. Finally, the liquefaction reactors (batch, hydrogen-purged, and continuously fed) will be designed, constructed, and tested.

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Fe Content (% of total Fe)

Figure 1 Fe₂S₃ disproportionation versus time and temperature.

Pyrrhotite/Pyrite Molar Ratio

Figure 2 Pyrrhotite to pyrite molar ratio as a function

X-ray powder diffractographs.

Figure 3 Typical x-ray powder diffractographs of products of Fe_2S_3 disproportionation.

Table 1 Product Distribution from the Catalytic
Liquefaction of Pittsburgh Seam Coal (%daf)

<u>350 °C, no tetralin</u>	<u>Non- Catalytic</u>	<u>Fe₂S₃ Mixed</u>	<u>NaFeS₂ Mixed</u>	<u>NaFeS₂ Impreg.</u>
*Gas + oil	9.1	19.5	7.6	5.0
Asphaltene	14.2	14.0	12.5	12.3
Asphaltol	20.0	17.2	16.2	20.5
Total Conversion	43.3	50.7	36.3	37.8
 <u>350 °C, tetralin</u>				
*Gas + oil	0.5	5.7	6.4	7.6
Asphaltene	10.7	7.6	11.9	11.9
Asphaltol	43.8	44.3	48.2	40.4
Total Conversion	55.0	57.6	66.5	59.9
 <u>400 °C, no tetralin</u>				
*Gas + oil	26.3	32.2	27.1	25.4
Asphaltene	15.3	12.5	18.1	16.1
Asphaltol	7.4	11.8	21.2	13.9
Total Conversion	49.0	56.5	66.4	55.4
 <u>400 °C, tetralin</u>				
*Gas + oil	26.1	18.5	20.0	21.9
Asphaltene	22.7	22.7	25.0	22.1
Asphaltol	37.8	44.7	43.9	45.1
Total Conversion	86.6	85.9	88.9	89.1

*Gas + oil by difference

Table 2 Effect of Disproportionation of Fe_2S_3 on Product Yields (%daf)

	<u>Pyrrhotite/Pyrite Ratio</u>		
<u>350 °C, tetralin</u>	<u>0.3</u>	<u>1.0</u>	<u>6.5</u>
*Gas + oil	10.3	11.2	12.0
Asphaltene	9.6	5.8	6.2
Asphaltol	43.2	55.8	43.0
Total Conversion	63.1	72.8	61.2

400 °C, tetralin

*Gas + oil	23.6	38.8	16.5
Asphaltene	25.5	15.5	20.1
Asphaltol	40.9	36.1	53.7
Total Conversion	90.0	90.4	90.3

 *Gas + oil by difference

Table 3 Effect of Catalyst Addition Method on Product Yields (%daf)

<u>350 °C, no tetralin</u>	<u>Non-</u> <u>Catalytic</u>	<u>Fe₂S₃</u> <u>Mixed</u>	<u>Fe₂S₃</u> <u>Impreg.</u>
*Gas + oil	9.1	19.5	14.8
Asphaltene	14.2	14.0	7.3
Asphaltol	20.0	17.2	52.7
Total Conversion	43.3	50.7	74.8

*Gas + oil by difference

Project I.4 Generic Structural Characterization and Liquefaction Research

(G.P. Huffman, F.E. Huggins, N. Shah, G.T. Hager, M.M. Taghiei, J. Zhao, B. Ganguly, K.R.P.M. Rao and R.A. Keogh)

I. INTRODUCTION

Our research program in the period May 1, 1990 to April 30, 1991 focused on three topics, all of which dealt primarily with characterization of catalyst structure and reactions, with emphasis on iron-based catalysts. These may be briefly summarized as follows:

Mossbauer spectroscopy studies: B. Ganguly, a graduate student in Physics, working closely with K.R.P.M. Rao, a visiting professor at UK, developed a theoretically sound model for superparamagnetic Mossbauer spectra of the type observed experimentally for many of the as-prepared iron-based catalysts currently under investigation in the CFFLS. As discussed below, an important point confirmed by the model is that our earlier approximation of defining a critical volume as a function of temperature on the basis of a semiclassical approximation is valid, and that size distributions derived on the basis of the semiclassical model are reasonable.

Additionally, Mossbauer results were obtained for a wider variety of iron-based catalysts. Samples investigated included a variety of sulfated Fe_2O_3 samples, iron incorporated into coal by chemical impregnation/intercalation, cation-exchanged lignites, carbide catalysts produced by laser pyrolysis and sulfide species produced during liquefaction or hydrotreatment.

The Mossbauer results are summarized in Section II.

XAFS spectroscopy: M.M. Taghiei, a graduate student in Materials Science, with the assistance of J. Zhao, a new postdoctoral fellow at UK, carried out our program of X-ray absorption fine structure (XAFS) spectroscopy analysis of CFFLS catalysts, and also initiated work on incorporating ultrafine iron species into lignite by cation exchange. All of the iron-based catalysts noted above were investigated by XAFS spectroscopy at ambient conditions. Additionally, a number of samples were investigated by in situ XAFS at elevated temperatures under hydrogen or helium at the iron and sulfur K-shell absorption edges.

The XAFS results are summarized in Section III.

In situ sample probe: G.T. Hager, a graduate student in Chemical Engineering, designed, built and tested an in situ sampling probe for use with a one liter stirred autoclave reactor. The objective was to be able to extract samples from the reactor at any time without disturbing conditions in the reactor significantly, while maintaining the condition of both the catalyst and liquefaction product. The results are discussed in detail in Section IV.

II. MOSSBAUER SPECTROSCOPY STUDIES OF IRON-BASED CATALYSTS

In previous work, Mossbauer spectroscopy has been used to determine approximate size distributions of ultrafine particle ferric oxide catalysts. Such catalysts exhibit supermagnetic spectra, as illustrated by Figures 1 and 2. Both hematite ($\alpha\text{-Fe}_2\text{O}_3$) and the most common iron oxyhydroxide, goethite ($\alpha\text{-FeOOH}$), are antiferromagnetic and would normally exhibit only six-line magnetic hyperfine spectra at room temperature and below. However, as seen in Figures 1 and 2, the catalyst samples exhibit a significant quadrupole component. Such behavior is typical of superparamagnetic systems[1-6].

By use of a simple semiclassical approximation, it is possible to use such superparamagnetic(SP) behavior to derive approximate sizes of the catalyst particles. As discussed elsewhere [1-3], a critical volume, V_c , can be defined by

$$V_c = \frac{kT}{K_a} \ln(f_0/f_L) \quad (1)$$

where T is the absolute temperature, k is the Boltzmann constant, K_a is the magnetic anisotropy constant, f_0 is a constant frequency determined by the material properties, and f_L is the Larmor precession frequency of the ^{57}Fe nucleus. If it is assumed that particles exceeding the critical volume give rise to magnetic hyperfine spectra, while particles smaller than that volume exhibit quadrupole spectra, the Mossbauer spectra can be used to derive particle size information. For example, the spectra of Figure 1 indicate that all of the particles in the FeOOH/SO_4 catalyst are smaller than 65 Å in diameter, assuming spherical particles. Similarly, under the same assumption, the two $\text{Fe}_2\text{O}_3/\text{SO}_4$ samples of Figure 1 contain 60(40)% and 2(98)% of particles less (greater) than 85 Å in diameter. By measuring spectra at a number of temperatures, one

can determine an approximate size distribution, as illustrated for the samples of Figure 2 in Figure 3.

It is important, however, to verify the accuracy of this approximation by calculating theoretically correct SP Mossbauer spectra using quantum mechanical relaxation models [7,8]. In very finely divided substances, the grains contain only a single domain and the magnetization vector in a single domain particle is held in an easy direction by the crystalline field. The energy required to go from one easy direction to another is the magnetic anisotropy energy, $E = K_1 V$ where V is the particle volume. At any non-zero temperature, the thermal fluctuations cause a Brownian rotational motion of the magnetization vector around an easy axis and there is a finite probability that the magnetization vector will change its direction spontaneously. The relaxation time, τ , which indicates how rapidly this transition occurs is given by:

$$\tau = \tau_0 \exp (K_1 V/kT) \quad (2)$$

where τ_0 is a temperature independent constant (1).

A model based on the Gutowsky, McCall, and Slichter (GMS) equations [7,8] was used to generate relaxation spectra of Fe oxides. The hyperfine field is usually generated by the polarizing effects of unpaired electron spins. The spin direction can alter or "flip" after a period of time by one of the several mechanisms; this is the relaxation phenomenon.

The total Hamiltonian for the absorber contains the ground and excited state hyperfine interaction, the spin-spin relaxation term and a term representing incident radiation from an unpolarized single line source. Starting with this Hamiltonian and using the model described above, it can be shown how spin relaxation alters the Mossbauer spectra.

Typical calculated spectra for Fe_2O_3 are shown in Figures 4 and 5, which illustrate the effect of both size and temperature on the SP relaxation spectra. Here, spherical particles are assumed and Eq.(2) is used to calculate the relaxation times. It is seen that the approximation that particles exhibit a magnetic hyperfine spectrum if their diameter exceeds the critical diameter, d_c , which is 85 Å for Fe_2O_3 at room temperature, is quite good. However, the collapse to a quadrupole doublet occurs over a range of diameters below the critical diameter. At 45 Å, a significant SP relaxation component is still evident, in addition to a quadrupole component. These results indicate that, although size distributions based on Eq.(1) are reasonable, the SP

relaxation component of the spectra needs to be better fitted. In the next quarter, we will explore a three component fit for such spectra. These components are a magnetic hyperfine component for particles with $d > d_c$, a quadrupole component for particles with diameters less than some minimum diameter, d_m , and a SP relaxation component with a mean relaxation time appropriate for particles with $d_m < d < d_c$.

It is also possible to use the size distributions derived from the temperature variation of the Mossbauer spectra to derive theoretical spectra that may be compared to the experimental spectra. For example, the size distribution reported previously for a catalyst consisting of Fe_2O_3 on carbon black [3] (Figure 6a) was used to calculate the theoretical spectrum of Figure 6b. The agreement with the experimental spectrum is fairly good, and could be improved by adjusting linewidths and quadrupole splitting.

Mossbauer experiments were carried out on fine-particle Fe carbide particles made in the laser pyrolysis apparatus developed by X. X. Bi and P. C. Eklund. It was found that the carbide phase formed by this method is very dependent on the reactant gas flow rate. Figure 7 shows the 12K Mossbauer spectra of three different carbide samples prepared under the same experimental conditions except for changing the flow rate from 6 sccm to 30 sccm. Iron carbides dominate the spectra and a minor amount of metallic iron ($\alpha\text{-Fe}$) is the only other phase present. Cementite (Fe_3C) is the most abundant carbide, but as the flow-rate increases, increasing amounts of a second carbide phase occurs. Based on both X-ray diffraction data and Mossbauer data, this second iron carbide is most likely to be Fe_7C_3 . Mossbauer data for other reported carbides such as Fe_3C_2 and Fe_{22}C do not exhibit Mossbauer parameters similar to those observed for the second carbide phase produced in the laser pyrolysis experiments. Mossbauer experiments were done on three separate batches of samples prepared by the same flow rate of gas and same experimental conditions and the results were identical. Mossbauer data for the phases in these experimental runs are summarized in Table 1.

Despite their small size (estimated - 100Å from (TEM), the iron carbides do not exhibit superparamagnetic Mossbauer spectra at temperatures of 295K and below, but yield only well-resolved magnetic hyperfine spectra. Hence, to deduce size information from the Mossbauer spectra of these carbides, it will be necessary to induce superparamagnetic behavior at temperatures greater than room temperature. A preliminary experiment at elevated temperatures did indeed show evidence of collapse of the magnetic structure to a superparamagnetic doublet

at temperatures well below the Neel temperature for the iron carbides. However, the iron content for this sample was very low and the signal-to-noise ratio was not good. An improved high-temperature Mossbauer cell has been designed for this purpose and is now under construction.

Formation of pyrrhotite during liquefaction: As noted previously, most iron-based catalysts are converted to pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$) during liquefaction. The amount of pyrrhotite formed is primarily dependent on the amount of sulfur available. As illustrated by Figure 8, if insufficient sulfur is available in the system to convert all the added iron to pyrrhotite, the unconverted iron remains in the form of a SP oxide, but is transformed from hematite to what appears to be SP magnetite.

It is seen that the pyrrhotite spectrum is comprised of several components. This reflects the fact that Fe atoms having different numbers of Fe second nearest neighbors(nn) have a different magnetic hyperfine field. Since the largest field will be experienced by those atoms that have no vacancies in their second nn shell, the vacancy content can be determined from

$$P_0 = (1 - x)^6 \quad (3)$$

where P_0 is the Mossbauer-determined fraction of iron atoms that exhibit the largest magnetic hyperfine field. Montano et al. [9,10] have pointed out that the catalytic activity of pyrrhotite seems to be related to its vacancy content. The value of this parameter, determined from Eq. 3, is given in Table 2. It is seen that the vacancy content is relatively constant for a variety of catalysts and also for pyrrhotite derived from pyrite. This indicates that the vacancy content is related primarily to conditions of temperature and atmosphere, not to the nature of the precursor. Although electron microscopy indicates that the pyrrhotite particles remain quite small (~ 100 Å), the Mossbauer spectra do not exhibit significant SP character at room temperature and below. This will be further investigated.

III. XAFS SPECTROSCOPY RESULTS

The complete XAFS spectrum of bulk Fe_2O_3 is shown in Figure 9. The structural information is contained in both the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. The former is the shaded region in Figure 9

extending from approximately 20 eV below to 50 eV above the absorption edge, while the latter region extends from 50 to several hundred eV above the edge. In the current report we will focus mainly on the EXAFS. It can be shown [11,12] that the EXAFS can be extracted from the raw spectrum, converted to a wave-vector representation (Fig. 9, middle), and Fourier transformed to yield a radial structure function (RSF) (Fig.9, bottom) that is similar to a radial distribution function for the absorbing iron atoms. That is, each peak in the RSF represents the photoelectron scattering component from a shell of neighboring atoms surrounding the iron atom at the origin. This is shown clearly in Figure 10 where the RSF is compared to the true radial distribution function of bulk Fe_2O_3 ; the RSF has been shifted forward slightly in Fig. 10 to account for the effects of phase shifts [11,12].

In Figure 11, the RSF of bulk Fe_2O_3 is compared to that of several catalysts; a 30 Å Fe_2O_3 sample prepared by a company called Mach I, and two sulfated Fe_2O_3 samples prepared by the CFFLS group at the University of Pittsburgh. It is seen that the amplitudes of the iron shell peaks of the catalysts are significantly smaller than those of the bulk standard. By performing a least squares analysis of the back transform of a peak or set of peaks in the RSF, it is possible to determine both the interatomic distances and coordination numbers of the neighbor shells in question [11-13]. The results of such analyses for the catalysts of Figure 11 are presented in Table 3. It is seen that while the interatomic distances are within the standard deviations of those of bulk hematite for the most part, the coordination numbers of the iron shells are markedly decreased from those of bulk hematite. This reflects that fact that the iron atoms on or near the surfaces of these ultrafine catalyst particles have on average less iron neighbors in these shells. Similar results have been observed for catalysts that assume the FeOOH structure in the as-prepared or as-dispersed state, such as those prepared by cation-exchange or by the Shabtai treatment [14-16].

Greggor and Lytle have observed similar results in their EXAFS studies of supported metal catalysts [13] and have developed a model relating average coordination numbers for different neighbor shells to the size and shape of the catalyst particles. We are currently developing a model to do the same thing with catalysts of both the Fe_2O_3 and FeOOH structures.

In the current year, we have also initiated some high temperature XAFS studies in order to investigate the reactions of catalysts in situ during hydrotreatment. The initial experiments utilized coals impregnated with iron using cation exchange and using the Shabtai treatment.

These experiments have demonstrated that RSFs derived from high temperature XAFS spectra under flowing hydrogen can be used to indicate the reactivity of highly dispersed iron with sulfur to form pyrrhotite. In the coming quarter, we will carry out further experiments of this type using model compounds.

In situ XAFS studies have also been conducted at the sulfur K-shell absorption edge to determine the change in sulfur structure for sulfated iron oxide catalysts during drying. The clearest results are shown by a FeOOH/SO_4 catalyst, as illustrated by Figure 12. For sulfur structures, the XANES are most valuable, because of the fact that the $s \rightarrow p$ transition peak occurs at characteristic energies for sulfur species of different valence [17]. By far the dominant feature of the XANES of the as received catalyst is the sharp $s \rightarrow p$ peak of the sulfate species, which occurs at 10.0 eV in Figure 12. During treatment at 125 and 250 C, a small additional peak forms at approximately 9.0 eV, which corresponds to the $s \rightarrow p$ transition of sulfone. Approximately 5% of the total sulfur undergoes this reduction. We believe this could correspond to the loss of H_2O by some surface sulfur cations. The loss of OH bonds by surface sulfur cations could effectively reduce them to a sulfone-like oxidation state (+4). It is seen from Figure 12 that this process is reversible, as the small sulfone peak can be made to disappear by passing helium bubbled through water at room temperature over the "dried" catalyst. It is also seen that heating the sample to higher temperatures (400 and 500 C) seems to have no greater reductive effect than heating to 125 C. These results are in accord with reports that drying the sulfated iron oxide catalysts changes their activity, although it is not clear why the hypothesized reaction should have that effect.

IV. IN SITU SAMPLE PROBE

One of the problems with determining the relationship between catalyst structure and catalyst function is the fact that, in most liquefaction experiments, the structure of the catalyst is known only at the beginning and end of the experiment. In situ experiments are difficult because of the combination of high pressure and high temperature required to simulate a liquefaction environment. In order to circumvent this problem, we have constructed an in situ sampling probe for use with a one liter stirred autoclave reactor. By sampling the contents of the reactor as a function of time, the state of the catalyst inside the reactor should be clearly indicated. Further, the rate of growth of the catalyst particles as a function of time could also

be determined.

The reactor is designed so that a coal slurry can be introduced into the autoclave and brought to temperature very rapidly, thereby eliminating errors associated with long heating times (Figure 13). The slurry, consisting of coal, solvent and catalyst, is loaded into the slurry tank which is then purged and pressurized to 1500 psig with hydrogen. Note that the hydrogen may be added from either the top or the bottom of the slurry tank. The bottom fill may be used to keep slurry in suspension if the solvent has a low viscosity. The autoclave and all associated piping are purged with hydrogen before the autoclave is heated to approximately 415 C. After reaching operating temperature, the valve between the slurry tank and the autoclave is opened, allowing the slurry to be forced into the autoclave by the hydrogen pressure in the slurry tank. The pressure in the system is maintained at 1500 psig. The system can be adapted to allow for either constant flow or no flow of hydrogen. Figure 13 shows a schematic diagram of the system.

The sampling system consists of a series of pressure stepdowns terminating with the sample cell. The sampling system is purged with either hydrogen or nitrogen prior to the run and between each sample collection. The valves at the bottom of the reactor are opened and closed in series until the sample reaches the pressure stepdown tube. The pressure of the sample in the stepdown tube is approximately 250 psig. Gas is released through the vent to further reduce the pressure to 25 psig. The sample then flows into the XAFS sample cell. The sample cell uses two beryllium windows to contain the sample in a body of brass or aluminum. A series of additional sealed stainless steel sample cells are used to collect samples for other measurements. The sampling system is then disconnected and purged with heated hydrogen/nitrogen to remove any sample residue. The heated hydrogen may also be forced up through the bottom of the autoclave to clean the sample tube prior to sample extraction.

The initial run used an $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst with a Wyodak coal and tetralin solvent. While the catalyst concentration in the sample cells collected was less than desired, the results are considered good for a first run. Some typical XAFS data are shown in Figure 14. These radial structure functions clearly show the transformation from a highly dispersed hematite structure to pyrrhotite through the gradual replacement of the oxygen first nearest neighbor shell by sulfur shells, and the shift in position of the principal iron shell.

V. SUMMARY AND CONCLUSIONS

Excellent progress has been made this year in the development of both Mossbauer spectroscopy and XAFS spectroscopy methodology for the characterization of iron-based direct coal liquefaction catalysts. In future work, more emphasis will be placed on in situ measurements, at high temperatures under hydrogen in appropriate solvents or oils, and on samples extracted using a newly constructed in situ sample probe interfaced with a one liter stirred autoclave reactor.

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Table 1: Mössbauer Parameters for Fe carbide samples

Sample	H(kG)	I.S.(mm/s)	Q.S.(mm/s)	% Fe	Phase
Fe Carbide	326	.01	0.0	5	Fe metal
Run #40	211	.23	.03	37	Fe ₃ C
RT	193	.21	.01	29	Fe ₃ C
	267	.30	-.07	6	Fe ₇ C ₃
	169	.20	.02	16	Fe ₇ C ₃
Fe Carbide	326	-.02	0.0	13	Fe metal
Run #37	212	.25	.03	35	Fe ₃ C
RT	190	.23	.03	24	Fe ₃ C
	264	.37	-.12	20	Fe ₇ C ₃
	164	.20	.03	24	Fe ₇ C ₃
Fe Carbide	318	.07	0.0	8	Fe metal
Run #49	216	.24	-.01	26	Fe ₃ C
RT	192	.21	.01	23	Fe ₃ C
	264	.29	-.09	8	Fe ₇ C ₃
	164	.20	.02	33	Fe ₇ C ₃

Table 2. Results for the catalysts after reaction.

SAMPLE DESCRIPTION	PYRRH. TYPE	VACANCY CONTENT(X)
Ill #6 + Fe ₂ O ₃ /SO ₄ (3.4% SO ₄)		.11
Ill #6 + Fe ₂ O ₃ /SO ₄ (6.1% SO ₄)	Antiferromagnetic (Random vac. distb.)	.10
Ill #6 + Fe ₂ O ₃ (non sulfated)		.125
Illinois #6 (no catalyst)		.115
Ill #6/ Maya (no catalyst)		.11
Ill #6/ Maya + Fe(CO) ₅	Transition type	.12
Ill #6/ Maya + Fe(CO) ₅ + Mo as Mo(CO) ₆		.11
Ill #6/ Maya + Fe(CO) ₅ + Mo as Naphthanate		.09
Wyodak/ Maya (no catalyst)		.115
Wyodak/ Maya + Fe(CO) ₅		.115
Up. Frp./ Maya (no catalyst)	Ferromagnetic (Ordered vac. distb.)	.115
Up. Frp./ Maya + Fe(CO) ₅		.11

Table 3. Results of least squares analyses of the back transforms of the iron shell peaks of several catalysts. Standard deviation are ± 0.02 - 0.05 Å for distances, and ± 0.5 - 1 for coordination numbers.

Sample	Dist.(Å)		CN	
Hematite (Bulk Fe ₂ O ₃)				
Fe-O	1.96	} <2.02>	3	} < 6 >
Fe-O	2.09		3	
Fe-Fe	2.88	} <2.94>	1	} < 4 >
Fe-Fe	2.96		3	
Fe-Fe	3.36	3.36	3	3
Fe-Fe	3.69	3.69	6	6
Fe ₂ O ₃ /SO ₄ ²⁻ (1991 sample)				
Fe-O	1.90		5.9	
Fe-Fe1	3.00		2.3	
Fe-Fe2	3.42		1.5	
Fe-Fe3	3.74		3.0	
Fe ₂ O ₃ /SO ₄ ²⁻ (1990 sample)				
Fe-O	1.97		5.6	
Fe-Fe1	3.00		1.6	
Fe-Fe2	3.41		1.1	
Fe-Fe3	3.73		1.9	
Fe ₂ O ₃ (30Å sample)				
Fe-O	1.92		5.6	
Fe-Fe1	2.97		0.7	
Fe-Fe2	3.41		0.9	
Fe-Fe3	----		---

Figure 1. Mössbauer spectra of sulfated ferric oxide catalysts. Before calcination, only a quadrupole doublet is observed, while the two calcined samples exhibit significantly different quadrupole and magnetic percentage

Figure 2. 12K spectra of lignite after cation exchange in an FeCl_2 soln. (top) and an $\text{Fe}(\text{OOCCH}_3)$ soln. (bottom). By measuring spectra at several temperatures, approximate size distributions can be obtained using Eq. 1.

Figure 3. Approximate size distributions determined for cation-exchanged lignites from Mossbauer spectra at three temperatures.

Figure 4. Theoretical relaxation spectra calculated for Fe₂O₃ particles of several diameters at room temperature. The critical diameter from Eq. 1 is 85 Å.

Figure 5. Theoretical relaxation spectra for 45 Å diameter Fe_2O_3 at room temperature and 12K.

Figure 6a. Size distribution of Fe₂O₃ on carbon black.

Figure 6b. Experimental and theoretical spectra of Fe_2O_3 on carbon black catalyst calculated from the size distribution of Figure 6a.

Figure 7. Growth of Fe₇C₃ peaks with the increase in the gas flow rate in laser pyrolysis

Figure 8. Mössbauer spectra illustrating the case where all pyrite and added catalyst is converted to pyrrhotite (top), and where only half of the added catalyst is converted to pyrrhotite.

Figure 9. Complete XAFS spectrum of bulk Fe₂O₃ with the XANES region shaded (top). EXAFS oscillations plotted against wave vector (middle). Radial structure function (RSF) derived by Fourier transforming the EXAFS (bottom).

Figure 10. Comparison of the RSF of bulk hematite to the radial distribution function.

Figure 11. Comparison of the RSF of bulk hematite to those of several Fe_2O_3 catalysts.

Figure 12. Sequence of the sulfur K-edge XANES spectra for FeOOH/SO₄⁻² at indicated temperatures and atmosphere.

Stirred Autoclave with Sample Cell

Figure 13

Figure 14. RSF's obtained using the in situ sampling probe showing the transformation of a $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst to pyrrhotite as a function of time of reaction.

Project I.5 Macerals, Catalyst Dispersion and a Model Compound

(Edward M. Eyring, David A. Sommerfeld and H. Paul Wang)

SUMMARY

Hiawatha (Utah) coal macerals have been impregnated with iron chloride catalyst and hydrotreated at 290°C. A variety of spectroscopic tools have been used to explain pronounced differences in the depolymerization reactions experienced by vitrinite and resinite macerals. A coal model compound has also been subjected to mild hydrotreatment conditions. More of the model compound is being synthesized. Interstitial gas has been identified as the cause of photoacoustic enhancement of infrared active modes of adsorbed molecules in colite channels.

HYDROTREATED MACERALS

One way of achieving a better understanding of iron chloride catalyzed coal depolymerization is to separate the coal into maceral groups and observe differences in the reactivity of two different macerals. Hiawatha (Utah) coal was ground in two stages to produce a uniform particle size. The ground coal was the demineralized under nitrogen with concentrated solutions of HCl and HF. Next the ground, demineralized coal was divided into narrow density fractions of resinite and vitrinite macerals by a density gradient centrifugation (DGC) technique using aqueous cesium chloride solutions to which a nonionic surfactant had been added [1]. It was found that the dominant liptinite maceral in Hiawatha coal by a narrow margin is resinite rather than sporinite.

Resinite and vitrinite macerals from Hiawatha coal were impregnated with 15% by weight FeCl_3 from an acetone solution. The impregnated samples were then dried at 50° C in a vacuum oven (80 torr). In a tubing bomb reactor the impregnated samples were subjected to mild hydrotreatment conditions (275 C, 2500 psi H_2 , 3 hours) approximating the first stage of the Shabtai coal depolymerization procedure [2]. Maceral samples before and after hydrotreatment, were examined by electron probe microanalysis (EPMA), petrographic microscopy, thermogravimetry (TG), Curie-point Evaporation/Pyrolysis GC/MS, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

The 64 μm x 64 μm photomicrographs obtained by EPMA show the distribution of chemical elements within solid maceral particles (under high vacuum). One expected result is that the elements iron and chlorine do not map exactly onto one another in an impregnated maceral particle since the FeCl_3 salt is dissociated into iron (III) and chloride ions that migrate separately through the pores of a maceral particle. A less predictable EPMA result is that the FeCl_3 is more successful in reaching the interior of microscopic vitrinite particles than in gaining the interior of resinite particles. This has an important consequence for the susceptibility of the two macerals to iron chloride catalyzed depolymerization as shown below.

Enhanced reflectance of hydrotreated, impregnated resinite observed with a polarizing reflected-light microscope suggests [3] that thermal dehydrogenation reactions and condensation reactions leading to larger aromatic clusters are taking place at 275°C. These reactions may be caused by a poor dispersion of iron chloride in the resinite particles leading to limited hydrogenolysis.

The hydrotreated, FeCl_3 - impregnated resinite particles experience a ~40% weight loss below 280°C (determined by TG/DTG analysis). The hydrotreated, FeCl_3 -impregnated vitrinite particles experience only a ~8% weight loss below 280°C. This contrast is further evidence of the pronounced difference in chemical reactivity of the two impregnated macerals.

If hydrogenolytic cleavage of methylenic linkages predominates in the hydrotreatment step, an increase in concentration of methyl groups in partially depolymerized (hydrotreated) maceral should be detectable by DRIFTS at approximately 2862 cm^{-1} . There is indeed an increase in the intensity of the CH stretching bands of methyl groups in the vitrinite sample after hydrotreatment (see Figure 1). Hydrotreatment of resinite gives rise instead to an increase in intensity of an aromatic ring breathing vibration at 1600 cm^{-1} and a reduction in intensity of a carbonyl band at 1690 cm^{-1} . These infrared spectral changes suggest a transformation of the resinite from aggregates of partially unsaturated cyclic compounds containing some carbonyl groups to saturated and aromatic hydrocarbons during hydrotreatment. The contrast in the infrared data for the two macerals may arise from differences in dispersion of the iron chloride catalyst in the two macerals.

GC/MS data indicate that the impregnated resinite undergoes depolymerization of dimer, trimer and higher polymer components to monomers as hydrotreatment proceeds. All of the above results are from a manuscript [4] that has been submitted for publication.

COAL MODEL COMPOUND

A small sample of 4-(1-naphthylmethyl) bibenzyl, shown below, was generously provided by Malvina Farcasiu.

This coal model compound was mixed with iron (III) chloride and subjected to mild hydrotreatment conditions (275°C, 2500 psi H₂, 3 hrs.) in a tubing bomb reactor. No change in the model compound was detected by DRIFTS in this experiment. In the presence of high surface area carbon black the same compound undergoes decomposition at temperatures as low as 320°C [5].

A sustained effort in our laboratory to synthesize more of this model compound has thus far been unsuccessful.

PHOTOACOUSTIC SIGNAL ENHANCEMENT

Photoacoustic (PA) detection of infrared spectra of solid surfaces would compete more successfully with DRIFTS if the PA signal were not so weak. (Signal averaging times in microphonic FTIR/PAS can be as long as hours at mid-infrared wavelengths). The signal from an IR-active mode of adsorbed pyridine in the channel/cages of HZSM-5 and HY zeolites was measured by PA, transmittance, and diffuse reflectance FT-IR spectroscopies. The measured PA signal enhancement factor was 2.1 in the HY and 3.3 in the HZSM-5 zeolite. Interstitial gas expansion plays an important role in the PA signal enhancement of the surface IR mode. This study was reported in a recent paper [6] acknowledging CFFLS support.

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Figure I.5.1. Deconvoluted diffuse reflectance FTIR spectra for vitrinite (solid line) and hydrotreated FeCl₃-impregnated vitrinite (dashed line).

Project I.6 Characterization of Catalysts Used in Coal Hydrogenation Systems

(Nelly M. Rodriguez and R. Terry K. Baker)

INTRODUCTION

Recent studies performed at various laboratories in the Consortium have shown that iron compounds particularly those containing sulfur exhibit unusually high activities for the transfer of hydrogen in coal liquefaction processes. It is believed that the identity of the catalyst is that of a non-stoichiometric iron sulfide. In an attempt to understand the fundamentals of this behavior it is worthwhile to examine the extensive surface science literature dealing with the modification of metal surfaces arising from the substitution of some of the metal atoms by sulfur. It has been suggested that approximately 1/4 of a monolayer coverage of metal by sulfur can result in a dramatic increase in the activity of such a catalyst. On the other hand, it is well known that the presence of excess sulfur results in poisoning and a complete suppression of the catalytic activity of the metal. Various workers have demonstrated that this promotional/poisoning effect is not restricted to sulfur but can be achieved by the incorporation of other electronegative atoms such as nitrogen and halogens into the metal surface.

In the current program, we have used a combination of controlled atmosphere electron microscopy and in-situ electron diffraction techniques to characterize iron catalyst samples prepared by various groups in the Consortium. In addition, these and other experimental approaches have been used to establish the effect of sulfur on the reactivity of selected metals. For these experiments we focused our attention on the influence of sulfur additions to cobalt, since the catalytic activity of this metal has been found to be extremely sensitive to surface modifications. The probe reaction chosen for this purpose was the catalytic decomposition of unsaturated hydrocarbons which results in a range of gas phase products.

EXPERIMENTAL PROCEDURES

I. In-Situ Electron Microscopy

In-situ electron microscopy is a novel and powerful technique capable of overcoming

some of the limitations of conventional electron microscopy. These include the necessity of examining a material in a vacuum environment, which precludes dynamic studies of any structural changes which accompany the reactions. At Auburn we have successfully overcome this restriction by modifying a JEOL 200CX transmission electron microscope to function as a sophisticated micro-reactor system. This has been accomplished by fitting the microscope with a special gas reaction cell, which enables the specimen to be observed continuously by electron transmission while exposed to a gas environments at pressures up to 5.0 Torr and a temperature up to 1000°C. Dynamic events are recorded on video tape via a closed circuit television link and under stable conditions it is possible to achieve a resolution on the TV monitor of 0.4 nm. A further feature of this technique is the ability to perform chemical and structural analysis of a reacting specimen using micro-electron diffraction analysis. We are using this approach to identify the chemical nature of the catalyst particles and also determine the crystallographic orientation of the particle surfaces as the specimen is undergoing reaction. To our knowledge this is the first time that it has been possible to analyze the chemical state of particles as they are reacting and from the data presented here it will be seen that major differences are obtained under this conditions compared to a post-reaction examination of a specimen which has been cooled to room temperature.

Model Systems

Transmission specimens of single crystal graphite and amorphous carbon films were prepared by standard procedures. In one series of experiments spectrographically pure iron was vacuum deposited onto a specimen consisting of overlapping films of graphite and carbon. This type of specimen design offers two important features: (i) one can simultaneously observe the behavior of the metal particles on two different support media under identical conditions, and, (ii) one can gain insight into events occurring at the interface between the two supports and the metal. These specimens were reacted in hydrogen and the behavior compared to that observed in the presence of argon.

Real Systems

Samples of iron catalysts obtained from various laboratories were initially ultrasonically dispersed in iso-butanol and then a drop of the suspension introduced onto a transmission

specimen of single crystal graphite. This combination was subsequently heated in the microscope in the presence of hydrogen and changes in both the structure of the catalyst and the graphite support continuously monitored.

II. Macro-scale Studies

Testing of the catalyst activity was accomplished by following the evolution of ethylene, when it is mixed with hydrogen to produce methane, ethane and solid carbon. Two approaches were used:

- (a) To study the effect of the presence of trace amounts of H₂S in the feed on the catalytic activity of cobalt catalyst powder towards ethylene decomposition.
- (b) To determine how H₂S pre-treatment can affect the reactivity of ethylene.

The experiments reported in this section were performed in a quartz flow reactor (40 mm i.d. and 90 cm long) located in a Lindberg horizontal tube furnace. Flow rates of gases were controlled with needle valves and measured with rotameters. Catalyst samples (50-100 mg) contained in ceramic boats were treated in mixtures of H₂S:argon for variable periods of time at 600°C. Following this step a desired mixture of hydrocarbon, hydrogen and inert gas was introduced into the reactor. The composition of the gas-phase before and after reaction was analyzed with a gas chromatograph (Varian 3400) using a 30 m megabore column (GS-Q). The column was temperature programmed to give hydrogen, methane, ethylene, acetylene and ethane at 35°C and higher molecular weight hydrocarbons (C₃ to C₅) as the temperature was progressively raised to 180°C. The amount of carbon deposit produced on the catalyst was also determined after 1.5 hours by weight difference.

RESULTS AND DISCUSSION

i. Fe₂O₃.SO₄ with 0.5% Mo (From University of Pittsburgh)

Examination of the catalyst at room temperature showed that it consisted of thin platelet structures which tended to cluster together into larger entities. Measurements of a number of individual platelets showed that their typical length was 45 nm and widths of about 15 nm. Although it was not possible to obtain an accurate measure of their thickness, it was significant

that various features of the underlying graphite support could be seen through the platelets, which would suggest a thickness of about 5 nm. Although these observations appear to be in disagreement with particle sizes determined by other techniques, such as Mossbauer spectroscopy or X-ray line broadening, it should be appreciated that with the latter techniques one assumes that the particles have symmetrical geometries, i.e. hemispherical or cubic structures and under these circumstances values of about 5 nm would be predicted.

When these specimens supported on graphite were heated in hydrogen, no change in appearance was observed until the temperature was raised to 375°C at which point it was possible to discern the presence of small electron dense particles of about 1 nm diameter in the catalyst. On continued heating some of the smaller catalytic fragments started to exhibit mobility on the surface and tended to accumulate at graphite edges. At 590°C, inspection of the edges of the graphite support showed that particles which had collected in these regions were undergoing a wetting and spreading action and this behavior was accompanied by hydro-gasification of the support. At the same time, it was evident that catalyst material which remained on the inactive basal plane regions of the graphite had lost its sharp outline and become quite globular in appearance.

ii. FexSy Stiller's #1 Catalyst (West Virginia University)

Initial observation of this catalyst material supported on graphite showed that it consisted of irregular shape islands containing numerous pores and inclusions of small electron dense particles, 2 to 3 nm in size. When the system was subsequently heated in hydrogen, a major transformation occurred at 230°C, which involved volatilization of matrix material leaving a fibrous residue. At the same time, thin faceted particles 5 to 10 nm diameter started to form on the surface. As the reaction temperature was gradually raised to 350°C it was observed that of graphite edge regions were adopting a roughened profile suggesting that the catalyst was inducing hydro-gasification reaction. This behavior became more intense as the temperature was increased to 460°C at which point particles had grown in size to about 30 nm and were occasionally observed to exhibit mobility on the graphite surface. Further heating to 600°C resulted in extensive particle sintering, however, it was significant that there did not appear to be a corresponding increase in the rate of removal of the graphite.

iii. Iron/Graphite - Carbon Model System

When these specimens were heated in the presence of argon, the deposited metal film nucleated to form discrete particles at about 300°C, this behavior occurring more easily on graphite than on carbon. On continued heating up to 800°C particles increased in size and started to show a significant increase in sintering rate at around 670°C due to particle mobility. Examination of their morphological characteristics showed that they were relatively dense globular entities which exhibited very little evidence of a metal particle support interaction.

In contrast, when the same specimens were reacted in hydrogen, then the particles acquired well defined structural characteristics, being predominantly thin, flat and rectangular in outline, features which were apparent on both graphite and amorphous carbon and clearly point to the existence of a strong interaction of the crystallites with the supports. Motion of these particles commenced at 755°C and this action resulted in both an increase in the average particle size to 20 nm and an increase in the number of particles reaching graphite edge sites. These particles did not show any tendency to catalyze the hydro-gasification of the support until the temperature was increased to 890°C. At this temperature, particles located on edges were observed to create channels across the graphite basal planes.

iv. Macro-Scale Studies

(a) Effect of H₂S in the Feed

Table 1 summarizes the result of the continuous addition of trace amounts of hydrogen sulfide to the feed. It can be observed that small but nevertheless important changes at the surface of the catalyst are occurring. One important aspect is the reduction in the amount of carbon deposited on the catalyst surface. However the ability of the catalyst to decompose ethylene decreases with time as more sulfur is adsorbed at the surface and possibly the benefits resulting from modifications of the crystal structure are overridden by poisoning of the catalyst in excess sulfur.

(b) Effect of H₂S Pre-treatment

When similar cobalt catalyst were pre-treated in 4 ppm sulfur and subsequently reacted in the hydrocarbon environment a dramatic increase in the reactivity of the sulfided catalyst was

observed. Examination of the data presented in Table 2 shows that under these conditions there is almost a four fold increase in the ability of the catalyst to decompose ethylene and this behavior persists up to 60 minutes into the reaction.

Table 3 shows the product analysis for the decomposition of ethylene at the surface of cobalt powder (polycrystalline) in the presence and absence of hydrogen sulfide and also the effect of continuous addition of sulfur to the reactant feed. The presence of the different products is an indication of the mode whereby the catalyst operates and allows one to postulate the possible mechanism by which a given reaction has occurred. One of the major differences observed is in the amount of solid carbon deposited on the catalyst, and this can be correlated with the ability of the catalyst to break carbon-carbon bonds. In fact pre-treatment for 30 minutes with trace amount of hydrogen sulfide makes cobalt an extremely reactive catalyst for the decomposition of ethylene into a variety of products. The presence of methane and ethane in the product spectrum is indicative of the hydrogenation ability of the catalyst.

TABLE 1 EFFECT OF ADDITION OF H₂S (4 ppm) IN THE FEED ON THE DECOMPOSITION OF ETHYLENE BY COBALT POWDER

SPECIES	15 min	25 min	40 min	60 min	80 min	100 min	115 min
Solid C	19.7	18.3	15.6	13.4	13.0	12.3	12.4
CH ₄	0.46	0.46	0.48	0.52	0.58	0.64	0.71
C ₂ H ₄	77.34	78.63	81.1	82.85	82.86	83.7	82.53
C ₂ H ₆	2.25	2.27	2.34	2.54	2.76	3.06	3.27
C ₃	0.25	0.33	0.48	0.68	0.8	0.94	1.09
C ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE 2 EFFECT OF H₂S (4 ppm) PRETREATMENT ON THE DECOMPOSITION OF ETHYLENE ON COBALT POWDER

SPECIES	15 min	25 min	40 min	60 min	80 min	100 min	115 min
Solid C	65.7	70.0	71.20	70.9	70.5	69.0	67.6
CH ₄	5.33	7.11	7.2	7.28	6.41	5.54	4.96
C ₂ H ₄	21.98	13.92	11.89	11.71	13.38	16.63	18.88
C ₂ H ₆	6.84	8.77	9.49	9.86	9.45	8.84	8.30
C ₃	0.15	0.20	0.22	0.25	0.25	0.25	0.25
C ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE 3. PRODUCT ANALYSIS AFTER 2 HOURS REACTION OF ETHYLENE-HYDROGEN 4:1 MIXTURE

SPECIES	UNTREATED COBALT POWDER	COBALT PRETREATED WITH 4 ppm H ₂ S*	COBALT WITH 4 ppm H ₂ S CONTINUOUS
Solid C	4.6	67.6	12.4
CH ₄	0.14	4.96	0.71
C ₂ H ₄	94.01	18.88	82.53
C ₂ H ₆	1.25	8.30	3.27
C ₃	—	0.25	1.09
C ₄	—	0.0	0.0

* Pretreatment performed for 30 min at 535°C

Task II

Exploratory Research on Coal Conversion

Program Coordinators: Henk Meuzelaar and Mohindar Seehra

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Report Period: May 1, 1990 - April 30, 1991

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Project II.1 Coal Structure/Liquefaction Yield Correlation by Means of Advanced NMR Techniques (Ronald J. Pugmire and Anita M. Orendt)

Over the past year, the majority of our effort has been in the measurement and interpretations of ^{13}C chemical shift tensor data on model polycyclic aromatic hydrocarbon compounds. These results are discussed in Section A. In addition, some work was completed on ^1H relaxation data on coals, as presented in Section B.

A. Solid State ^{13}C NMR Studies of Chemical Shift Tensors in Model Aromatic Compounds

The work over the last several years has resulted in a manuscript that was recently submitted for publication entitled " ^{13}C Chemical Shift Tensors in Aromatic Carbons. 4. Substituted Naphthalenes" (submitted to the Journal of the American Chemical Society) [1]. Included were the measured chemical shift tensors, using the technique of variable angle spinning (VAS), for 1,4,5,8-tetramethylnaphthalene (I), 1,2,3,6,7,8-hexahydropyrene (II), and pyracene (III), along with ab initio calculations of the complete shielding tensor.

The calculations were used to provide the orientation of the tensor components in the molecular frame. The good agreement between experiment and theory is shown graphically in Figure 1. Figure 1 includes compounds I, II, III, along with naphthalene (IV), triphenylene (VI) and phenanthrene (VII) from alpha protonated carbons only, for a total of 18 sets of chemical shift

tensor components. The carbons included are marked by the heavy dots on the structures given above. The equation of the least squares fit line in Figure 1 is $\sigma_{\text{calc}} = 1.07 \sigma_{\text{obs}} - 2.5$ ppm, and the fit has a correlation coefficient of 0.990. Figure 2 shows the calculated orientations of σ_{11} in naphthalene (V), bicyclobuta[deij]naphthalene (IV) along with compounds I-III mentioned above. σ_{22} is in the aromatic plane and perpendicular to σ_{11} , while σ_{33} is always perpendicular to the aromatic plane. In the case of both substituted and protonated carbon, the changes in both the orientations and the principal values with comparison to those in naphthalene (V) could be rationalized in terms of the strain in the attached alkyl groups, with the largest changes observed in pyracene (III). The trends observed are continued in bicyclobuta[deij]naphthalene (IV), an unknown compound. Calculations on two other polycyclic aromatic hydrocarbons that contain four or five membered rings also show the effects of strain due to the small alkyl rings, with σ_{avg} and σ_{33} of the substituted carbons shifted downfield from those in other substituted carbons. Future efforts will include experimental measurements on several other compounds with strained substituents, such as biphenylene and fluorene.

A second observation that can be made from these results is that at the current level of theory, a problem exists in making confident orientational assignments in cases where two of the components are within 10 ppm. This is the case in the bridgehead carbons for the compounds studied in this work. The small difference observed between σ_{11} and σ_{22} (<10 ppm) coupled with the inherent errors in the calculated value of σ_{11} do not allow for any discussion of orientations. However, the fact that σ_{11} and σ_{22} are so similar in all compounds as they are in naphthalene suggests that the substituents do not significantly affect the π electron system. In addition, the fact that these two components are nearly identical is an indication that all three C-C bonds have nearly the same π bonding character. The π electron structure can be described as a single delocalized π system over the two aromatic rings. This, however, was not the case observed in triphenylene (VI) [2]. The bridgehead carbons in triphenylene show a difference of about 40 ppm between the two in-plane components (σ_{11} and σ_{22}), an indication that not all three bonds

are of the same approximate π bonding order, a conclusion supported by MNDO calculations. Therefore, in triphenylene (VI), the bonding can be described as three aromatic rings connected by C-C bonds. The same situation is believed to exist in phenanthrene (VII), where two isolated benzene rings are connected by C-C bonds; however, only theoretical results exist for the bridgehead carbons in this compound. The work on phenanthrene and triphenylene, completed by Grant, et al. [2] has been submitted for publication.

The above discussion demonstrates the power of ^{13}C NMR chemical shift measurements when coupled with calculations in gaining insight into the electronic structure and bonding of aromatic compounds.

In order to explore more complicated, less symmetrical aromatic model compounds, the use of new experimental techniques which separate the chemical shift tensor patterns of different carbons in a second dimension (2-D NMR) is necessary. The available techniques were presented in last year's annual report. In past reports we have discussed the acquisition of equipment to perform dynamic angle spinning (DAS) experiments. This equipment finally arrived in January 1991. Unfortunately, the design had several flaws which did not allow for reproducible flipping (i.e., changing of the angle that the sample makes with the magnetic field) over a long time period. These problems are currently being addressed by the manufacturer. In light of these technical problems, our effort is turning to the rotational resonance method developed by Z.H. Gan in our laboratory about a year ago [3]. This rotational resonance technique requires the ability to set exactly two different power levels during each acquisition, a function that are recently added to our NMR spectrometer (May 1991). Therefore, due to the delays in the DAS instrumentation, the use of the rotational resonance 2-D technique will be explored.

B. Measurement of ^1H relaxation parameters in coal and coal chars.

By the measurement of the ^1H relaxation times, T_1 , $T_{1\rho}$, and T_2 , in coal one can gain information about motion and composition of the sample. Coals have long been known to be very inhomogeneous in terms of both their overall structure and their magnetic environment. Previous measurements of the ^1H spin-spin relaxation time, T_2 , of coal samples have been fit by a multiple exponential function, with each term corresponding to a different motional regime, reflecting this inhomogeneity [4,5]. In addition, measurements of T_1 , or the spin-lattice relaxation

time, have been correlated with the rank of the coal via the oxygen content [6]. The direct measurement of the $T_{1\rho}$ relaxation time, the time constant associated with the decay of magnetization along a spin locking field, can be used to validate the more common indirect measurement [7] as well as to gain insight into the pyrolysis process, as will be discussed below.

Experimentally, we have been measuring the proton T_1 and $T_{1\rho}$ relaxation times of coal and coal chars produced at various maximum temperatures by a slow heating (0.5 K/sec) process. All measurements were made on static ^1H line shapes using standard inversion recovery techniques for T_1 and spin lock experiments for $T_{1\rho}$ measurements. Generally 16 to 20 different times were used for the measurements. All experiments were performed on a Bruker CXP-100 spectrometer.

The ^1H $T_{1\rho}$ relaxation data of Pittsburgh #8 from the Argonne Premium Coal Sample Bank and its slow heating chars were best fit by three different relaxation times as shown in Figure 3. The fastest relaxation component is mainly due to the interaction between protons and electrons present in the samples and the large gyromagnetic ratio of the electron makes this relaxation time very short [6]. The medium component corresponds to the portion of the sample which is relatively mobile in comparison to the rigid macromolecular structure. Molecular motion, particularly slow motion, will effectively shorten the relaxation since the $T_{1\rho}$ relaxation process is dominated by motion with correlation times of about $1/\gamma H_1$, [8] or in the range of 10^{-5} s $^{-1}$ for the 47 KHz rf spin-locking field used in our experiments. The slow component corresponds to the contribution from the remaining rigid macromolecular structure in the sample. The lack of a strong proton-electron interaction together with slow lattice motion renders this component the slowest of the three rates observed. However, the ^1H spin diffusion from this portion of the sample to other faster relaxing portions will shorten the relaxation time of this slow component in comparison to $T_{1\rho}$ values observed in model compounds.

The percentages and relaxation times of these three $T_{1\rho}$ components for the Pittsburgh #8 coal and its chars are listed in Table 2 and are shown graphically in Figure 4. The $T_{1\rho}$ values for the chars exhibit a decreasing trend, relative to the coal, with temperature until the chars have become almost completely aromatic. The relaxation times pass through a minimum and then increase sharply beyond approximately 800K. The distribution of total proton magnetization is also given in Figure 4. The percent of total proton magnetization associated with the medium and rapid $T_{1\rho}$ time constants passes through a maximum at approximately 800K and then

decreases rapidly. In the case of the slow component, the contribution to the total magnetization runs parallel to the $T_{1\rho}$ value. One feasible explanation of the $T_{1\rho}$ relaxation data which is consistent with a simple picture of the pyrolysis process is given below. As the temperature increases, the mobility of the molecular structure increases as linkages between clusters are broken and some loosely linked clusters are released from the macromolecular structure into the mobile component. These changes in the structure will shorten the relaxation times and also increase the percentage of the fast and medium component. As the temperature increases, the condensation or recombination between the reactive centers in the clusters makes the macromolecular structure the main component in the chars, and this corresponds to the increase of the percentage of the slow component and the decrease in the medium and fast components observed in the relaxation data. In addition, the proton distribution becomes more dilute as the temperature goes higher making the proton-proton interaction smaller and reducing its contribution to the relaxation process. Also, the spin diffusion among the protons will also be reduced; these two effect will cause longer relaxation times for the slow component.

^{13}C CPMAS variable contact time experiment can give the indirect measurement of ^1H $T_{1\rho}$ relaxation [7], but the fast relaxation component cannot be seen in this experiment because the cross polarization time (20 μs to 1 ms) is as long as the relaxation time of the fast components and even some of the medium components listed in Table 2. In the deconvolution of the ^{13}C CPMAS variable contact time data, the fast component of the ^1H relaxation must be considered in order to obtain the total magnetization; this is extremely important in spin counting experiments. However, it will not have much effect in the parameters such as aromaticity because the contribution of the fast relaxation term of ^1H $T_{1\rho}$ is comparable for both the aromatic and aliphatic intensity. The indirectly measured ^1H $T_{1\rho}$ relaxation times listed in Table 2 are approximately the weighted average of the medium and the slow component from the direct measurement as they should be. In addition, the trends in the relaxation times for the different temperature chars are similar to the trends observed for both the medium and the slow components in the direct measurement.

The ^1H spin-lattice (T_1) relaxation data for Pittsburgh #8 coal, shown in Table 3 and Figure 5, is almost a single exponential for the parent coal and for the chars below 673K; above this temperature the data becomes bi-exponential as the contribution from the fast component rises to a significant level. Generally, the relaxation time becomes shorter for the higher

temperature chars. These T_1 relaxation data do not show any obvious trends with respect to the temperature of the chars and this may be due to the fact that there is no direct relationship between fast molecular motion and the temperature of the chars since the spin-lattice relaxation is affected mainly by fast lattice motion with correlation times of $1/\gamma H_0$, 8 or about 10^{-8} s^{-1} at 100 MHz. The interesting result is the exceptionally short ^1H T_1 of 28 μs (69% of the total intensity) observed from the 1173K char. Possible ^1H spin-lattice relaxation mechanisms in coals and coal chars remains to be further investigated.

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Figure 1. Least squares fit of calculated versus experimental chemical shift tensor components for the substituted naphthalenes, triphenylene, and phenanthrene. Circles are σ_{11} , squares σ_{22} , and triangles σ_{33} .

Figure 2. Calculated orientations of σ_{11} . σ_{22} is in the aromatic plane and perpendicular to σ_{11} ; σ_{33} is perpendicular to the aromatic plane.

Figure 3. Fits of ^1H $T_{1\rho}$ relaxation data of Pittsburgh #8 coal, using: A) Single exponential; B) Two exponentials; and C) Three exponentials.

PITTSBURGH #8 CHARS (SLOW COMPONENT)

Figure 4. Graphs of change in percentage of total proton magnetization and relaxation time of the T₁ρ components as a function of char temperature for Pittsburgh #8 coal and its slow heating chars

PITTSBURGH #8 CHARS (FAST COMPONENT)

PITTSBURGH #8 CHARS (SLOW COMPONENT)

Figure 5. Graphs of change in percentage of total proton magnetization and relaxation times of the T_1 components as a function of char temperature for Pittsburgh #8 coal and its slow heating chars.

Project II.2 Mass Spectrometric Analysis and Modeling of Coal Liquefaction Processes (H.L.C. Meuzelaar and

H. Huai)

1. NOVEL METHODS FOR OBTAINING MOLECULAR WEIGHT DISTRIBUTION PROFILES

Yield and average molecular weight are the most frequently used parameters to measure the relative performance of coal liquefaction procedures in general and for gauging the effect of changes in experimental conditions, in particular. Unfortunately, neither parameter can be measured in an unambiguous manner. Since yield is often determined on the basis of solubility in a particular solvent allowance has to be made for the tenuous link between conversion rate and solubility (macromolecular substances that have undergone little or no conversion may be quite soluble). Average molecular weight, although providing a more direct measure of the degree of conversion achieved, provides little information about the relative proportion of small vs. large molecules, due to the large variations in the shape of the molecular weight distributions profiles encountered. Obviously, calculation of both "number average" and "weight average" MW values provides additional information about the shape of the distribution curve. The importance of unambiguously interpretable yield and molecular weight parameters has prompted us to undertake the development of a combined GC/CIMS and vacuum TG technique to measure complete molecular weight distributions as well as simulated distillation profiles for vacuum distillable coal-derived liquids.

During the preceding year the combined (GC/CIMS + vacuum TG) technique was shown to provide reliable (RSD < 10%) MW distribution data for a set of 64 model compounds in the 90-350 dalton range. Moreover, when applied to a series of coal derived liquids obtained by the Shabtai HT-BCD procedure, the MW profiles obtained agreed well with available coal structural data and measurements by other techniques.

This year our standard mixture was extended to 103 compounds including 5 n-alkanes, 9 hydroaromatics (including 5 oxygen containing compounds) and 89 aromatics (11 oxygen containing compounds and 18 sulfur containing compounds). Figure 1 shows the relationship between MW and GC elution temperature when using a short (40 cm), BP-1 coated capillary

column (0.1 μm film thickness) operating at high linear carrier gas velocities (~ 140 cm/sec).

A second emphasis area has been to study the effect of changes in various experimental parameters on the relationships between MW and GC elution (simulated distillation) temperature (GC/CIMS experiment) as well as between MW and vacuum distillation temperature (TG experiment). In spite of the very basic nature of the physicochemical phenomena involved relatively few literature data are available. Most information found in the literature strictly concerns hydrocarbons for which GC based SIMDIST (simulated distillation) methods are standard practice among petroleum chemists and fuels engineers. Essentially, we were asking the question: "can GC based SIMDIST methods be extended to the kind of heteroatomic compounds encountered in coal-derived liquids, (viz. hydroxyaromatics and aromatic ethers)?" As shown in Figure 1, chemical shifts due to the presence of O and S containing heteroatomic functionalities tend to be small enough not to cause major systematic errors. Moreover, the basic MW/elution temperature relationship shown in Figure 1 was found to be relatively insensitive to differences in column heating rate, instrumental response factors or sample inlet split ratios. However, at the much lower linear carrier gas velocities typically used in conventional SIMDIST experiments a marked increase in systematic shifts due to differences in compound chemistry was observed. As shown in Figure 2, MW/(simulated) distillation temperature relationships are strongly influenced by pressure (compare atmospheric pressure TG and vacuum TG curves in Figure 2) and by carrier gas velocities (compare the calculated boiling point curve with the short column GC/MS profile). Further note the close agreement between the vacuum TG and short column GC/MS profiles.

Apparently, the high carrier gas velocities used in the GC/MS experiment are approximately equally effective in transporting evaporated molecules away from the evaporation region as the vacuum environment present in the TG experiment. Thus, in both experiments the equilibrium between evaporation and condensation processes is shifted decisively in the direction of the former. Although our present insight into the liquid and gas phase transport behavior of complex mixtures falls well short of the rigorous, quantitative level of understanding required for the development of reliable mechanistic models, experiment observations appear to allow a successful empirical calibration of the proposed MW determination method.

2. ON-LINE MS MONITORING OF COAL CONVERSION PROCESSES AT HIGH PRESSURES

Over the past decade, sophisticated chromatographic and spectroscopic techniques have greatly increased our knowledge of the composition and structure of coal-derived liquids as well as of the corresponding feed coals. Notwithstanding these advances, relatively little is known about the precise reaction pathways as well as the intermediate reaction products involved. This is particularly true of conversion reactions carried out in batch reactors such as autoclaves. Due to the relatively long residence times primary reaction products formed in autoclaves are notoriously susceptible to secondary, or even tertiary reactions. Application of real-time, on-line chromatographic and/or spectroscopic techniques capable of throwing light on these processes is hampered by the high temperatures and pressures inside the reactor which complicate direct interfacing to standard analytical instruments.

Using a novel automated air sampling technique developed at the University of Utah, Center for Micro Analysis and Reaction Chemistry (U.S. Patent No. 4,970,905), the authors have undertaken the development of an on-line mass spectrometry interface for high pressure (>1000 psi) reactor environments. The interface consists of a valveless, all quartz, heated inlet device suitable for automated, repetitive vapor sampling. The automated vapor sampling (AVS) module connects directly to a 1 m long, 150 μm i.d., fused silica capillary GC column, thereby providing a highly useful degree of chromatographic preseparation. The effluent from the capillary column is fed directly into the ion source of a highly sensitive ion trap mass spectrometer (ITMS) capable of operating in GC/MS as well as tandem MS (MS^n) mode while providing electron ionization (EI) as well as chemical ionization (CI) options.

Since the AVS inlet is designed to operate at near-ambient pressures in order to ensure a constant, stable flow of carrier gas through the capillary transfer line column into the high vacuum of the MS system, the high pressures in the autoclave reactor need to be first reduced to near ambient pressure by means of a 1 m length of narrow bore (e.g. 10 μm) fused silica capillary tubing. This tubing is kept at relatively high temperatures (< 300°C) to minimize condensation losses. Moreover, utmost care is taken to eliminate dead spaces at the high pressure end of the transfer line in order to avoid unduly long response times due to the very low liquid flows (e.g. 0.1 $\mu\text{l}/\text{min}$) in the narrow bore capillary tube.

Figure 3 shows a schematic picture of the on-line system. At this point, model

compounds, such as diphenyl methane have been studied under three different reaction conditions: (a) thermal reaction without any catalyst; (b) thermal reaction with $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst; and (c) mild hydrotreatment (HT) with $\text{FeCl}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst. In Figure 4 the total ion chromatograms from these three reactions recorded at different reactor temperatures are illustrated. Figure 5 shows the concentration change of the feed (diphenyl methane) and the products (benzene, toluene and xylene) as a function of reaction time at 350 C. Under mild hydrotreatment conditions with $\text{FeCl}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst cleavage reactions occurred at the lowest temperature and gave the highest yield. The thermal reaction with $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst has a much smaller effect on the diphenyl methane cleavage reaction.

Figure II.2.1. Relationship between molecular weight and GC elution temperature for 103 model compounds.

Figure II.2.2. Distillation and GC elution (simulated distillation) curves produced by different techniques.

Figure II.2.3. Schematic configuration of the on-line system.

Relative Intensity

Figure II.2.4. Total ion chromatograms for a) thermal reaction in without any catalyst; b) with $\text{SiO}_2\text{-AlO}_3$ catalyst and c) mild hydrotreatment with $\text{FeCl}_3/\text{SiO}_2\text{-AlO}_3$ catalyst using diphenyl methane at different reactor temperatures. Note nonreactive biphenyl used as internal standard.

Figure II.2.5. Concentration change of the feed (diphenyl methane) and the products (benzene, toluene and xylene) as a function of reaction time at 350 C. a) thermal reaction (N_2 atmosphere) without any catalyst; b) thermal reaction with $SiO_2-Al_2O_3$ catalyst; and c) mild hydrotreatment (H_2 atmosphere) with $FeCl_3/SiO_2-Al_2O_3$ catalyst.

Project II.3 Catalytic Cracking, Hydrogenation and Liquefaction of Coals Under Milder Conditions

(Mohindar S. Seehra and Manjula M. Ibrahim)

OBJECTIVES

During this period, our objectives were: (i) to bring to a successful conclusion the research on the effect of Lewis acids (ZnCl_2 , ZnBr_2 , ZnI_2) on the cracking and hydrogenation of coals; (ii) to set up a high-temperature (500°C) and high pressure (1000 psi) ESR cavity system for in-situ investigation of the free radicals during cracking, hydrogenation and liquefaction; and (iii) to initiate research on the characterization of catalysts using SQUID magnetometry and x-ray diffraction.

SUMMARY OF RESULTS

Using the techniques of in-situ ESR spectroscopy, TGA/DTG and GC/MS, we showed that zinc halides promote depolymerization of coals at temperatures as low as 100°C . The details of these experiments and results have now appeared in the following publication:

"Depolymerization of Coals Promoted by Zinc Halides near 100°C ", M. M. Ibrahim and M. S. Seehra, *Energy and Fuels*, 5, 74-78 (1991).

Another accomplishment was that we fabricated and successfully tested a high pressure-high temperature ESR cavity system for in-situ studies to 500°C and pressures to 750 psi. During the coming year, we plan to extend the system to at least 1000 psi and then carry out cracking/hydrogenation experiments using Mo and Fe sulfide catalysts. Finally we have successfully employed x-ray diffraction to identify a large number of iron sulfide catalysts prepared by the Zondlo-Stiller team (who will report details of these studies) and used line broadening in x-ray diffraction and SQUID magnetometry to determine the particle-size distribution of an $\alpha\text{-Fe}_2\text{O}_3$ based catalyst.

BACKGROUND/INTRODUCTION

The history and background of the zinc halide catalysts in coal liquefaction was given in last years' annual report and other details of the results are given in our recent publication [1]. Therefore we omit details of this aspect of the work in this report. The remaining report will deal with the use of x-ray diffraction and SQUID magnetometry in characterizing catalysts and in determining their particle size distribution.

The use of SQUID magnetometry to determine the particle size distribution of Fe-based catalysts is based on the fact that many Fe-based compounds order magnetically and below a critical size and above blocking temperature T_B , these particles exhibit superparamagnetic behavior [2-5]. This superparamagnetic (SP) behavior can be used to determine the average particle size although the determination of the particle size distribution poses a more serious problem [2-11]. Assuming a log normal distribution, Richardson and Desai [6] have outlined a procedure for determining particle size distribution and a variation of this procedure has been developed for our work. First, in the SP region, the magnetization M must scale as H/T when H is the applied field and T is the absolute temperature. Second, for SP particles, M follows the Langevin function L

$$\frac{M}{M_{\infty}} = L(M_s V H / k_B T), L(x) = \coth x - \frac{1}{x} \quad (1)$$

where M_{∞} and M_s are respectively the saturation and spontaneous magnetizations per unit volume, V is the volume of the particle and k_B is the Boltzmann constant. M_s is usually obtained from a bulk sample whereas M_{∞} is obtained for the superparamagnetic particle in the limit $1/H \rightarrow 0$. Assuming a spherical particle so that $V = 4\pi r^3/3$, and using the low-field (lf) and high-field (hf) approximations of $L(x)$, Eq. 1 is inverted to yield

$$(r^3)_V = \left(\frac{9k_B T}{4\pi M_s M_{\infty}} \right) \left(\frac{M}{H} \right)_V \quad (2)$$

If a sample has uniform particle size, then $(r^3)_L = (r^3)_{hf}$. For a sample with particle size distribution, $(r^3)_L$ is dominated by the larger particle and $(r^3)_{hf}$ by the smaller particles. To

$$(r^3)_{hf} = \frac{3k_B T}{4\pi M_s H[1-(M/M_s)]_{hf}} \quad (3)$$

determine a probable particle size distribution, one assumes that each particle size follows the Langevin equation (Eq. 1) weighted by the probability density function $f(r_i)$, leading to

$$\frac{M}{M_s} = \sum L(r_i, H) f(r_i). \quad (4)$$

Following Richardson and Desai [6], a number of other groups [8-10] have assumed that most catalysts can be described by a log normal distribution given by with

$$f(r) = \frac{1}{\sqrt{2\pi r \ln \sigma}} \exp \left\{ -\left(\frac{\ln r - \ln r_o}{\sqrt{2 \ln \sigma}} \right)^2 \right\} \quad (5)$$

$$\overline{r^n} = \exp(n \ln r_o + \frac{n^2}{2} (\ln \sigma)^2) \quad (6)$$

where the parameter r_o and σ are related to the n th moment $\overline{r^n}$.

From Eq. 4 and Eqs. 2 and 3, it follows [6] that

$$(r_p)^3 = \overline{r^3} \text{ and } (r_{hf})^3 = 1/\overline{r^{-3}}$$

Determination of $(r_p)^3$ and $(r_{hf})^3$ from the M vs H data determines $\overline{r^3}$ and $\overline{r^{-3}}$. Then Eq. 6 can be used to determine r_o and σ , leading to the evaluation of $f(r)$ of Eq. 5.

An average particle size can be determined from line broadening of the Bragg peaks using the Scherrer Eq. [12].

$$2r = 0.9\lambda/B \cos \theta \quad (8)$$

where B is the extra width (in radians), λ is the x-ray wavelength and θ is the Bragg angle of the line. Usually B is calculated from [12]

$$B^2 = B_s^2 - B_o^2 \quad (9)$$

where B_o is the width of a line in a standard (like silica) near θ and B_s is the width for the sample.

EXPERIMENTAL SECTION

The sample of $\alpha\text{-Fe}_2\text{O}_3$ used in this work (labelled here as sample A) was provided by Dr. Huffman on which some Mössbauer and XAFS studies have been reported recently [7]. This sample is partially (up to about 6%) sulfated to $\alpha\text{-Fe}_2\text{O}_3/\text{SO}_4$. For XRD studies, a Rigaku/DMax diffractometer available in our laboratory was employed. For magnetic measurements, a SQUID magnetometer (Quantum Design Model MPMS) was used, employing about 10 mg of sample, temperature range of 5 K - 400 K and magnetic fields up to 55 kOe. For comparison purposes, we also report measurements on some bulk samples of $\alpha\text{-Fe}_2\text{O}_3$ (sample B).

EXPERIMENTAL RESULTS AND DISCUSSION

First we report and discuss XRD data on the $\alpha\text{-Fe}_2\text{O}_3$ samples (Fig. 1). All the major lines in Fig. 1 have been identified as due to $\alpha\text{-Fe}_2\text{O}_3$. Using $\lambda = 1.542 \text{ \AA}$ for $\text{CuK}\alpha$ radiation used in this work and line near $2\theta = 33^\circ$, we determine $r = 86 \text{ \AA}$ by using Eqs. (8) and (9). Note that Eq. (9) assumes the lineshape to be like an error function and it may be possible to determine particle size distribution by a closer examination of the lineshape in XRD. This issue will be addressed in future works.

We next consider the main component of this report viz. the magnetic studies. In Fig. 2, temperature dependence of the magnetic susceptibility χ , measured at 50 Oe, in the field-cooled (fc) and zero-field-cooled (zfc) conditions, is shown. The temperature below which the fc and zfc curves differ is usually associated with T_B (blocking temperature) which can be related to the larger particle size [3-5]. Data in Fig. 2 show that for sample A, $T_B \sim 150 \text{ K}$. The significance of T_B is that only above T_B , the sample can be superparamagnetic. From Fig. 2, we also note a weak Morin transition (T_M) near 240 K which is lower than the value for a bulk $\alpha\text{-Fe}_2\text{O}_3$ sample (Fig. 3). The significance of T_M in $\alpha\text{-Fe}_2\text{O}_3$ is that for $T > T_M$, bulk $\alpha\text{-Fe}_2\text{O}_3$ is a weak ferromagnet whereas for $T < T_M$, it is an antiferromagnet. The sharp drop in the

magnetization for bulk $\alpha\text{-Fe}_2\text{O}_3$ in Fig. 3 attests to this ferromagnetic-antiferromagnetic transition as temperature is lowered.

Since the χ vs T behavior in sample A (Fig. 2) is rather complicated, it is important to first establish the superparamagnetic region. In Fig. 4, we have plotted M vs H/T at several temperatures (30, 220, 300, 350 K). It is evident that at 220, 300 and 350 K, the criterion for superparamagnetism is obeyed. M vs H data for H up to 55 kOe were taken in the superparamagnetic region. Then with the use of Eqs. 2 to 7, the particle size distribution $f(r)$ is determined. In Fig. 5, we plot $f(r)$ vs r as histograms from the fit of the data at 220 K and 300 K. We show the two distributions obtained from the two sets of measurements at the temperatures of 220 K and 300 K in order to demonstrate how $f(r)$ is affected by changes in the M vs H fits. At 300 K, the distribution is a bit broader with most the particles between 35 and 115 Å, $r_0 = 65$ Å and $\sigma = 0.24$. The corresponding numbers for 220 K are: $r_0 = 69$ Å, $\sigma = 0.17$ and particle range 45 to 105 Å.

A self consistency check on the procedures used here can be made by calculating M/M_∞ using Eq. 4 with the results of $f(r)$ vs r from Fig. 5 a & b and comparing it with the experimental values of M/M_∞ vs H. The calculations are rather involved in that one has to calculate $L(r_i, H)$ for each r_i . We wrote a computer program to do these calculations and the results so obtained are plotted as solid lines in Fig. 6 where we have also plotted the experimental data (using $M_\infty = 2.65$ and 2.55) at 220 K and 300 K, respectively. There is excellent fit to the data at low and at high fields and some noticeable departures at intermediate fields. Note that in our experiments a complete saturation is not obtained even at 55 kOe so that this may be the source of some of the discrepancy. The other possibility for the discrepancy is that the log normal distribution may not be completely adequate to describe the sample. Additional iterations may provide some further improvements and these improvements are being looked into.

Next we compare the above results with the results obtained from XRD and from Mössbauer data [7]. The average size of 86 Å determined from line broadening in XRD is well within the range of the distribution determined above although the average value is about 20% larger than the mean of the distribution. The Mössbauer studies of Huffman et al [7] yielded the following information on particle sizes for this catalysts: 12% of the particles < 29 Å diameter, 45% of the particles have diameters from 29 Å - 85 Å and the remaining 43% have diameters larger than 85 Å. No actual distribution is available from the Mössbauer work. Overall the

average particle size determined from the Mössbauer analysis is somewhat smaller than the average determined from the magnetic studies. Considering the uncertainties in both magnetic and Mossbauer studies is about $\pm 10\text{\AA}$, the two measurements give reasonable results. Both measurements suffer from the assumption of a spherical particle in the analysis so that if the actual particles depart strongly from a sphere e.g. thin platelets, the actual uncertainties could be quite considerable.

In summary, detailed analysis of the magnetic studies have provided a particle size distribution for an $\alpha\text{-Fe}_2\text{O}_3$ based catalyst, the average of which agree reasonably well with the averages determined from XRD and Mössbauer studies. What is really needed is a test of the accuracy of these techniques on well-characterized near spherical and on non-spherical particles so as to determine the accuracies of these techniques. We are now undertaking such a study the results of which will be reported in due course.

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Fig. 1a & b: X-ray diffractograms of bulk $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{SO}_4$ (sample A) respectively. Note that all the lines are broader for sample A indicating that the particle size is very small.

Fig. 2: Variation of χ with T. Above T_B , χ for ZFC and FC conditions merge.

Fig. 3: Morin transition in bulk Fe_2O_3

Fig. 4: Super position of M vs H/T data at different T's.

Fig 5 a&b: Particle size distribution obtained from data at 220K and 300K respectively.

Fig 6 a &b: Calculated and experimental values of M/M_∞ at 220K and 300K respectively.

Project II.4 ENDOR Investigations of Coal Liquefaction Under Mild Conditions

(Naresh Dalal and Jeffrey P. DeLooze)

INTRODUCTION

In order to understand the accomplishments for this subtask in terms of both the proposed work schedule and actual accomplishments, the following introductory statements are referenced in terms of specific quarters. Following our proposed plan of research for the first quarter, we have completed our electron nuclear double resonance (ENDOR) measurements on the Illinois #6 coal as a function of mild heating (25° - 250°C) in the presence of ZnCl_2 . The objective of this undertaking was to obtain chemical-structural data which would be helpful in elucidating the chemical mechanism of the catalytic conversion of coal by Lewis acid-type catalysts, such as ZnCl_2 . Zinc chloride and Illinois #6 were selected as the model systems for study because ongoing research by other workers (notably, M. Seehra, J. Shabtai, and L. Anderson) at universities involved in the Consortium for Fossil Fuel Liquefaction Science (CFFLS) Program has indicated that ZnCl_2 leads to a significant enhancement in the breakdown of the coal polymer matrix at about 200°C, a range of temperature that was much lower than the temperatures needed to achieve the same effect in the coals under consideration without the catalyst. In particular, Seehra and coworkers have demonstrated that in general coals heated to approximately 200°C in the presence of Lewis acid catalysts, such as ZnCl_2 , exhibit a rate of free radical formation much higher than without the catalyst. Since the extent of free radical formation provides a good measure of coal conversion efficiency, it is of fundamental importance to elucidate the chemical structure of the free radicals formed in the catalytic reactions around 200°C. Specifically, our goal was to find if this enhanced radical generation apparently caused by ZnCl_2 (around 200°C) results from the increase in the formation of the same radical species which were known to be present in the unheated samples, or did the catalytic reaction generate a new type of free radical.

We utilized the ENDOR technique for this purpose because earlier studies had suggested that the resolution available with EPR spectroscopy, the standard method for identifying and characterizing free radical species, was insufficient. On the other hand, through our earlier CFFLS report, we have shown that the ENDOR methodology provides about a factor of 100

higher resolution than that possible with EPR. We thus undertook systematic ENDOR measurements of the temperature dependence of the ZnCl_2 -catalyzed free radical formation upon heating of Illinois #6 coal.

Following our work schedule and plan established for the second quarter, we continued on our investigation of the role of free radicals in the superacid-catalyzed electron transfer reactions of aromatic compounds which was initiated at the closure of the last quarter. The compounds selected were substituted, resonance-stabilized, aromatic species that are generally considered as good models for the organic moieties in coal. These materials are currently being investigated by other Consortium members, most notably Irving Wender. The objective of this subtask was to answer the following questions:

1. Are free radicals generated in triflic-acid catalyzed electron-transfer reactions of aromatic compounds?
2. Does oxygen play any significant role in the free radicals generation, if, in fact, such radicals are produced?
3. Can the ESR spectra obtained from the model compounds be combined/manipulated to simulate coal-like spectra? If so, what are the approximate ratios needed to produce these spectra?

To our knowledge, these results constituted the first direct evidence for the role of free radicals in acid-catalyzed reactions of coal-model compounds. It was also found that the radical formation did not significantly depend on the presence of molecular oxygen, since the observed ESR spectra were not affected when the reactions were carried out under anaerobic conditions¹.

As per our schedule, for the third quarter our goals were:

1. To utilize ENDOR spectroscopy for identifying the charge on the radicals, *i.e.*, whether the radicals are neutral, anionic or cationic species. The charge information was to be obtained via measurements of proton hyperfine splittings, and hence, the unpaired electron spin density distribution, as measured by ENDOR spectroscopy. For example, for a given molecule, the cations exhibit typically 15-20% larger spin densities as compared to the anions, with the neutral species exhibiting an average behavior. Such differences are easily measurable via ENDOR spectroscopy.¹
2. To employ computer modeling techniques to simulate the ESR signal observed from coal. As discussed in previous reports and at the last CFFLS technical Meeting, the objective of this undertaking is to ascertain the presence of certain specific compounds in the coal structure; these will be the molecules whose radicals add up to reproduce the signal from the radicals present ubiquitously in coal.

In the final quarter of the year, we undertook initial examinations of iron-based catalysts mixed with various clays and coals as provided by the University of Utah. This undertaking was begun in the understanding that iron-based catalysts are and will continue to be important in the field of fossil fuel liquefaction.

EXPERIMENTAL

The Illinois #6 coal was obtained from Dr. Robert W. Clarkson of the University of Illinois, Urbana-Champaign. The coal was crushed in a dry, inert atmosphere to about 100 micron size and loaded into 5 mm (o.d.) EPR/ENDOR sample tubes, especially designed and fabricated by and within this research initiative, for gas exchange of evacuation (10^{-6} torr). Zinc chloride was dried under inert atmosphere and ground to 100 micron size in a dry nitrogen atmosphere because it is an extremely hygroscopic material. The amount of ZnCl_2 mixed with each coal sample catalyzed was 1:1 w/w, as done by other CFFLS workers (notably, Seehra). As a control, an identical amount of coal corresponding to the weight of coal in each catalyzed sample was identically prepared and treated. The ENDOR measurements were made with a Bruker ER-200-D EPR/ENDOR spectrometer system. The ENDOR insert dewar which permitted variable temperature ENDOR studies at high temperatures was of our own design, as described by us in previous CFFLS reports concerning this subtask. Temperature was controlled by a Bruker VT-4111 nitrogen gas flow system, which allowed temperature steps of 1°C . Other spectrometer variables, found via previous ENDOR investigations on Illinois #6 coal outlined in reports from previous years, were again used to: (1) yield optimum ENDOR response, and (2) provide consistency between data treatments of previous investigations. As a result, they will not be reproduced herein.

Table 1 lists the model compounds studied as well as a summary of the unprocessed ESR data. All ESR measurements were made with a Bruker ER-200-D ESR spectrometer system. A special ESR sample cell was designed and constructed to enable the investigation of the role of oxygen in the radical generation process. The sample holder was specially designed to enable in-situ evacuation to 10^{-4} torr, or to pressurize with helium or any other gas at a known pressure and temperature. Oxygen was first removed by freeze-thaw methodology utilizing an Edwards High Vacuum EM-2 packaged pumping system to 10^{-8} torr, and the sample tubes were either kept evacuated or back-filled with argon to atmospheric pressure (two independent trials for each sample). Temperature was controlled by a Bruker VT-4111 nitrogen gas flow system, which

allowed temperature steps of 1°C. All simulations were carried out using an ASPECT-2000 microcomputer and laboratory-developed ESR lineshape simulation programs.

In the fourth quarter, due to equipment difficulties, we utilized a Varian E-3 spectrometer available in the teaching laboratory. Even though it could not perform the in-depth analysis of the Bruker system, it was adequate for the cursory initial investigations on a number of systems. For data collection and analysis of the more interesting systems, we "purchased" time on the research instrument of Dr. Larry Halliburton in the Department of Physics.

Compound	Formula	ESR Sig.	Strength	Hyperfine Structure	Line Width
2-methylnaphthalene	C ₁₁ H ₁₀	Yes	Strong	None	2.24
anthracene	C ₁₄ H ₁₀	Yes	Very weak	None	12.6
naphthalene	C ₁₀ H ₈	Yes	Weak	None	14.7
anthracene, 9-COOH	C ₁₅ H ₁₀ O ₂	Yes	Very weak	None	13.5
dibenzothiophene	C ₁₀ H ₆ S	Yes	Medium	None	6.84
phenanthrene	C ₁₄ H ₁₀	Yes	Medium	None	7.10
7,8-benzoquinoline	C ₁₃ H ₉ N	Yes	Strong	Yes, 23 lines	0.7
1,3-dihydroxynaphthalene	C ₁₀ H ₈ O ₂	Yes	Medium	None	4.2
1-naphthol	C ₁₀ H ₈ O	Yes	Med.-Str.	Yes, 15 lines	0.9
anthraquinone	C ₁₄ H ₈ O ₂	No	NA	NA	NA
benzoin	C ₁₄ H ₁₂ O ₂	Yes	V. Strong	None	5.04
2-methyl,1-nitronaphthalene	C ₁₁ H ₉ NO ₂	Yes	Weak	None	5.4
naphthoic acid	C ₁₁ H ₈ O ₂	Yes	Very Weak	None	6.51
anthranilic acid	C ₈ H ₇ NO ₂	No	NA	NA	NA
anthrone	C ₁₄ H ₁₀ O	Yes	Very Strong	Yes, 20 lines	0.5
phenanthraquinone	C ₁₄ H ₈ O ₂	Yes	Med.-Str.	Yes, 14 lines	0.4
trifluoromethanesulfonic acid	CF ₃ SO ₃ H	No	NA	NA	NA

Table 1: Listing of model compounds investigated during the second quarter.

RESULTS AND DISCUSSION

Figure 1 shows a sample of the ENDOR spectra obtained from the Illinois #6 coal that had been heated to 200°C while being continuously evacuated to 10⁻⁵ torr, following the procedure described by Seehra. Figure 1(a) depicts the spectra of the control samples (heated under evacuation without ZnCl₂), while Figure 1(b) shows the corresponding spectra from an identical coal sample heated under evacuation but in the presence of 1:1 w/w ZnCl₂. From a detailed computer-based analysis, we have determined that the ENDOR spectra in Figure 1(a) and Figure 1(b) are essentially identical in line shape as well as positions (ENDOR transition frequencies). However, the spectra for the ZnCl₂-treated samples, Figure 1(b), were weaker by about a factor of three, which is quite consistent with the increase in the overall radical content, essentially as reported by Seehra.

ENDOR Spectra as a Function of Temperature and ZnCl_2 Presence

Figure 1: ENDOR spectra as a function of temperature for evacuated Illinois #6 coal, (a) without ZnCl_2 , (b) with 1:1 w/w of ZnCl_2 .

In conclusion, our EPR results confirm Seehra's finding that ZnCl_2 causes an increase in the radical concentrations at much lower temperatures than in the absence of ZnCl_2 . The ENDOR results now show that the catalytic effect of ZnCl_2 does not involve the formation of any new types of free radical, but more of the same radical specie(s) that were present in the coal before heating.

Figure 2a -2c shows a set of respective ESR spectra obtained *in vacuo* from the model compounds. Figure 2a is the free radical spectrum obtained from benzoin ($\text{C}_{14}\text{H}_{12}\text{O}_2$) at room temperature; figure 2b is the free radical spectrum obtained from 2-methylnaphthalene ($\text{C}_{11}\text{H}_{10}$) at room temperature; and figure 2c is the free radical spectrum obtained from methylnaphthalene (C_{10}H_8). It can be noted from the spectra that each

Figure 2: ESR spectra of superacid catalyzed (a) benzoin, (b) 2-methylnaphthalene, and (c) naphthalene at 10^{-7} torr and 300 K.

individual model compound has an individual linewidth. These differing linewidths may be obtained from Table 1. These results provide unequivocal evidence that free radical species are generated in triflic acid catalyzed breakdown of model organic compounds. Figure 3 shows spectra of the model compound anthrone ($C_{14}H_{10}O$) as a function of atmospheric pressure. Figure 3a was obtained at 300K and 760 torr, while figure 3b was obtained at 300K and 1×10^{-7} torr. As can be seen, Figure 3 clearly shows that free radicals are, indeed, generated in the presence of oxygen. The effect of oxygen removal is simply to improve the resolution of the ESR spectrum obtained.

Figure 3: ESR spectra of superacid catalyzed radical from anthrone as a function of atmospheric pressure: (a) 760 torr and (b) 1×10^{-7} torr.

Figure 4 shows a typical ESR spectrum of Illinois #6 coal. The signal lineshape is a composite of at least one sharp and one broad peaks. As discussed in detail by Retcofsky², the presence of two peaks implies that this coal sample consists of at least two types of compounds the sharper component representing the highly aromatic, ring-condensed (fusinite) fraction whereas the broader component arises from the less-condensed fraction. Also included in Figure 4 are the ESR spectra from the three compounds (naphthalene, benzoin, and 2-methylnaphthalene) whose superposition yielded the best simulation of the coal spectrum. Other combinations of compounds utilized for this simulation were the 17 compounds listed in Table 1.

Figure 4: Experimentally-observed and computer simulated ESR spectra of Illinois #6 Coal.

In house ENDOR measurements could not be performed during the end of the third and all of the fourth quarter because of the breakdown of our data acquisition and processing accessories, which are required to perform ENDOR spectroscopy. It is expected that the ENDOR instrumentation will be operational during the first week of the new funding year at which time we plan to complete the ENDOR measurements on the organic compounds.

During the fourth quarter of the year, even though we could not perform in-house data acquisition and analysis, we utilized the teaching grade instrument present in the Department of Chemistry as well as the research grade instrument in the laboratory of Dr. Larry Halliburton of the Department of Physics to analyze iron-containing moieties which were received from the University of Utah. Our conclusions concerning these samples, later confirmed by discussions with Gerald Huffman concerning his Mossbauer spectroscopy results, is that the iron catalysts are coordinating with a carboxylate-containing moiety of the coal polymer matrix. Further, we see evidence of the formation of clusters containing super-paramagnetic iron species. At this point, however, we cannot elucidate more information without a more detailed analysis. We shall undertake the analyses of both the ENDOR data from the organic model compounds and the EPR/ENDOR data from the iron-containing catalyst mixtures in the initial quarters of the new funding year.

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Project II.5 Catalytic Dehydrogenation of Model Compounds in Relation to Direct Coal Liquefaction (I. Wender and J.W. Tierney)

INTRODUCTION

It is generally assumed that coals and liquids derived from coal contain varying amounts of hydroaromatic hydrogen. The determination of this so-called hydroaromatic hydrogen is important for several reasons: (a) the source of donatable hydrogen in recycle solvents is critical in the direct liquefaction of coal, (b) coals contain hydrogen atoms that are involved in intra and interchange as well as hydrogen transfer not only from hydroaromatics but from aromatic entities; in other words, hydrogen atoms in coals are quite labile, (c) knowledge of the nature of hydroaromatic and transferable hydrogen, which differs with rank of coal, will be of great help in elucidation of the structure of coal and the nature of the reactions in coal liquefaction and (d) it has been claimed that a catalyst which gives a higher hydrogen yield in dehydrogenation also shows higher activity in coal liquefaction.

The objectives in this work are to study the catalytic dehydrogenation of model compounds so as to obtain a better understanding of coal constitution and to learn more of the manner in which coal hydrogen takes part in the liquefaction process.

BACKGROUND

Catalytic dehydrogenation of a series of coals was carried out by Reggel et al.¹⁻² to study coal structure and the yield of hydrogen. The highest hydrogen yield was obtained using phenanthridine as the solvent, Pd as the catalyst and CaCO₃ as the support. Dehydrogenation reactions were carried out at the boiling point of the solvent since vigorous boiling provides agitation and nucleation for the hydrogen atoms. The rates of hydrogen evolution were not measured in any of the experiments. The possibility of side reactions was expressed, though their contributions were said to be negligible. Reggel et al. extended their study to catalytic dehydrogenation of a number of different coals (Figure 1). The flaw in their work is very likely the assumption that the gaseous hydrogen evolved came only from hydroaromatic entities.

Considering the complex nature of coal and the high reactivity and lability of hydrogen in coal, this assumption is highly unlikely. An objective of the present work is to use model compounds in catalytic dehydrogenation to determine the source and nature of evolved hydrogen.

In a review by Neuworth³, catalytic dehydrogenation was discussed as a potential method for estimating the hydrogen donor capability of various substances involved in coal liquefaction. It was pointed out that few efforts had been directed towards finding optimum temperatures or reaction times for dehydrogenation. Palladium and platinum, used as finely divided metals on a support, are considered the most satisfactory catalysts for catalytic dehydrogenation.

In a study conducted by Heredy et al.⁴, catalytic dehydrogenation with Pd/CaCO₃ was investigated for determining the hydroaromatic content of coal, process solvents, and coal extract fractions. They stated that condensation reactions of phenanthridine might lead to erroneous results. They decided to use quinoline as the vehicle but found that this solvent dimerized during dehydrogenation, giving unusually high rates of hydrogen evolution.

Recycle solvents were dehydrogenated in a study by Finseth in the absence of a vehicle⁵. Coal-derived pyrite and Pd/BaCO₃ (found to be better catalyst than pyrite) were used as dehydrogenation catalysts. Pyrite is not a good hydrogenation catalyst and hence it is not expected to be a good catalyst for dehydrogenation. Curtis et. al.⁶ studied the contribution of transferable hydrogen to coal conversion in liquefaction. Coal liquefaction was carried out in the presence of solvents such as creosote oils and recycle solvents. Catalytic dehydrogenation was again carried out with Pd/CaCO₃ and phenanthridine. The results showed that higher amounts of transferable hydrogen in the solvent gave higher coal conversion yields.

It is expected that, akin to the principle of microreversibility, a dehydrogenation catalyst should be a hydrogenation catalyst and vice versa. Catalytic dehydrogenation is carried out at atmospheric pressure while coal liquefaction requires high pressures. Yokono et al.⁷ studied the catalytic dehydrogenation of coal as a rapid measure of catalyst activity for coal hydrocracking. Dehydrogenation of tetralin and decalin was carried out by Dziewiecki et al.⁸ using Ni-Mo catalysts. Hydrogen yields from these dehydrogenations were compared with the activities of catalysts in the hydrogenation of coal extract solutions. From their results, it was concluded that a catalyst with better activity for dehydrogenation also gave higher conversions for the liquefaction of coal.

These results indicate that dehydrogenation experiments may be useful for determining

the activity of coal liquefaction catalysts. Dehydrogenation experiments can be carried out on very small amounts of substrate (<0.1g) in a short time with comparatively simple equipment. Experiments are performed at atmospheric pressure and analysis of the products is relatively easy. The method gives a direct measure of hydrogen evolved; analysis of the residue (especially when using model compounds) reveals the nature of the dehydrogenated product. Indirect methods (evolved H_2 is not measured) of determining results of catalytic dehydrogenation are not as effective. Spectra are too diffuse and require many assumptions in regard to sample composition and response factors.

RESULTS AND DISCUSSION

Dehydrogenation reactions were carried out using different solvents to investigate the role of the vehicle in catalytic dehydrogenation. To determine the effect of the reduction potential of the vehicle in dehydrogenation, several solvents with varying reduction potentials were used for dehydrogenation of 9,10-dihydroanthracene (DHA) with $Pd/CaCO_3$ as catalyst. A solvent with a lower reduction potential should accept an electron more easily⁹. Blank runs of the vehicles and the catalyst were carried out. The following vehicles were used in this investigation: phenanthridine, phenanthrene, fluoranthene, pyrene and acridine.

All the experiments were carried out at the boiling point of the vehicle used. The amount of hydrogen evolved in a blank run was normally very small (1-3 cc). Gas samples were taken at regular intervals during the runs. Hydrogen was the main component of the evolved gases; small quantities of CO_2 and H_2O were also present. The final yield of hydrogen evolved is calculated from the amount of hydrogen evolved from the model compound after subtraction of hydrogen evolved in blank runs. The yield is reported as the percentage of theoretical available hydrogen in the model compound.

Reduction potentials of several vehicles are plotted against the hydrogen yield in Figure 2. The lower the reduction potential of the vehicle, the higher is the hydrogen yield. Use of phenanthridine as the vehicle results in a high yield (93.3%) of hydrogen from DHA. The blank reaction with phenanthridine gave a hydrogen yield of 0.8 cc of hydrogen, indicating that condensation reactions do not contribute significantly. We have found phenanthridine, fluoranthene and pyrene to be particularly useful solvents for the catalytic dehydrogenation of model compounds.

The yield from DHA was 92% with pyrene (b.p. 393°C) as the solvent, approximately the same as that obtained using phenanthridine (b.p. 350°C). Use of the aromatic hydrocarbon, fluoranthene (b.p. 375°C) as the vehicle gave 88.5% of the theoretical hydrogen yield from DHA. The high yields of hydrogen with fluoranthene and pyrene are significant because neither contains nitrogen. Nitrogen-containing polynuclears are generally better solvents and have lower reduction potentials than polynuclear aromatic hydrocarbons.

Acridine (b.p. 346°C) is a nitrogen-containing polynuclear molecule which has a very low reduction potential (-1.04V). Not unexpectedly, the yield of hydrogen from DHA was very high (160%) when acridine was used as the vehicle. However, when the considerable amount of evolved hydrogen (22.8 cc) in the blank (no DHA) was taken into account, the yield of hydrogen from the catalytic dehydrogenation of DHA was 98.9 percent. Residues from the blank and the experiment using DHA had a significant black appearance, suggesting that a considerable amount of condensation reactions had taken place during dehydrogenation with acridine.

In almost all experiments, most of the hydrogen evolution occurred in the first 5-15 minutes of the catalytic dehydrogenation reaction. We speculate that this sudden surge in hydrogen may be due to multiple reaction pathways leading to dehydrogenation. During the first phase, hydroaromatic hydrogens are likely removed; the later phase may involve other more complex reactions. Rate curves of hydrogen evolution for dehydrogenation of DHA with three different vehicles and Pd/CaCO₃ are given in Figure 3.

Several other model compounds were dehydrogenated. The hydrogen yields from 9,10 - dihydrophenanthrene (DHP) (with phenanthridine and Pd/(CaCO₃)) were similar to those obtained with DHA; both are known as good hydrogen donors. 1,2,3,4,5,6,7,8 - octahydroanthracene, OHA, and 1,4,5,8,9,10-hexahydroanthracene, HHA, shown in Figure 4, were dehydrogenated using several vehicles. Yields are reported on the basis of theoretical available hydrogen. The hydrogen yields with HHA and OHA were unexpectedly low compared to those with DHA and DHP. For example, OHA (amount of available hydrogen four times that of DHA) was dehydrogenated (with phenanthridine and Pd/CaCO₃) to give only 25.2% of the theoretical yield. These results imply that these compounds may be poor hydrogen donors in coal liquefaction (but see below). The rates of hydrogen evolution, (using Pd/CaCO₃ in phenanthridine) from these compounds, along with hydrogen yields from DHA and DHP, are shown in Figure 5.

The surface area of 5% Pd on carbon is 1000 m²/g as compared to 25 m²/g of 5% Pd on

CaCO_3 ; we might expect a more rapid reaction with Pd/C as catalyst. It is necessary to reduce the Pd/C catalyst with hydrogen before its use in catalytic dehydrogenation. The hydrogen yield in both these cases was the same (93.3% with Pd/ CaCO_3 and 93.5% with Pd/C) but the rate of hydrogen evolution with Pd/C is slightly higher than that with Pd/ CaCO_3 . OHA was dehydrogenated using Pd/C with phenanthridine as the vehicle; the hydrogen yield obtained in this dehydrogenation was 89.3% of theoretical. This is much larger than the 25.2% obtained when OHA was dehydrogenated with phenanthridine using Pd/ CaCO_3 . An analysis of the residue from OHA using the two catalysts has not as yet been made.

Reaction products after dehydrogenation were analyzed using GC-MS. Surprisingly, the dehydrogenation of DHA yielded small amounts of 1,2,3,4-tetrahydroanthracene (THA) in the residue. The structure of THA is similar to that of tetralin and tetralin is a good hydrogen donor. The formation of THA and its continued presence after 5 hrs of reaction is therefore unexpected. THA has been formed by complexation of anthracene with catalysts such as zerovalent Rh and Ru^{10} ; its formation with Pd, which is also in the zerovalent state, may be explained by formation of a similar complex.

More recently, we tested the efficiency of $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, a good coal liquefaction catalyst, for the catalytic dehydrogenation of DHA. We were surprised to find that no hydrogen was evolved using this catalyst. However, analysis of the residue showed that the DHA had been quantitatively dehydrogenated to anthracene. Evidently a stoichiometric oxidative dehydrogenation of DHA had taken place with the oxygen derived from the added $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$. The hydrogen was removed as water and part of the Fe_2O_3 was reduced to Fe_3O_4 . Dehydrogenation is equivalent to an oxidation.

CONCLUSIONS

Some preliminary conclusions follow. The relationship between the reduction potential of the vehicle and the hydrogen yield in catalytic dehydrogenation has been established. The lower the reduction potential of the vehicle, the higher is the hydrogen yield. The rate of hydrogen evolution in catalytic dehydrogenation varies with the nature of the vehicle. Phenanthridine, fluoranthene and pyrene were found to be good vehicles. Side reactions with these compounds were insignificant. The catalyst affects both the rate of hydrogen evolution and the hydrogen yield in catalytic dehydrogenation. Pd/C, with a large surface area, is a very good

catalyst for catalytic dehydrogenation. Analysis of the reaction products indicated that the dehydrogenation of hydroaromatic compounds takes place through a number of pathways.

FUTURE WORK

The concepts derived from this project have grown since its inception. It provides a novel approach to the large number of investigations of coal liquefaction, promising to provide insights into the mechanisms of reactions involving catalysts, coal and hydrogen. Yet to be explored in "catalytic dehydrogenation" are the effects of the usual coal liquefaction catalysts such as ZnCl_2 , SnCl_2 , MoS_2 , Fe_2O_3 and $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$. We are investigating the catalytic dehydrogenation of Wilsonville recycle oils and using these oils as vehicles in the dehydrogenation of model compounds.

There is little doubt that some hydrogen evolved during catalytic dehydrogenation is derived from cyclodehydrogenation reactions such as the conversion of o-terphenyl to a benzphenanthrene. We will investigate this type of reaction. We will allow a dehydrogenated sample of a model compound (9,10-DHA, 9,10 DHP, etc) to be exposed to deuterium (D_2) gas at room temperature immediately after catalytic dehydrogenation and then observe which, if any, carbon atoms pick up deuterium. We will add phenols to our model compounds to determine their effects on rates of catalytic dehydrogenation. It is possible that catalytic dehydrogenation proceeds through a radical cation mechanism and we will endeavor to determine the pathway such an intermediate involves.

The dehydrogenation apparatus is now automated and interfaced to an IBM PC/XT using a DT 2806 mother board. This will improve data collection and allow more rapid progress in dehydrogenation studies.

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Figure 1. Dehydrogenation of coals using phenanthridine solvent and Pd/CaCO_3 catalyst².

REDUCTION POTENTIAL

VS

HYDROGEN EVOLUTION

(as % of theoretical yield)

9-10 DHA Pd/CaCO₃

5 hr run

DEHYDROGENATION PLOTS

9-10 DHA Pd/CaCO₃

Figure 3. Kinetic plots for dehydrogenation of 9,10-DHA using Pd/CaCO₃ catalyst.

1,2,3,4,5,6,7,8-
Octahydroanthracene

1,4,5,8,9,10-
Hexahydroanthracene.

Phenanthridine

1,2,3,4-
Tetrahydroanthracene

Figure 4. Structures of some model compounds and the vehicle phenanthridine.

Figure 5. Kinetic plots for dehydrogenation of different model compounds over Pd/CaCO₃ catalyst.

Project II.6 Surface Characterization of Catalyst Added Coal Samples (P. J. Reucroft and J. Y. Kim)

INTRODUCTION

The highly dispersed forms of certain catalysts are believed to be very active in the conversion of coal to liquids via direct liquefaction.[1-3] A catalyst with a higher specific surface area and fine particulate size can be utilized at small concentrations to achieve better performance in terms of overall coal conversion and selectivity to lighter products (oils) in direct coal liquefaction.[4]

X-ray photoelectron spectroscopy (XPS) has been used to study the surface characteristics of six catalysts and a catalyst impregnated Illinois #6 coal. This technique provides the surface elemental distribution and chemical information about the outermost 3-4 nm of the exposed solid surface. This preliminary characterization has shown that the concentration of elements at the outermost layer measured by XPS is representative of that in the bulk by chemical analysis.

XPS was also employed to determine the oxidation states of Fe, Mo, and Sn in catalyst samples. Each element showed the expected values for the most stable oxidation states. To obtain the chemical environment of oxygen, peak synthesis was carried out. The results showed that Fe_2O_3 and XSO_4 accounts for the total oxygen signal in catalyst IV.

1. Experimental

Six catalysts and catalyst ($\text{FeOOH}/\text{SO}_4^{2-}$) impregnated Illinois #6 coal were used in the surface characterization studies. These samples were obtained from Vivek R. Pradham and the sample lists are shown in Table 1. The powdered samples were examined in their as-received form and their particle sizes were less than -100 mesh.

The powdered samples were mounted on the spectrometer probe tip by means of double-sided adhesive Scotch insulating tape. The samples were pressed with the aid of a metal spatula and the excess that had not adhered was tapped off. To exclude the possibility of recording contaminants associated with the tape, the tape was also analyzed separately. It was found that the constituents of tape were not detected by XPS, and that the photoionization signals are characteristic of the coal samples alone.

The samples were examined by XPS on a Kratos XSAM 800 spectrometer using Mg K

alpha (1253.6 eV) radiation. The spectrometer was run in fixed retarding ratio (FRR) mode at a pass energy of 13 KV and 15 mA. Under these conditions, the full width at half maximum (FWHM) of the Ag (3d_{5/2}) peak is ≈ 1.1 eV). Spectra were recorded at $< 5 \times 10^{-7}$ torr.

Radiation damage to the sample from long-term exposure to the X-ray beam was not observed. All binding energies were referred to carbon (1s) at 285 eV to compensate for sample charging. Elemental concentrations were obtained from peak area and corrected for atomic sensitivity factors.

The peak was deconvoluted using a peak synthesis procedure which employed a Gaussian line shape at fixed binding energies determined from model compound studies.[5] The data system permitted the intensity of the components and their FWHM to be varied in order to obtain the best fit between the experimental and the synthesized spectrum.

RESULTS AND DISCUSSION

2.1 Surface Compositions

Representative XPS wide-scan spectra for catalysts I and III are shown in Figure 1. The spectra show a distinct peak for major elements, oxygen, iron, and tin, as well as the minor component, sulfur, in each catalyst sample. The C 1s peak was observed in all catalysts and this can be ascribed to carbon contamination. Cl 2p was only observed in the tin oxide catalyst (III). This could be associated with the fact that chlorine was introduced as SnCl₄/5H₂O in the starting materials that were used for the preparation of the tin oxide. This excess chlorine was left at the surface after sample preparation.

To determine the oxidation states of the Fe, Mo, and Sn, narrow survey scans were carried out. The binding energies of the Fe 2p, Mo 3d and Sn 3d levels showed the expected values for the most stable oxidation states of these elements. Multiple splitting was observed in the transition elements, such as Fe and Mo. Figures 2 & 3 show the results for Fe 2p and Mo 3d, respectively. This is the result of spin interaction between an unpaired electron from the photoionization process and other unpaired electrons present in the system. The point of real interest is that the separation between the two peaks varies depending upon the environment of the atom concerned. In Fig. 2, the Fe 2p peak shows the 13.6 ± 0.05 eV splitting between the 2p (1/2) and 2p (3/2) peaks. This was observed in all tin oxide containing catalysts. The

observed splitting corresponds well with the Fe 2p peaks of Fe_2O_3 and FeOOH (Goethite) in model compound studies (5). The Fe compound can thus be ascribed to either Fe_2O_3 or FeOOH .

Mo 3d showed the 3.2 eV splitting between the 3d (3/2) and 3d (5/2) peaks in the catalyst II, IV, and V samples. Molybdate (MoO_4^{2-}) was used as a starting material in the preparation of these catalysts. This anion is readily oxidized at the surface and produces the stable oxidation state MoO_3 at the catalyst surface. Sn 3d also showed the multiple splitting of 8.45 eV. This can be ascribed to SnO_2 and is shown in Figure 4. O 1s signals are shown in Figure 5. These peaks were deconvoluted using a peak synthesis procedure which employed Gaussian shaped peaks at binding energies of 530.7 eV (for Fe_2O_3), 532.1 eV (for SO_4^{2-}), and 531.9 eV (for MoO_3). Estimation of the concentrations of these components by peak synthesis gave the following relative proportions: 47.4:41.0:11.9, respectively. The results thus show that approximately 90% of the oxygen peak exists in the form of sulfate and iron oxide. Peak synthesis results are shown in Figure 6.

Emphasis has been focused on the S 2p peaks of raw coal samples in earlier reports (6). It has been shown that the S 2p peak always displays two photolines with a separation of 5.6 eV in raw coal samples. However, the XPS spectrum of S 2p in the catalyst samples showed only one S 2p peak at 168.8 eV, corresponding to SO_4^{2-} . This result is shown in Figure 7 where a catalyst spectrum is compared with that of catalyst impregnated coal. In the upper spectrum, the peak at 164 eV can be ascribed to sulfide in the coal.

From the above results, it appears that XPS can be used to obtain useful analytical information about the surface chemistry of catalyst samples and catalyst impregnated coal samples.

2.2. Quantitative Analysis

Determination of the relative concentrations of the various constituents in the surface of a material is an important application of XPS. To obtain the quantitative analysis of the samples, peak area sensitivity factors have been used. Quantitative analysis results are shown in Table 2. Iron and oxygen are the major components of the iron oxide catalysts, while tin is the major component of the tin oxide catalysts. Sulfur concentrations are variable through catalysts I, II, and III, ranging from 4.5 to 6.9 wt %. Sulfur concentrations are reduced, however, in the tin oxide containing catalysts (catalysts III & VI). Mo is also present in the surface with average values of 6.5 wt% in the iron oxide catalysts. This value increase by a factor of 4 with the absence of sulfate (catalyst VI).

A comparison between the wide scan spectra of the raw Ill. #6 coal and the catalyst (FeOOH/SO₄²⁻) impregnated Ill. #6 coal is shown in Figure 8. The spectra show the presence of carbon, oxygen, aluminum, silicon and small peaks of nitrogen and sulfur. The catalyst impregnated coal sample shows distinct Fe 2p peaks in the 700-730 eV region. From this it can be assumed that Fe is well distributed (as Fe₂O₃ or FeOOH) throughout the coal surface region.

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Table 1. Summary of Materials

Catalyst	Symbol	Elemental Analysis
FeOOH/ SO_4^{2-}	I	3.0 wt% Sulfur
Mo/FeOOH/ SO_4^{2-}	II	1.0 wt% Mo and 2.0 wt% Sulfur
FeOOH/SnO(OH) ₂ / SO_4^{2-}	III	
Mo/ Fe_2O_3 / SO_4^{2-}	IV	0.5 wt% Mo and 1.3 wt% Sulfur
Fe_2O_3 / MoO_4^{2-}	V	2.0 wt% Mo
SnO ₂ / SO_4^{2-}	VI	
FeOOH/ SO_4^{2-} on Ill. #6		10.0 wt% Fe and 2.0 wt% Sulfur

Table 2. XPS Analysis (wt %)

Catalyst	Fe	O	S	Mo	Sn
I	40.79	52.24	6.97		
II	40.43	48.65	4.51	6.40	
III	27.09	30.55	0.46		41.89
IV	40.71	46.22	6.34	6.74	
V	34.69	39.97		25.94	
VI		19.07	2.05		78.88

FeOOH/ SO_4^{2-} on Ill. #6 --- C: 43.46, O: 38.54, Fe: 6.67, S:1.87, Al: 3.48, Si: 3.97

Raw coal (Illinois #6) --- C: 66.58, O: 22.53, S: 1.52, Al: 3.99, Si: 4.3

Figure 1 Typical XPS wide scan spectra for Catalyst I and III

Figure 2. Typical XPS Fe 2p spectra for Catalyst I and IV

Figure 3. Typical XPS Mo 3d spectra for Catalyst IV and V

Figure 4. Typical XPS Sn 3d spectra for Catalyst III and VI

Figure 5. XPS spectra for O 1s for Catalyst IV and V

Start eV: 538.20
End eV: 528.00

Fit: 1.3

100% Intensity: 102720
100% Area: 2604621

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS 0 I		530.7	76.0	1.5	47.4
GAUSS 0 II		532.1	30.0	3.3	41.0
GAUSS 0 III		531.9	16.0	1.8	11.9

Figure 6. XPS O 1s spectrum deconvoluted into Gaussian components for Catalyst IV

Figure 7. XPS S 2p spectra for Catalyst I and Catalyst impregnated Coal

Figure 8. Comparisons of XPS wide scan spectra for Catalyst I with Catalyst Impregnated Illinois #6.

Project II.7 Computational Chemistry of Model Compounds and Molecular Fragments of Relevance to Coal Liquefaction (K.R. Subbaswamy)

During the past contract year the following investigations were completed:

1. A comparative study of bond dissociation calculations, in the presence and absence of a catalyst, for a model compound using three semi-empirical quantum chemical methods;
2. Calculations of the heats of reaction for the hydrogenation of a model compound in the presence and absence of a catalyst. The first has been accepted for publication in the Journal of Physical Chemistry. The second has been published in Fuels Preprints of the Division of Fuels Chemistry of the American Chemical Society, Atlanta Meeting, April, 1991. Both of these projects were undertaken in conjunction with the experimental work of Dr. Malvina Farcasiu and her collaborators. Some PY-MS data from the laboratory of Dr. Henk Meuzelaar were also utilized.

In addition, several other investigations have been initiated, and are at various stages of completion:

3. Theoretical investigation of the effect of an electron-removing catalyst on bond cleavage in a series of model compounds. These compounds, containing various combinations of fused rings, ethylene and methylene linkages, have recently been studied by Dr. Farcasiu and her collaborators and show very interesting trends with regard to catalytic selectivity. Our objective is to identify or develop semi-empirical methods that reproduce the experimental results, and can hence be used to predict reaction pathways and mechanisms in direct coal liquefaction.
4. Development of first-principles, finite temperature molecular dynamics method suitable for application to large, complex systems such as coal fragments and model compounds. We have almost completed the formulation of a tight-binding (analogous to extended Hueckel) method that can handle large systems, and are trying it out on simpler systems such as diamond, graphite, and the fullerenes.
5. Exploration of methods for the study of the surface electronic structure of Fe-S alloy series, with a view towards their catalytic properties for coal liquefaction.

The two projects completed during the year are summarized below:

1. Comparative Study of Bond Dissociation Energy Calculations for Model Compounds. Since bond dissociation energy calculations for large molecules are not very common, a

comparative study of the common semi-empirical methods is of value in assessing the range of applicability for the methods and parameters used. This work has now been accepted for publication by the Journal of Physical Chemistry.

In this study we have used three semi-empirical methods that are referred to in the literature as MNDO, AMI, and ASED-MO methods. As we have indicated before, extended Huckel Molecular Orbital (EHMO) and Atom Superposition and Electron Delocalization Molecular Orbital (ASED-MO) calculations have been successfully used to treat a wide variety of problems, from molecular stability in the gas phase to condensed phase phenomena. The EHMO method has been used to study geometries, isomerism and rotational barriers for a number of saturated and unsaturated hydrocarbons.[1] We have previously reported on the results for bond dissociation energies for coal fragments and model compounds.[2] In the present work a study of bond dissociation energies, both in the presence and in the absence of an electron-accepting catalyst, is reported for the compound, 4-(1-naphthylmethyl)biphenyl, a forty-seven atom molecule, using the MNDO and AMI methods of Dewar.[3,4] The results from these calculations are compared our earlier study[2] in which the ASED-MO method of Anderson[5] was used. An experimental investigation of this compound has been carried out by Farcasiu and Smith,[6] who carefully monitored the decomposition of the compound under thermal and catalytic reaction conditions. Product distributions were also determined for both types of reaction conditions.

The Modified Neglect of Differential Overlap (MNDO) method with configuration interaction has been used to calculate reaction paths for thermolyses of trans and cisazoethane and 1,1-diethyldiazene,[7] and for recombination reactions of methyl radicals with allyl, 1-azaallyl and 2-azaallyl radicals.[8] The proposed mechanisms were in agreement with experiment when such information was available. The MNDO method has also been successfully used to calculate relative stabilities of aryl radicals, in support of an experimental study of the reactivity of polycyclic aromatic aryl radicals.[9]

The calculations reported in this paper have been done with Anderson's ASED-MO method[2,5] adapted for the IBM 3090 computer by Onwood in an internal coordinate version. The MNDO and AMI calculations have been done with the quantum chemical program, MOPAC 5.0, of Stewart.[10]

The minimum energy conformation for the compound studied by Farcasiu and Smith, $C_{10}H_7CH_2C_6H_4CH_2CH_2C_6H_5$, 4-(1-naphthylmethyl)biphenyl was found with all three methods.

To begin, an initial geometric conformation was assumed for the molecule, which was then followed by a minimum energy geometric conformation search.

In ASED-MO calculations it is common to freeze the lattice or backbone of the system studied and vary only certain portions of interest. For instance, Anderson,[11] in a study of the

activation of methane on iron, nickel, and platinum surfaces, froze the transition metal clusters at experimental distances, kept the methyl group rigid but allowed it to tilt. Therefore, we follow the common practice of freezing the backbone of the system at typical experimental distances. All aromatic C-C and C-H bond lengths and aromatic C-C-C and C-C-H bond angles were kept fixed at 1.394 Å, 1.084 Å, and 120, respectively, throughout the ASED-MO calculations. All aliphatic C-H bond lengths were fixed at 1.07 Å and all C-C(sp³)-H bond angles at 108. These bond lengths and bond angles are not necessarily the ASED-MO theory equilibrium distances and angles. Bond lengths, bond angles and dihedral angles for all nonaromatic carbon atoms were then allowed to vary, one by one, until the desired self-consistency in the ASED-MO total energy and geometry was reached. The dihedral angles from a typical minimization are given in Table 1.

The magnitudes of the coefficients of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for all three methods show a striking similarity. The HOMO coefficients are shown in Table 2. These two molecular orbitals essentially involve the p-z orbitals, except for the bridgehead carbon atoms, of the naphthyl portion of the molecule. The HOMO exhibits localized pi-bonding between the 1-6, 2-3, 7-8, and 9-10 pairs of carbon atoms.

The LUMO is an orbital that exhibits localized pi-bonding between the 1-2 and 8-9 carbon atoms and has isolated F-z orbitals on carbon atoms 3,6,7, and 10.

The energies of the orbitals calculated by the ASED-MO and the MNDO-AMI methods are, of course, different. The orbital pictures of the three methods for the HOMO and LUMO's for naphthalene are essentially the same as that for the substituted naphthalene compound. The coefficients for naphthalene with the three methods are also listed in parentheses in Table 2. These dissimilar methods give like descriptions of the molecular orbitals, but different energies for the orbitals.

Bond dissociation energies were calculated for the model compound with all three methods. Since we have frozen the aromatic rings and hydrogen atoms at experimental distances and angles in the ASED-MO calculations, relaxation of the radicals after cleavage of the bond would be inconsistent. Thus, the bond dissociation energy calculated with the ASED-MO method should be considered to be an upper bound to the 'true' bond dissociation energy. However, with the MNDO and AMI methods the minimum energy geometry and total energy of each of the radicals was found by allowing all atoms in the radical to move, but under the restraint of planar aromatic rings.

These latter calculations will be referred to as OPT (for optimized). Therefore, the energy difference between the radicals and the parent compound calculated with the MNDO and AMI methods can more closely be considered to approach the 'true' bond dissociation energy.

We also did a series of MNDO and AMI calculations in which the aromatic rings and hydrogen atoms were frozen at the distances and angles used in the ASED-MO calculations and only the geometry of the aliphatic carbon atoms optimized. The radicals formed after cleavage of the bond were not optimized either. This series of calculations will be designated as Limited OPT. The results of the Limited OPT calculations should be more directly comparable to the ASED-MO results.

The results of the bond dissociation energy computations for the neutral molecule are summarized in Table 3, with bond labels given in Figure 1. All three methods indicate that the symmetric cleavage of the bibenzyl bond (bond d) has the smallest dissociation energy for the neutral molecule. However, the ASED-MO method predicts that bond b has the next lowest dissociation energy while OPT MNDO and AMI methods predict bond a. The Limited OPT MNDO and AMI minimizations give an order for the bond dissociation energies of e, d and d, e respectively. The order and magnitude of the bond dissociation energies is relatively insensitive to geometric conformation, as can be seen by comparing the bond dissociation energies for the extended vs. the folded conformations in Table 3 for all the methods. The bond dissociation energies for the folded conformation are in parentheses.

An examination of the molecular orbital coefficients of the neutral molecule shows that many of the energy levels, even deep-lying levels, are a mixture of atomic orbitals from all parts of the molecule. Thus, cleavage of any bond leads to a rearrangement of electron density over the whole molecule and makes it very difficult to attempt a simple explanation as to the ordering of the bond breaking energies.

Farcasiu and Smith [6] studied the thermolytic decomposition reactions of the compound. This compound has also been studied by Meuzelaar and Huai[13] with the low voltage (12 eV) Py-MS method. The percent product distributions are summarized in Table 4. It might be expected, based on the stability of benzyl radicals due to resonance, that the bond dissociation energy for bond d should be lower than that for a or b, which in turn should be lower than that for c or e. The py-MS data are in accordance with this expectation, while the thermolysis data are not.

The product distributions for the cleavage of the different bonds at 400°C were estimated with a Boltzman distribution, from the computed bond dissociation energies of the three methods and are given for comparison in Table 4.

When a catalyst, carbon black (BP 2000), is added to the compound in the absence of a hydrogen donor, Farcasiu and Smith [6,12] find that products resulting from the cleavage of bond a now predominate, accompanied by large, relative decreases in products from the cleavage of bonds d and c. The catalytic cleavage of bond a occurs at temperatures as low as 320°C. No cleavage at all is observed in the absence of the catalyst at temperatures below

400°C.

Since the same preference for bond cleavage is found both in the presence and absence of the hydrogen donor, a mechanism other than a "solvent mediated hydrogenolysis", is most likely.[6,12] Through Charge Distribution Analysis (CDA) it has been shown that the surface of the catalyst becomes positively charged at 320°C. In order to mechanistically explain the different preferences in bond cleavage in the presence of a catalyst, Farcasiu and Smith [6,12] have proposed that the compound gives up an electron to the positively charged surface of the catalyst, forming a positive radical ion. This radical ion, with the +1 charge localized on the naphthyl moiety, then decomposes through selective cleavage of bond a, the bond adjacent to the naphthyl unit.

We have modeled this mechanism with all three computational methods by placing a +1 charge on the compound. In all three cases the electron removed by the computations came largely from the p-z orbitals of the naphthyl functional group, excluding the bridgehead carbon atoms. This is not an unexpected result, since it is known from UV-photoelectron spectroscopy that naphthalene has a lower first ionization energy(8.15 eV) than benzene (9.15 eV) or aliphatic carbon atoms (about 12 eV).

In the ASED-MO method no relaxation of the molecule after removal of the electron nor relaxation of the fragments after rupture of the bond has been allowed as noted before. With the MNDO and AMI methods the geometry of the molecule is reoptimized after removal of the electron. Certain numerical difficulties, unimportant for our purposes, were encountered during reoptimization of the positive radical ion formed from the model compound by removal of an electron. Although self-consistency was achieved and an acceptably low gradient norm could be obtained, continued iteration tended to keep the gradient norm oscillating. The problem was associated with the geometry of the terminal $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ group. We have verified the insensitivity of the computed bond dissociation energies to the precise geometry of this group by comparing with those obtained by freezing the terminal $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ group at its pre-ion formation minimum energy geometry. The geometries of the ion and the free radical fragments resulting from the cleavage of the various bonds were also optimized with the MNDO and AMI geometry optimization methods. These calculations will be referred to as OPT+. No numerical difficulties were encountered during this process. When calculating bond dissociation energies with all three methods, the positive charge was always placed on the fragment containing the naphthyl functional group. The bond dissociation energies for the positive radical ion were calculated as before for the neutral molecule. The MNDO and AMI calculations for the free radical fragment were RHF calculations with the half electron (HE) correction.

Some AMI optimization were carried out in which the free radical geometry was optimized with the UHF option. The total energy of the radical, with the geometry from the

UHF optimization, was then calculated with a single point RHF calculation in order to make a direct comparison. Insignificant differences in bond dissociation energies were observed, as can be seen in Table 5. MNDO and AMI calculations were also done for the positive radical ion which more closely mimic the ASED-MO calculation. In these, referred to hereafter as Limited OPT+, the geometry of the molecule, calculated by freezing the geometry obtained in the Limited OPT case, is not reoptimized after the electron is removed to form the positive radical ion, nor are the fragments formed after bond cleavage reoptimized.

The bond dissociation energies from the three methods for the positive radical ion are summarized in Table 5 and the percent distributions in Table 6.

It was noted above that in ASED-MO theory all bonds become easier to break for a singly positive charged molecule, not just the bonds closest to the naphthyl unit that has lost the electron. This may be understood from the following argument. In the ASED-MO calculation no relaxation of the molecule after formation of the positive radical ion nor relaxation of the fragments after cleavage of bonds was allowed. The electron removed in the formation of an ion comes from the HOMO of the whole molecule or from the HOMO of the fragment containing the naphthyl portion. Thus, with no relaxation allowed, the change in bond energy for any bond upon going from dissociation of the neutral molecule to that of the radical ion is simply the difference between the HOMO energy of the neutral compound and the HOMO energy of the fragment containing the naphthyl moiety after the bond is broken. In the ASED-MO calculation the HOMO of the whole molecule is always more negative than the HOMO of the fragment, thus explaining why the change in bond dissociation energy is negative for all bonds in the ASED-MO calculation.

The HOMO of the fragment containing the naphthyl group changes as the various bonds are cleaved because, as previously noted, the cleavage of bonds b, d and e yield naphthyl-containing fragments with terminal alkyl radicals. In the other two cases, (bonds a and c), the fragments containing the naphthyl moiety have terminal aryl radicals. In the ASED-MO calculation, an electron in a fragment terminating with an aryl radical is in a HOMO that is higher in energy than an electron in a fragment terminating in an alkyl radical.

Three semi-empirical methods, namely, ASED-MO, MNDO, and AMI, have been used to compute bond dissociation energies of 4-(1-naphthylmethyl)bibenzyl, a model compound of experimental interest in the context of the direct liquefaction of coal. All three methods give similar results for the computed bond dissociation energies for the neutral molecule in predicting that symmetric cleavage of the bibenzyl bond, bond d (refer to Figure 1), is most likely to occur. The ASED-MO results and the py-MS experiments are in qualitative agreement with results expected from simple stability arguments for benzyl radicals. The two other theoretical methods and thermolysis experiments give results that do not conform to the simple

expectations. Further experimental and theoretical work would be most helpful in clarifying the situation. In the presence of a catalyst (BP 2000) that removes an electron from the naphthyl group of the compound (thus creating a positive radical ion), the ASED-MO method, predicts, in agreement with experiment, that the bond closest to the naphthyl group, bond a, is the bond most likely to be cleaved. However, the AMI results, which appear to correctly predict ionization potentials, are not in agreement with the observed changes in bond cleavage preferences in the presence of the catalyst. The AMI method predicts that bond d will still be the bond that is cleaved and that bond a will be even less likely to break in the presence of the catalyst. The ASED-MO method, while not predicting ionization potentials correctly, appears to best describe the catalytic action of the electron-removing catalyst in bond cleavage. This may simply reflect a need for reparameterization of the semi-empirical methods for charged species. We hope this work stimulates further experimental and theoretical work on bond dissociation in model hydrocarbon compounds.

In the remaining quarter of this contract period, we will apply these methods to a series of model compounds with ethylene and methylene linkages connecting single and fused benzene ring structures to look for trends regarding catalytic action such as reported in this work.

This work was done in collaboration with Drs. Harriet Ades and Audrey Companion. We are grateful to Dr. Malvina Farcasiu for suggesting the study of 4-(1-naphthylmethyl)bibenzyl and for providing experimental data. We also thank Dr. H. Meuzelaar for sending us the mass spectrometry data.

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• Figure 1. Skeletal structure of the compound studied. The cleaved bonds are indicated and labeled. The numbering for the dihedral angles listed in Table 1 is included.

Dihedral angle	Extended Conformation		
	ASED	MNDO	AM1
5-10-11-12	85°	97°	96°
10-11-12-13	77°	88°	87°
14-15-18-19	90°	90°	86°
15-18-19-20	180°	179°	179°
18-19-20-21	90°	90°	90°

Table 1: Dihedral angles for a minimum energy conformations of 4-(1-naphthylmethyl)biphenyl.

Atom No.	Coefficients of HOMO		
	ASED	MNDO	AM1
1	0.2520 (0.2553)	0.2697 (0.2682)	0.2657 (0.2677)
2	-0.2358 (-0.2533)	-0.2672 (-0.2682)	-0.2556 (-0.2677)
3	-0.3842 (-0.4064)	-0.4008 (-0.4220)	-0.3891 (-0.4223)
4	0.0049 (0.0000)	0.0020 (0.0000)	0.0078 (0.0000)
5	-0.0274 (0.0000)	-0.0094 (0.0000)	-0.02650 (0.0000)
6	0.3781 (0.4064)	0.4031 (0.4220)	0.3893 (0.4223)
7	0.4157 (0.4064)	0.4124 (0.4220)	0.4234 (0.4223)
8	0.2444 (0.2553)	0.2705 (0.2682)	0.2662 (0.2677)
9	-0.2769 (-0.2553)	-0.2910 (-0.2682)	-0.2986 (-0.2677)
10	-0.4013 (-0.4064)	-0.4295 (-0.4220)	-0.4294 (-0.4223)
11	0.0937	0.0411	0.0591
12	-0.1153	-0.0505	-0.0581

Table 2: Molecular orbital coefficients for the HOMO of 4-(1-naphthylmethyl)bibenzyl. The coefficients are for p_z orbitals only. All other orbital coefficients for these atoms and the ones not listed are much smaller compared to the ones given. The p_z coefficients for naphthalene are included in parentheses for each method. The numbering for the atoms is given in Figure 1.

Bond	Bond Dissociation Energies (eV)				
	ASED	MNDO	MNDO*	AM1	AM1*
a	4.09 (4.11)	3.41	4.56	3.80 (3.80)	4.85
b	3.89 (3.90)	3.57	4.79	3.82 (3.82)	4.90
c	4.23 (4.35)	3.54	4.56	3.93 (3.81)	4.74
d	3.77 (3.68)	2.64	4.45	3.01 (2.97)	4.53
e	4.18 (4.29)	3.54	4.44	3.93 (3.80)	4.62

Table 3: Bond dissociation energies for 4-(1-naphthylmethyl)bibenzyl in the absence of a catalyst (neutral molecule). The bond labels are shown in figure 1. The values in parentheses are for bond dissociation energies for the folded conformations. The * refers to the Limited OPT series of calculations.

Bond	ASED	MNDO	MNDO*	AM1	AM1*	Thermolysis ^α	Py-MS ^β
a	0.4%	-	6%	-	0.3%	17%	26%
b	11%	-	0.1%	-	0.2%	3%	34%
c	0.04%	-	6%	-	2%	16%	-
d	88%	100%	40%	100%	80%	64%	40%
e	0.08%	-	48%	-	17%	-	-

^αFrom Farcasiu and Smith (ref. 6)

^βEstimated from Meuzelaar and Huai (ref. 13)

Table 4: The percent distributions for dissociation of the neutral molecule in its extended conformation. The theoretical distributions were calculated assuming a Boltzmann distribution at 400° C. The * refers to the Limited OPT series of calculations.

Bond	Bond dissociation energy (eV)					
	ASED	MNDO	MNDO*	AM1	AM1 [†]	AM1*
a	2.80 (2.82)	5.29	5.83	4.18	4.15	6.07
b	3.08 (3.09)	2.42	4.23	2.63	2.62	4.23
c	3.01 (3.13)	4.18	5.89	4.39	4.38	5.95
d	3.00 (2.88)	1.68	4.29	1.90	1.90	4.16
e	3.40 (3.59)	3.16	5.53	3.43	3.42	5.44

Table 5: Bond dissociation energies of the positive radical ion. The energies for the folded form are included in parentheses for comparison. The [†] refers to the UHF-RHF combination calculation. The * refer the Limited OPT+ series of calculations.

Bond	ASED	MNDO*	AM1*	Thermolysis
a	94%	-	-	51%
b	0.7%	74%	23%	7%
c	2%	-	-	8%
d	3%	26%	77%	34%
e	-	-	-	-

Table 6: The percent distributions for dissociation of the radical ion. The distributions were calculated assuming a Boltzmann distribution at 400° C. The * refers to the Limited OPT+ series of calculations. Distributions for the dissociation of the radical ion were 100% for bond *d* for the MNDO and AM1 calculations.

2. Calculations of Heats of Reaction for Hydrogenation of Model Compounds.

In the earlier work^{1,2} we used Anderson's modified version of the extended Hückel molecular orbital method³ and the MNDO and AM1 methods of Dewar, *et al.*^{4,5} to study bond cleavage in neutral and positively charged radical ion formed from Model Compound I. The interest in the positively charged radical ion formed from Model Compound I by removal of an electron, comes from the suggestion of Farcasiu and Smith^{6,7} that the BP 2000 catalyst acts as an electron acceptor and removes an electron from the naphthyl portion of model compound I.

Geometric conformations, molecular orbital coefficients for the HOMO's and LUMO's, and bond dissociation energies were computed and compared for the three methods. Qualitative agreement with experiment for bond cleavage was observed for the three methods for the neutral molecule. Our earlier calculations suggest that the ASED-MO method appears to best describe the bond cleavage in the presence of an electron-accepting catalyst. This can be seen from the results shown in Table 1, where the product and the positive radical ion, respectively) calculated by the ASED-MO method are compared with the thermolysis results. The bond labels referred to in the table are shown in Figure 1. The theoretical relative product distributions were calculated from the computed bond dissociation energies (shown in columns 2 and 5) using the Boltzmann distribution at the experimental temperature. The qualitative agreement between theory and experiment with regard to the bond-selectivity of the catalytic reaction is evident from the Table.

In our earlier papers the reactions in the presence of a hydrogen donor, which are more directly relevant to the study of coal liquefaction, were not studied. In the present work, we have calculated the energy differences for the five reactions

where $\alpha = a, b, c, d, e$ denotes the bond that is cleaved in the reaction (as labeled in Figure 1), and in each instance, $R^{(1)}$ denotes the product molecule containing the naphthyl portion of the starting Model Compound I and $R^{(2)}$ the product molecule containing the remainder of Model Compound I. This is a rather simplistic model of the reaction in the presence of the hydrogen donor; clearly, the energy of reaction for hydrogen extraction from the donor (e.g., 9,10-dihydrophenanthrene) will be involved. However, our interest is in the relative product stabilities for the different bond cleavages, and the hydrogen extraction contribution should be essentially the same in all the cases. We present results for ASED-MO, NMDO, and AM1 methods. It should be noted that only the relative energies of reaction for the five paths indicated above within any given method are significant. The absolute numbers calculated by the different methods depend on the calculated dissociation energy for the hydrogen molecule. For example, the dissociation energy for the hydrogen molecule is overestimated by about 5 eV by the ASED-MO method, and by about 1 eV by the AM1 method.

In Table 2 we show the energies of reaction for the hydrogenation reactions of the neutral Model Compound I calculated by the three methods. As explained above, only the relative magnitudes within each method are meaningful. The main conclusion from this table is that the energies of reaction for the five different paths are very similar; the product stabilities relative to the reactants are not greatly different, and further there is no correlation between product stability and the observed product distributions. In Table 3 a similar comparison is done for reactions involving the positive radical ion formed from Model Compound I. In the products, the positive charge is kept with the species containing the naphthyl fragment; the justification has been given in our earlier papers. Once again, the product stabilities are uncorrelated with the observed product distributions. From these calculations we conclude that the driving force behind the bond-selectivity found in the reaction is not the relative thermodynamic stabilities of the products formed.

Other possible factors for the bond selectivity are the differences in the activation energies for the different bond cleavages, and/or the charge distribution in the radicals formed after bond cleavage. We will consider first whether the experimentally found product distribution might be accounted for by the differences in the hydrogen affinity of the radicals formed by the bond cleavage. To test the importance of this factor, we have compared the charge localized on the terminal carbon atoms of the cleaved bond for the neutral and the charged Model Compound I in the different methods. We find no correlation between the charge build-up in the radicals and the observed product distributions.

Since the entropy changes in all the reactions are expected to be small, the bond dissociation energies, which are directly calculated by the theoretical methods, should be an upper bound to the activation energies and appears to be the most important factor in determining the product distributions. The ASED-MO method predicts the difference between the neutral molecule and the positive radical ion in qualitative agreement with experiment. The fact that this simple method succeeds where the more sophisticated semi-empirical methods fail is surprising. Of course, the MNDO and AM1 methods have not really been parameterized for charged species, and this may be the reason for their apparent failure. We are presently carrying out more calculations both to further elucidate the catalytic action and to test the methods for other model compounds.

This work was done collaboration with Dr. Harriet Ades and Audrey Companion.

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Bond	Neutral			Charged (+1)		
	BDE(eV)	Product %		BDE(eV)	Product %	
		ASED	Expt. ^a		ASED	Expt. ^a
a	4.09	0.4	17	2.80	94	51
b	3.89	11	3	3.08	0.7	7
c	4.23	0.0	16	3.01	2	8
d	3.77	88	64	3.00	3	34
e	4.18	0.1	-	3.40	0.0	-

^aFrom Farcasiu and Smith (Ref. 6)

Table 1: Bond dissociation energies (BDE) and product distributions for the thermolysis of Model Compound I. The results for the positively charged radical ion are appropriate to the presence of BP 2000 catalyst, as described in the text. From Ades, *et al.*, Ref. 5.

Bond	ASED-MO		MNDO		AM1	
	Neutral	Charged	Neutral	Charged	Neutral	Charged
a	0.90	0.96	-0.60	-0.54	-0.12	0.00
b	0.93	0.98	-0.43	-0.44	-0.02	-0.09
c	0.93	0.93	-0.37	-0.43	0.05	-0.02
d	1.07	1.07	-0.50	-0.55	-0.03	-0.10
e	0.93	0.93	-0.37	-0.42	0.05	-0.03

Table 2: The calculated energies of reaction (in eV) for the neutral and charged (+1) Model Compound I using three semi-empirical methods. As explained in the text the numbers are only meaningful for the comparison of the thermodynamic stability of the products relative to the reactants within a particular method.

Figure 1: The skeletal structure of 4-(1-naphthylmethyl)biphenyl. The methylene and ethylene linkages, whose cleavage is of interest here are labeled for use in the text.

Project II.8 Chemical Characterization and Hydrogenation

Reactions of Single Coal Particles (Asit Ray)

During this reporting period, we have devoted our efforts to physical and chemical characterization of single coal particles. Physical characterization involves determination of size and shape of single coal particles, and their abilities to adsorb various gases and vapors. Experiments were conducted in an electrodynamic balance mounted inside a vacuum chamber which can be evacuated to a pressure of 10 torr. The electrodynamic balance operates as a charge-to-mass ratio filter; depending on the frequency and amplitude of the applied a.c. potential, particles within a narrow band of charge-to-mass ratio can be stably contained inside the balance. The a.c. field creates a net time-averaged force which is directed towards the center of the balance. At the center, the time varying force vanishes. Therefore, a charged particle can be suspended free of perturbation for an unlimited time at the center by applying a d.c. potential across the endcap electrodes to balance the vertical (gravitational and drag) forces. In a environment, the balancing d.c. voltage is proportional to the mass of the particle. In our experimental system, we also flowed a controlled gas stream around the particle. In such a situation, the balancing d.c. voltage is proportional to the difference between the gravitational and drag forces on the particle. Thus, we obtained the mass and aerodynamic particle size from the voltages require to suspend a coal particle in the stagnant and flow environments. We have mounted a CCD based video camera to record the image of the particle. The camera and associated electronics are also used as a feedback devise to automatically maintain the particle at the center of the electrodynamic balance, and provide the balancing d.c. voltage as a function of time. We are currently developing a technique to characterize the shape using the image of the particle. We have used these techniques to analyze the ability of a coal particle to adsorb various gases. In these experiments, we suspended 5 micron to 20 micron size single coal particles in the chamber at atmospheric pressure. Then, we slowly evacuated the chamber to a pressure of 10 torr. We monitored the mass change of a particle as a function of total pressure.

Finally, we increased the total pressure by introducing desired gas or vapor. We have conducted experiments with helium, nitrogen and water vapor. For a given particle, the

percentage of adsorbed mass as a function of the total pressure shows a high degree of reproducibility. However, at a given pressure the percentage of adsorbed mass varies widely from particle to particle. For example, we find that at 99% saturation, the percentage of adsorbed water varies from 0.2 to 7%. The fractional adsorbed mass appears to depend on the size and shape of the particle, and increases as the size decreases. We are currently modifying the chamber to conduct experiments at high pressures (10,000 torr) in hydrogen environments.

For chemical characterization we have used Raman spectroscopy. The intensity of inelastically (i.e., Raman) scattered light from a microdroplet is very low. Therefore, detections of Raman scattering signals from small particles are quite tricky. In the current experimental system for Raman spectroscopy of single particles, only a small fraction of the total scattered light at a given wavelength is received by the detector (e.g, photo-multiplier tube). Due to the weak signal level in the system, obtaining a complete spectrum of a particle requires more than one hour. Moreover, the use of an Optical Multi-channel Analyzer (OMA), where the scattered light over a range of wavelengths can be recorded simultaneously, is not possible. To overcome these difficulties, we have modified our experimental system where more than 80% of the total scattered light from a particle is received by the detector. A schematic of the experimental system is shown in Figure 1. A two ring electrodynamic balance is mounted inside a parabolic mirror. The null point of the balance where the suspended particle remains stationary for a prolonged period of time coincides with the focal point of the parabolic mirror. All the light scattered by the particle that hits the parabolic mirror is reflected down, forming a beam of collimated light. More of the scattered light is collected by placing a focusing lens at its local length beneath the particle but above the large focusing lens shown in Figure 1. The parallel light rays are then focused by a lens and redirected by a flat mirror toward the entrance of a spectrometer (i.e., double-monochromator). A final focusing lens is used to focus the light precisely at the entrance slit of the spectrometer, and produce the correct f-ratio for maximizing the spectrometer performance. A chilled photomultiplier or an OMA is used to detect light at the exit of the spectrometer, and output signal is amplified for photon counting. Figure 2 shows a spectrum obtained from an 11 micron coal particle. The spectrum was obtained in the range 400 cm to 4000 cm in steps of 5 cm, using 500 mW power from an Ar-Ion laser (514.3). The spectral width was set at 5 cm, and the count time was 10 s. The background counts without

Single Particle Raman Spectroscopy Experiment

Figure 1. A schematic of the experimental system for Raman spectroscopy of a suspended particle.

the particle in the presence of the laser beam varied from 10 to 20 cps. In the Raman active region the counts as high 1800 photons/s was observed. The signal to noise ratio was significantly high, indicating that the technique can be applied to much smaller particles. We are currently examining ways to obtain particle composition and structure from Raman spectra.

Project II.9 The Role of Hydrogen During Liquefaction Using Donor and Non-Donor Solvents

(B. H. Davis, H. Dabbagh, R. D. Guthrie,
M. Venkatachalam, and R. A. Keogh)

INTRODUCTION

The current view of an ideal pating solvent is that it should have hydrogen donor properties. This view is illustrated by Neavel's data show in figure 1 (1). The conversion in tetralin, a good hydrogen donor, attains a higher value than in naphthalene, a non-donor solvent. An idealized version of figure 1 was presented by Whitehurst (2) and has been reproduced frequently in reviews. In this idealized version, coal solubilization is depicted as being independent of the hydrogen donor potential of the solvent (region 1, figure 2). During the intermediate times, the initially solubilized coal fragments may follow one of two pathways: (1) in the poor hydrogen donor solvent, naphthalene, retrogressive reactions become dominant so that insoluble material (labeled mesoform carbon in figure 2) is formed and (2) a good hydrogen donor assists in further conversion of the initial coal fragments by donating hydrogen to stabilize the lower weight materials. In region 3 of figure 2, solvent rehydrogenation occurs as the demand for donatable hydrogen for coal fragment conversion decreases.

It was therefore surprising when we obtained the data in figure 3 for the conversion of an Alston Western Kentucky #9 coal (3). During the early stages of coal solubilization, the extent of conversion was greater in 1-methylnaphthalene, a hydrogen non-donor, than in tetralin. Furthermore, the conversions in the two solvents approached a common value at longer reaction times (40 and 60 minutes). Even more surprising was the dependence of conversion in the 1-methylnaphthalene solvent upon gaseous hydrogen (figure 4); in the absence of added hydrogen the conversion was low and decreased with increasing time as shown by Neavel for naphthalene in figure 1 while the conversion was high and continued to increase with increasing reaction time when gaseous hydrogen was present. It is therefore evident that: (1) gaseous hydrogen is more effectively utilized when the solvent is 1-

methylnaphthalene than in tetralin, and (2) if the solvent participates in the hydrogen utilization mechanism it must be through hydrogen shuttling.

The high conversion is not limited to one unique coal. It has been observed that about one-third of some 300 coal samples from both eastern and western Kentucky coal fields exhibit conversions in 1-methylnaphthalene that are as great or greater than in tetralin provided gaseous hydrogen is present. The dependence of the conversion upon the gases, nitrogen and hydrogen is illustrated in figure 5 for an eastern and a western Kentucky coal. Representative data for the conversion of a number of eastern Kentucky coals are illustrated with results for samples showing essentially equivalent conversion in both solvents as well as results where the conversion is nearly twice as great in tetralin as in 1-methylnaphthalene (figure 6). The uniqueness of the 1-methyl substituent is illustrated by the data in figure 7.

It is apparent that some coals are very effective in utilizing gaseous hydrogen. The mode of hydrogen utilization, adding directly to the coal fragments or to coal through hydrogen shuttling through solvent molecules, is of interest. One way to decide this would be to utilize deuterium in runs with 1-methylnaphthalene. If deuterium is added to the coal fragments directly from the gas phase, deuterium exchange with the solvent should be similar whether coal is present or absent. If deuterium adds to the coal through hydrogen shuttling the incorporation of deuterium in the solvent should be as great or greater than in the coal. Furthermore, if hydrogen shuttling occurs by the formation of the dihydro species through α,β addition, exchange at α , β carbon positions should occur at the same rate.

EXPERIMENTAL

Materials

The coal sample was collected at the mine, ground to -100 mesh, stored in a nitrogen filled, sealed bottle in a glovebox, and dried prior to the liquefaction run. The properties of the coal are summarized in Table 1.

Table 1
Properties of Western Kentucky #9 Pyro Coal

<u>Property</u>	<u>Weight %</u>
Ash (dry)	10.31
VM (daf)	43.72
FC (daf)	56.28
C (daf)	82.15
H (daf)	5.72
N (daf)	1.71
S (daf)	3.93
O (daf)	6.49

The compounds used as solvent were obtained from Aldrich and were used without further purification. Deuterium was obtained from Cambridge Isotope Laboratories (99.8%).

Liquefaction Runs

The coal liquefaction experiments were carried out in a 50cc stainless steel microautoclave reactor. In a typical run, 5.0 grams of coal, 7.0 grams of 1-methylnaphthalene, and deuterium (800 psig at ambient temperature, about 2000 psig at reaction temperature) were added to a reaction vessel fitted with two stainless steel balls to effect mixing; the reactor was then immersed into a fluidized sand bath. Heat up time to 385°C was less than two minutes. The reactor was vertically shaken at 400 cpm. At the end of the experiment, the reaction was quenched by reducing the temperature of the reactor to less than 100°C by immersing it in a sand bath held at ambient temperature.

After the reactor had cooled to room temperature it was connected to an evacuated manifold of known volume; the residual gas was expanded into the manifold and the total pressure obtained. A gas sample was analyzed by a Cole Gas Analyzer.

Analysis for conversion was by solubility class. The sample was transferred to a Soxhlet thimble by slurring the reactor contents with either toluene or pyridine; Soxhlet extraction of the oil and asphaltenes was thus effected with toluene, whereas pyridine extracted oils, asphaltenes and preasphaltenes. The sample was then extracted with pyridine;

the difference in weight of the dried thimble following toluene and pyridine extraction was the weight of the preasphaltenes. Total conversion was calculated from the weight of the pyridine insoluble as:

$$\frac{\text{initial coal weight (maf)} - \text{pyridine insoluble weight}}{\text{initial coal charged (maf)}}$$

After removal of most of the pyridine with a Rotovap, about 500 mL of toluene was added to precipitate preasphaltenes which were removed by filtration. Most of the toluene was removed from the extract with a Rotovap and the residue added about 500 mL pentane. The pentane insoluble was collected by filtration and dried; the weight corresponded to the amount of asphaltenes formed. Oil yield was calculated as:

$$\frac{(\text{coal charged (maf)}) - \text{IOM-Ash-preashaltene-asphaltene-gaseous compounds}}{\text{coal charged (maf)}}$$

In the D₂ experiments to minimize contact with the metal reactor, a pyrex long-neck glass reactor was constructed (figure 8). The microautoclave was also modified so that the glass reactor bulb was in the main reactor vessel, but larger tubing was used so that the long glass neck could extent out of the fluidized sand bath. During the run dry ice was placed in a container around the reactor neck to effect reflux to prevent the solvent from distilling from the glass reactor. Glass beads were placed inside the glass reactor to effect mixing. The glass reactor was prevented from contacting the steel reactor wall by surrounding it in stainless steel wool. This reactor prevented the liquid from contacting the steel reactor and at the same time to be in contact with D₂ at high pressure at reaction temperature.

In some runs with both coal and the 1-methylnaphthalene solvent, the 1-methylnaphthalene was isolated from the oil sample using a microdistillation technique. The isolated 1-methylnaphthalene had a purity of greater than 97% as determined by GC analysis.

The deuterium contents of solvent molecules were obtained using a GC/MS. Spectra of pure compounds were obtained to effect corrections for corrections for the M + 1 and higher peaks. Spectra were obtained using 10 eV ionization energy. The deuterium NMR were performed on a 300 MHZ Varian instrument.

RESULTS AND DISCUSSION

The early studies with 1-methylnaphthalene at 385°C indicated that both the sealant used with the autoclave and the autoclave walls could catalyze deuterium exchange (Table 1). It is apparent that the walls of the steel autoclave exchange during 1 hour of reaction so that about 40% of the 1-methylnaphthalene had exchanged deuterium for one or more hydrogens. No evidence was obtained for methyl migration to produce 2-methylnaphthalene.

The deuterium distributions in some model compounds following exchange in the steel microautoclave for 1 hour in D₂ at about 2000 psig and 385°C are shown in Table 2. While the absolute values will vary from run to run with a particular compound, it is apparent that the substituent has an impact upon D exchange. The substitution of either ethyl and phenyl for H in the ring-1 position has little impact upon the extent of exchange. However, the exchange when methyl is substituted in the 1 position is increased, and the exchange is essentially in the ring only. The more electron releasing groups (OH and OCH₃) cause the exchange rate to increase over that of the methyl substituent. Thus, the order of increasing exchange rate for the substituents is as follows:

Exchange studies were attempted with 1-naphthoic acid; however, this compound underwent complete conversion during the one 1 hour reaction period to produce essentially naphthalene and 1-methylnaphthalene, with naphthalene the dominant product (Table 3).

1-Methoxynaphthalene undergoes conversion under the 1 hour reaction conditions to produce other products, predominantly 1-naphthol and 1-methylnaphthalene (Table 4). Similar data for the conversion of 1-methoxynaphthalene in the presence of coal is shown in Table 5. First, the extent of chemical conversion is greater in the presence of coal and the products appear to shift to favor the formation of 1-naphthol. However, the deuterium incorporation in the solvent and the reactants appear to follow a common pattern in the presence or absence of coal.

The extent of deuterium incorporation with time into 1-methylnaphthalene, based on the percentage of d₀ remaining, is shown in figure 9 for the presence or absence of coal. It is apparent that there is little difference in the extent of exchange whether coal is present or absent. Furthermore, the extent of deuterium incorporation does not show the initial rapid increase with time as does the extent of coal solubilization (figure 10).

The extent of exchange with naphthalene for any corresponding time, is less than with 1-methylnaphthalene; likewise, the extent of exchange with naphthalene is not greater when coal is present (figure 11). The data in figure 12 for the conversion using 1-methyloxynaphthalene again show little difference whether coal is present or absent.

The deuterium distribution at various ring and the methyl position can be learned from deuterium NMR of the exchanged compound. The spectrum in figure 13 shows that (1) essentially no exchange occurs in the methyl position at the 385°C reaction temperature and (2) the dominant ring substitution positions are the ring α positions or the positions ortho and para to the substituent. The deuterium exchange therefore occurs by a mechanism that is under chemical influences rather than by a mechanism that would produce a statistical distribution. Deuterium exchange with 1-methylnaphthalene was also effected using either $\text{CH}_3\text{CO}_2\text{D}$ or DCl in D_2O ; the deuterium distribution for the acid catalyzed exchange was very similar to that obtained with gaseous D_2 at 385°C (Table 6). Note that the % deuterium is calculated based on the total deuterium and cannot be added to the ring distribution percentages.

Table 6 also includes the deuterium distribution in 1-methylnaphthalene following conversion with coal. The 1-methylnaphthalene distilled from the oil fraction produced at 385°C shows a distribution that is essentially the same as was obtained for exchange in the absence of coal (Table 6). When the conversion was effected at 450°C with coal, 22% exchange did occur in the methyl group; however, the ring exchange distribution was essentially the same at 385°C and 450°C (figure 14).

Data is presented in Table 7 for the incorporation of deuterium into the coal derived products. The data for the oils (hexane soluble fraction) is for the residue after removing the 1-methylnaphthalene solvent by distillation. In contrast to the solvent, more deuterium is incorporated into the coal derived oils in the aliphatic position than in the ring positions. Furthermore, the dominant aliphatic exchange position was the α -position. The fraction of deuterium in the oil fraction increases with increasing conversion; this is expected since the oil fraction increases with time. The extent of exchange in the aromatic position in the asphaltene plus preasphaltene fraction is greater than in the corresponding oil fraction; this implies that oil formation results in aliphatic bond breaking with subsequent incorporation of D from the gas phase. The extent of exchange in 1-methylnaphthalene is presented together

with coal solubilization in Table 8. It is apparent that deuterium exchange is not very extensive in 10 minutes whereas coal has been stabilized to approach its maximum conversion.

The NMR spectrum of the pyridine soluble, pentane insoluble fraction from coal liquefaction at 450°C is presented in figure 15. It is observed that deuterium is incorporated into aromatic, aliphatic and active hydrogen positions. The spectrum also shows deuterium peaks for pyridine superimposed upon the spectrum for D attached to aromatic carbons. The pyridine used as for solubility class separations did not contain deuterated molecules; hence, the deuterium present in pyridine was incorporated during the analysis. Presumably, the H-D exchange in pyridine is a result of exchange with the active hydrogen in the coal derived species during extraction. Deuterated pyridine was always observed in the coal derived sample although in most cases it was not nearly as prominent as is observed in figure 15. Deuterium was incorporated into the methyl position (22%) of 1-methylnaphthalene in runs with coal at 450°C; however, the distribution of D in the ring was similar to that expected for substitution at α ring positions (figure 16). At 385°C, D is not incorporated into the methyl position of 1-methylnaphthalene in the presence or absence (figure 17A and B) of coal. Furthermore, a similar distribution of D in the ring of 1-methylnaphthalene is obtained at 385°C and 450°C.

The deuterium NMR spectrum of tetralin following conversion at 385°C for 1 hour in the presence of coal is shown in figure 18. The exchange on the aromatic ring corresponded to 68% of the total exchange. The exchange in the hydrogenated ring favored the α position by nearly 2:1 ($= \alpha:\beta$).

The exchange with 1-methoxynaphthalene was very selective. As shown in figure 19 the ring protons are sufficiently separated to permit analytical determinations for all ring positions. However, detectable deuterium exchange was observed to occur in one hour at 385°C only on the ring containing the methoxy substituent; furthermore, the exchange occurs only at the positions ortho and para to the methoxy group, with 70% of the exchange occurring in the para position.

As described in the experimental section, a special glass reactor was designed whereby reflux returned the volatile solvent to the heated reactor area but still exposed the solvent to D₂ at about 2000 psig at the 385°C reaction temperature. With about 0.5 g of 1-

methylnaphthalene in the reactor, deuterium exchange was below the detection level. Furthermore, the addition of 5% Pd-C catalyst to the 1-methylnaphthalene in another run clearly demonstrated that D₂ had access to the solvent since after 1 hour reaction time at 385°C, only four GC peaks were detected and these were assigned to the four 1-methyldecalin isomers. Furthermore, both D and H NMR showed only aliphatic peaks with the absence of peaks in the aromatic region. GC/MS analysis indicated that essentially only deuterium was present in the 17 ring positions. In addition, some of the methyl hydrogens had exchanged. Thus, there is potential for further studies where solvent exchange should not occur unless coal is present.

SUMMARY

Some coals utilize gaseous hydrogen very efficiently so that conversion during the early period of liquefaction is greater in 1-methylnaphthalene, a non-donor solvent, than it is in tetralin, a good hydrogen donor solvent. This enhanced conversion could be viewed to be due to hydrogen shuttling by the formation of di- or tetra-hydro methylnaphthalene. If the methyl group is to be effective in adding hydrogen we could visualize 1,2 deuterium addition as:

If deuterium shuttles by a 1,2-dihydro-1-methylnaphthalene intermediate [reaction 1], exchange should occur predominantly in the ring-2 position. If the shuttling occurred through reaction [2] exchange at the ring 3 and 4 positions should occur in equal amounts.

The data clearly eliminate the participation of reaction [2] since the 4- (para) position exchanges to a much greater extent than the 3- (meta) position. Likewise the ring α position in the unsubstituted ring exchanges more rapidly than the β position. We likewise eliminate reaction [2] because (1) the exchange in the 4-ring position is greater than in the 3-position and (2) the exchange in the unsubstituted α -ring position is greater than exchange in the 3-ring position. Dihydrogen intermediates, if they are responsible for shuttling, must be the result of 1,4-hydrogen addition, and this is considered unlikely.

Exchange appears to be different in coal structures and the 1-methyl-naphthalene solvent molecules since the alkyl hydrogens in coal fragments exchange at 385°C but do not do so in the solvent. Furthermore, coal solubilization appears to occur more rapidly than deuterium exchange. In addition the extent of deuterium incorporation into solvent molecules appears to be about the same extent in the presence or the absence of coal. Thus, the results of the deuterium studies appears to eliminate the shuttling of hydrogen by solvent molecules as being responsible for the apparent superior conversion in the non-hydrogen donor 1-methylnaphthalene.

McMillen et al. (4) have advanced a mechanism involving coal solubilization in which hydrogen-transfer-promoted bond scission is initiated by coal fragments. In this mechanism, strong linkages are cleaved as a result of hydrogen transfer from solvent-derived cyclohexadienyl radicals in a direct bimolecular step (figure 21).

If the coal linkage broken in figure 21 involved a propyl group in the presence of D_2 we would expect the following:

In the coal fraction, D was present predominantly in the α position. Thus, in this mechanism it would appear that the α position of the alkyl group would be substituted with D if the bridging group was a methylene group ($-\text{CH}_2-$). Since tetralin exchanged predominantly in the α position it is possible that the α -D exchange arises from exchange by the hydroaromatic

structures; however, the slower exchange of the hydroaromatic ring than the aromatic ring argues against this being the case. However, additional experiments where the reactor catalyzed exchange is eliminated are needed to determine the reliability of the data in Table 7.

The glass lined reactor offers the possibility to utilize deuterium label so that exchange will occur only when coal is present.

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Table 1

Deuteration of 1-Methylnaphthalene at 2000 psi D₂, 385°C, 1 Hr Reaction Time

Reactor		D ₀	D ₁	D ₂	D ₃	D ₄	D ₅
Reactor used with Coal		69	25	5	0	0	0
Reactor never used with Coal		58	25	6	1	0	0
Used Reactor with Ni Graphite Flakes		49	33	13	4	1	0
Reactor with Glass Liner		92.0	7.0	1	0	0	0
Stirred Tank Reactor With Glass Liner at 425°C ^a	Condensed Inside Glass	27.0	32	23	11	5	2
	Condensed Outside Glass	38.0	35	17	8.5	2.5	1
CH ₃ CO ₂ D in stirred, 1 atm glass reactor at 100°C, 24 hr.		31	44	21	3.5	.5	0

a A glass liner was fitted into a 75 cc stirred stainless steel autoclave.

Table 2

Deuteration of Model Compounds at 385°C, D₂ 2000 psi, 1 hr.

Model Compound	<u>Deuterium Content (%)</u>					
	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅
Naphthalene ^a	78	19.5	2.5	0	0	0
1-Methyl-naphthalene	58	28	6	1	0	0
1-Ethyl-naphthalene	82	14.5	2.5	0.7	0.3	0
1-Phenyl-naphthalene	85.0	13.0	1.5	0.5	0	0
1-Methoxy-naphthalene	51	38	9.0	1.0	0	0
1-Hydroxy-naphthalene	36	42	17.5	5.0	0	0

a. Reaction time, 30 minutes

Table 3

Deuterium and Product Distribution of the Decomposition Products of 1-Naphthoic Acid
in a 50 cc S.S. Reactor at 2000 psi D₂, 385°C, and 1 hr. without Coal

Products ^a	% G.C.	Deuterium Content %								
		d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	d ₇	d ₈
Naphthalene	85.3	3.6	15.6	30.2	30.0	15.8	4.1	.6	0	0
1-Methyl-naphthalene	12.5	0	2.0	12.6	19.8	32.4	19.0	11.0	2.8	.3

a 100% conversion of naphthoic acid.

Table 4

Deuterium and Product Distribution of the Decomposition Products of 1-Methoxynaphthalene
in a 50 cc S.S. Reactor at 2000 psi D₂, 385°C, and 1 hr. without Coal

Products	% G.C.	Deuterium Content %					
		d ₀	d ₁	d ₂	d ₃	d ₄	d ₅
Naphthalene	.6	52	39	8	0	0	0
1-Methyl-naphthalene	7.1	60	32	5	2	1	0
1-Methoxy-naphthalene	74.3	45	41	13	1	0	0
1-Naphthol	8.5	76	20	3	0	0	0
Others ^a	9.5	--	--	--	--	--	--

a Decalin and tetralin (trace amounts).

Table 5

Deuterium and Product Distribution of the Decomposition Products of 1-Methoxynaphthalene
in a 50 cc S.S. Reactor at 2000 psi D₂, 385°C, and 1 hr. with Coal

Products	% G.C. ^a	Deuterium Content %					
		d ₀	d ₁	d ₂	d ₃	d ₄	d ₅
Naphthalene	.60	49	42	7	4	0	0
1-Methyl-naphthalene	3.0	52	34.5	11	2	.7	0
1-Methoxy-naphthalene	57	45	41	13	1.6	.7	0
1-Naphthol	24.5	33	49	17	1.6	.3	0
Others ^b	14.5	--	--	--	--	--	--

a Average of two runs.
b Predominantly decalin and tetralin.

Table 6

Deuterium Distribution in 1-Methylnaphthalene with or without the Presence of Coal (W.Ky. #9 Pyro) in a 50 cc S.S. Reactor, 2000 psi, D₂

Position (ppm) ^c	Deuterium Content ^a , %						
	With Coal				Without Coal	CH ₃ CO ₂ D ^b	D ₂ O/H
	385°C		450°C		385°C	100°C	
A (7.36)	21	23	23	19	14.5	14	23
B(7.21)	23	26	25	19	14.5	11	17
C (7.09)	34	35	35	38	42	35	26
D (6.87)	4.0	3.5	3	4.5	5.5	3	5
E (6.86)	4.0	3.5	3	4.5	5.5	3	4
F (6.75)	4.0	3.5	6	4.5	3.5	3	4
G (6.68)	9.0	6.0	5	9.5	14.5	30	20
M (3.20) ^d	0 ^d	0 ^d	NA	22 ^d	2.0 ^d	0 ^d	.
Reaction Time (hr)	.5	1	1 ^e	1	1	48	24

a Experimental error $\pm$ 3%

b At one atmosphere.

c ²NMR signal.

d Distribution of deuterium (%) in the methyl group. The remaining (%) deuterium is distributed in the ring positions a-g.

e Long neck reactor with condenser and glass liner.

Table 8

Deuteration - Coal Liquefaction of Western Kentucky #9
Pyro at 385°C, 2000 psi D₂ in a 50 cc S.S. Reactor at Various
Reaction Times in the Presence of 1-Methylnaphthalene

<u>Reaction Time (min.)</u>	<u>% Conversion</u>	<u>Deuterium Content % of 1-methylnaphthalene</u>			
		d ₀	d ₁	d ₂	d ₃
10	76.0	93	6	1	0
30	80.5	75	21	4	0
60	80.5	69	26	5	0

Table 7

Deuterium Incorporation (Relative %) in Fractions of the Reaction Product from the Conversion of Western Kentucky #9 Pyro Coal at 385°C, 2000 psi D₂ in 1-Methylnaphthalene with Increasing Reaction Times

	Deuterium Distribution, % of Total					Deuterium in Solubility Fraction	Total ^b Deuterium in Coal
	Aromatics		Aliphatics				
Coal Fraction	(5.5-9.0) ppm	Pyridine ^a	α (2.2-4.1) ppm	β (1.3-2.2 ppm)	γ (.7-1.3 ppm)		
Hexane-Insolubles (HI)	33 (50.0) ^c	33	23 (34.8)	9 (13.6)	1.0 (1.5)	1.14	.50
Hexane-Solubles (HS) ^d	32	0	44	19	5		.64
Hexane-Insolubles (HI)	39 (46) ^c	16	30 (35.7)	13 (15.5)	2.0 (2.4)	2.21	0.45
Hexane-Solubles (HS) ^d	33	0	47	17	3		1.76
Hexane-Insolubles (HI)	44 (55) ^c	20.0	30 (37.5)	6 (7.5)	0	2.66	0.37
Hexane-Solubles (HS) ^d	46	0	42	10	2		2.29
Hexane-Insolubles (HI)	e		e	e	e	4.27	.870
Hexane-Solubles (HS) ^d	34	0	36	17	3		3.40

a. Percent of aromatic deuterium signals due to incorporated pyridine (7.10, 7.50 and 8.80 ppm); b. Normalized based on CD₃NO₂; c. Percentage based on pyridine free; d. Fraction boiling above 1-methylnaphthalene; e. Amount of deuterium too small to measure.

Figure 1. The conversion of coal in a good and a non-hydrogen donor solvent (from reference 1).

Figure 2. Idealized conversion-time curves for coal solubilization in a good and a non-hydrogen donor solvent during the solubilization, hydrogen transfer and rehydrogenation periods.

FIGURE 3. CONVERSION OF AN ALSTON WESTERN KENTUCKY #9 COAL
IN A NONDONOR AND DONOR SOLVENT

FIGURE 4. CONVERSION OF AN ALSTON W.KY. #9 COAL IN 1-METHYLNAPHTHALENE

FIGURE 5. CONVERSION IN A DONOR AND NONDONOR SOLVENT USING HYDROGEN AND NITROGEN ATMOSPHERES

FIGURE 9. EASTERN KENTUCKY COAL CONVERSIONS IN
TETRALIN AND 1-METHYLNAPHTHALENE

Figure 7. Comparison of the conversion of a Western Kentucky #9 and an eastern Kentucky Peach Orchard coal in variously substituted naphthalenes and in tetralin.

Figure 8. Schematic of glass reactor designed for deuterium exchange without solvent contacting the steel reactor.

Figure 9. Percentage of undeuterated methylnaphthalene following conversion at 385°C in the absence (▲) and presence (○) of coal.

Figure 10. Coal conversion versus time for the coal liquefaction of Western Kentucky #9 pyro in a 50 cc SS reactor, 2000 psi deuterium, at 385°C, 1 hr.

Figure 11. Percentage of undeuterated naphthalene following conversion at 385°C in the absence (▲) and presence (○).

Figure 12. Percentage of undeuterated methoxynaphthalene following conversion at 385°C in the absence (▲) and presence (○).

Figure 13. Deuterium NMR spectrum of 1-methylnaphthalene following exchange at 385°C and 2000 psi.

for 30 minutes.

Figure 15. Deuterium NMR spectrum of asphaltene plus preasphaltene fraction of coal liquefaction products following conversion at 385°C and 2000 psig D₂ for 30 minutes.

D₂, Coal
 450°C, 30 min.
 2000 psi

COAL
 PYRIDINE SOLUBLE
 PENTANE
 INSOLUBLES

CONVERSION OF THE α AND β RING H_2 IN 10 MINUTES.

Figure 17A. Deuterium NMR spectrum of 1-methylnaphthalene following exchange at 385°C and 2000 psig D_2 for one hour.

Figure 17B. Deuterium NMR spectrum of 1-methylnaphthalene following exchange at 385°C and 2000 psig D₂ for one hour in the presence of coal.

H2 NMR
 SAMPLE: #15
 SOLVENT: HEXANE OR THF
 REFERENCE: ACETONE-D6 = 2.04 PPM
 OPERATOR: RF
 10/25/90

exp3 pulse sequence: e2pu1

SAMPLE		DEC. & VT	
date	Oct 25 80	dn	H1
solvent	cdcl3	dof	0
file	exp	dm	yyy
ACQUISITION		dms	•
sfreq	48.044	daf	9900
tn	H2	dhp	67
at	2.000	PROCESSING	
np	16000	wtfile	
sw	4000.0	proc	ft
fb	2200	fn	not used
bs	40	meth	f
pw	7.0		
di	0	herr	
tof	-1102.5	wexp	
nt	400	wbs	
ct	0	wnt	
clock	n	DISPLAY	
gain	not used	ep	27.5
FLAGS		wp	465.8
il	n	ve	212
in	n	ec	0
dp	y	kc	400
he	nn	hzma	0.97
		ie	97053.93
		rfl	2069.6
		rfp	93.9
		th	18
		ins	1.000
	nm	cdc	ph

Figure 18. Deuterium NMR spectrum of tetralin following conversion at 385°C and 2000 psig D₂ for one hour in the presence of coal.

hour.

Figure 20. Deuterium NMR spectrum of 1-methoxynaphthalene following conversion at 385°C and 2000 psig D₂ for one hour.

Figure 21. Reaction scheme for rupture of strong bond linkage during coal liquefaction (from reference 4).

PATHWAY III

Project II.10 Solvent-Sorption and FTIR Studies on the Effects of Catalytic Depolymerization

Reactions in Coal (Peter Stansberry and Paul Jagodzinski)

INTRODUCTION

Coal is structurally and chemically a very complex sedimentary rock material consisting predominantly of organic matter.¹ The organic phase is considered to be a three-dimensionally cross-linked, reticulated macromolecular network containing extractable molecules.² The transformation of coal to useful liquid products via direct liquefaction is simple, in principle. All one has to do is add enough hydrogen such that the hydrogen-to-carbon atomic ratio of the original coal (<1) is raised to about 2 in its products. To achieve this level of hydrogen addition usually requires rather severe conditions of high temperature ($>400^{\circ}\text{C}$) and pressure (>7 MPa), though the addition of metal catalysts leads to lower process conditions^{3,4} and better product distributions.⁵⁻⁸

It is possible that even more mild reaction conditions could be attained by a more fundamental knowledge of coal structure, the nature and reactivity of its functional groups, and the role of catalysis. From this information catalysts could be tailored to act on certain bonds or functional groups to provide the hydrogenation and molecular weight reduction necessary for an economically successful liquefaction process.

BACKGROUND

Low-temperature catalytic coal hydrogenation experiments indicate that subtle structural changes occur in coal at temperatures well below those used in typical liquefaction schemes.⁹ Low-temperature catalytic pretreatment followed by liquefaction increases the yield of soluble liquids and production of oils compared to similar thermal treatments. It is also observed that catalytic pretreatment alone did little to increase the yield of soluble liquids; however, the pretreatment reaction causes an increase in the degree of coal swelling in pyridine.¹⁰ Since the degree of coal swelling increases, it is inferred that the reaction causes a decrease in the number of "cross-links."

Information on the chemistry leading to cross-linking reactions in coal can be obtained by a study of coal-solvent interactions. Coal-solvent interactions have been used by others to follow the chemical processing of coal¹¹⁻¹⁴ and to provide insight into the nature of chemical bonding between coal structures.^{15,16} Specifically, it is known that polar solvents, such as alkylamines or pyridine, bind to coal at particular sites.^{17,18} While the number of sites can be estimated, their identity is not known unequivocally though hydroxyl groups (e.g., phenolic hydroxyl) are most often implicated.

In this regard, we have focused on the role that iron-based catalysts have on preventing or mitigating retrograde reactions caused by phenolic groups (-OH). Our approach used the solvent-sorption technique reported by Green and Larsen¹⁷ in conjunction with the acetylation of acidic oxygenates. It is thought that by combining these two techniques with the observed frequency shifts associated with oxygen functionalities by FTIR, valuable insight into the mechanism of catalytic liquefaction would be obtained.

EXPERIMENTAL

The coals used for this study were supplied by the Center for Applied Energy Research, University of Kentucky and were chosen to cover a range of coal rank. The ground coals (<100 mesh) were shipped under an inert atmosphere in sealed glass containers. Some of their properties are listed on Table 1.

The coals were dried in vacuum at 110°C for about 24 hours before use. Catalysts were mixed with the coals while in a nitrogen-purged glove box using a blender designed for solids. Two iron sulfides were used for catalytic hydrogenation, Fe₂S₃ and NaFeS₂. These catalysts were developed in another CFFLS project. Both catalyst were calculated to give a loading level of 1 wt% based on daf coal.

Hydrogenation reactions were conducted without solvent in 316 SS tube reactors (nominal volume 25 mL) of a similar design described elsewhere.¹⁹ About 5 grams of material were sealed into Pyrex-lined reactors, purged, and pressurized with 7 MPa hydrogen (initial cold pressure). The reactors were then immersed into a preheated fluidized sandbath and reacted at either 275 or 350°C for 1/2 hour before being quenched to room temperature by immersion in cool water.

Following reaction, the reactor contents were removed and quickly stored in nitrogen

filled-bottles.

Treated and untreated coals were exposed to mixtures of pyridine and chlorobenzene while in sealed test tubes. After days, the height of swollen coal was measured and the supernatant solvent composition determined by gas chromatography. Details on the analytical procedure are reported elsewhere.^{17,20}

Coals were acetylated with acetic anhydride in pyridine using a method similar to that used by Blom et al.²¹ Details are provided elsewhere.²⁰

FTIR analysis of untreated and treated coals were conducted on a Nicolet 510P spectrometer. Potassium bromide (KBr) pellet preparation and data collection were similar to those published elsewhere.²²

RESULTS

A comparison of the -OH content determined by acetylation, Table 2, with the sudden change in absorbed solvent composition, Figure 1, indicates a correspondence between the amount of -OH groups and coal swelling behavior. We find these results encouraging because they suggest a means by which to follow the chemical changes associated with phenolic groups in coals under catalytic liquefaction conditions. Table 3 lists the measured -OH contents of the coals following thermal and catalytic hydrogenation. It can be seen that heating at 275°C causes a reduction in -OH content compared to the untreated coals, as would be expected. Heating to 350°C causes even more loss of -OH, again as expected. However, even though different catalysts were used, there are no significant changes in -OH contents compared to the strictly thermal experiments. The fact that the respective relative changes in the observed -OH contents for the three coals are the same is in agreement with the view that the predominant force in liquefaction is thermolysis.

Nevertheless, a comparison of solvent-sorption plots, Figures 2-3, shows that the added catalysts are affecting the structure or other types of coal bonds in an as yet undefined manner, especially for the subbituminous and hv bituminous coals. The lv bituminous coal, Figure 4, shows little change no matter what the reaction condition. This is not surprising for a coal of high rank. Its structure is very aromatic and cross-linked to start with and, hence, very unreactive.

FTIR analyses are inconclusive at this time. We encountered problems with water absorption in the KBr pellets such that spectral interpretation was not possible. However, we have recently acquired a Herrick chamber accessory for the FTIR spectrometer which will allow for infrared studies in controlled environments.

CONCLUSIONS

Acetylation of thermally and catalytically hydrogenated coals shows that -OH groups are lost as reaction temperature increases. The low-rank coal lost the greatest amount of -OH as the result of thermolysis while the high-rank coal the least. There appears to be no effect of iron catalysis on -OH elimination. However, solvent-sorption behavior of treated coals shows that added iron catalysts have altered coal structure or bonding in an undetermined manner.

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Table 1 - Coal Characteristics

<u>¹CAER Sample Number</u>	<u>91875</u>	<u>91864</u>	<u>91874</u>
Seam	Wyodak	WKY #9	Pocahontas 3
State	Wyoming	Kentucky	Virginia
Rank	sub	lv bit	lv bit
Mean-Maximum Reflectance of Vitrinite	0.37	0.80	1.52
<u>Ultimate Analysis (%daf)</u>			
Carbon	79.80	82.15	94.89
Hydrogen	4.99	5.72	4.39
Nitrogen	1.12	1.71	1.27
² Oxygen	13.54	6.49	0.00
Organic Sulfur	0.35	2.07	0.56
Proximate Analysis (as determined)			
Moisture	20.73	2.32	0.78
Volatile Matter	37.80	38.30	17.70
Fixed Carbon	36.10	49.31	76.84
H-T Ash	5.37	10.07	4.68
Petrographic Composition (%vol)			
Vitrinite	87.7	87.0	89.0
Liptinite	1.6	2.5	0.0
Inertinite	10.7	10.5	11.0

¹Center for Applied Energy Research, University of Kentucky

²Oxygen by difference

Table 2 - Amount of -OH Functionality in Raw Coals (mmol/dmmf coal)

<u>Coal</u>	<u>Amount -OH</u>
Sub	6.1
hv bit	3.3
lv bit	1.0

Table 3 - Amount of -OH Functionality in Treated Coals (mmol/dmmf coal)

<u>Treated at 275°C</u>	<u>Sub</u>	<u>hv bit</u>	<u>lv bit</u>
Non-Catalytic	4.9	2.8	0.9
Fe ₂ S ₃	4.8	2.9	0.8
NaFeS ₂	4.9	2.7	0.9
<u>Treated at 350°C</u>			
Non-Catalytic	1.9	2.3	0.2
Fe ₂ S ₃	1.2	2.3	0.8
NaFeS ₂	1.2	2.6	0.8

Figure 1 Solvent sorption of raw coals. A) Sub; B) hv bit; and C) hv bit

Figure 2 Solvent sorption of treated subbituminous coal.

Amount of Pyridine Absorbed, mmol/dmmf coal

Figure 3

Solvent sorption of treated hv bituminous coal, A)-(C) 275 °C, n)-(F) 250 °C

Amount of Pyridine Absorbed, mmol/dmmf coal

Figure 4 Solvent sorption of treated bituminous coal.
A)---C) 275 °C; D)---F) 350 °C

Task III

Novel Coal Liquefaction Concepts

Program Coordinators: D. Bhattacharyya, A.R. Tarrer, and J.S.Shabtai

Task III

Novel Coal Liquefaction Concepts

Program

Coordinators: D. Bhattacharyya, R. Tarrer, and J. S. Shabtai

Report Period: May 1, 1990 - April 30, 1991

Project III.1 Bioprocessing of Coal (D. Bhattacharyya, M.V.S. Murty, R.I. Kermode, H. Venkatachalam, M.I.H. Aleem, and M. Venkatachalam)

SUMMARY

In order to study the hydrogenation of coal for enhanced liquefaction, experiments were conducted with different bacteria on various coals and model compounds. Our preliminary results obtained using Warburg apparatus showed the hydrogen uptake by coal (KCER#91182), Diphenyl Methane (DPM) and Methylene Blue (MB) by *Sulfolobus brierleyi* and *Desulfovibrio desulfuricans*. Even our later experiments in presence of *Desulfovibrio desulfuricans* the hydrogen uptake by different powdered (200 mesh) raw Coals (KCER#71637 or WKY#9, KCER#4677, KCER#91182 or KY#11), pretreated Coal (KCER#91182P), asphaltene, DPM and MB showed promising results. The hydrogen uptake by pretreated Coal (KCER#91182P) and asphaltenes were 2370 and 1793 5mol/g of coal respectively. These uptake values are much higher than any of the raw coals studied. Similarly, in the presence of *S. brierleyi* hydrogen uptake by Coals KCER#91182 and KCER#91182P has been observed only at the end of 144 hours of incubation. However, hydrogen uptake by asphaltene and diphenylmethane has been observed right from the end of 18 hours of incubation.

Effect of *S. brierleyi*, *D. desulfuricans* and Oil-2 isolate on DPM and Coal (KCER#91182) were observed in the presence of organic solvent, benzene. Although maximum bacterial growth was observed in the absence of benzene, the experiment showed that the bacteria did grow even in the presence of 80% benzene in the medium. Analysis of aqueous phase (extracted with methylene chloride) of the run in presence of benzene, by GC-MS showed a major fragment with

m/z value 94 resembling phenol was observed.

Sulfolobus brierleyi has been used to study the formation of in-situ mixed metal catalysts (Mo and Ni) containing active iron. The amount of iron released into aqueous phase depends on the amount of coal used as substrates. *Sulfolobus brierleyi* showed a definite growth in presence of 200 ppm of ammonium molybdate. Chemical liquefaction results of different coals under varied conditions treated with *D. desulfuricans* and *S. brierleyi* showed enhancement in liquefaction to a maximum extend of 7%.

It was clearly noticed that *S. brierleyi* utilized dibenzothiophene and thiophene which were present in coal-liquid to the extent of 27% and 36% respectively. However, it did not utilize other compounds viz. coal-liquid as such, methyl disulfide, ethyl disulfide and ethane thiole.

MATERIALS AND METHODS

Growth and collection of the cells of *Desulfovibrio desulfuricans*. Composition of growth medium (g/l) is given in Table 1. Pre-reduced sterilized medium was prepared under hydrogen atmosphere. It was inoculated with 10% culture broth and incubated at 37°C for 7 days. The broth was centrifuged and the cells were collected under anaerobic conditions. Cells were finally washed with phosphate buffer (0.1M & pH 7.0) containing 10 mM dithiothriitol as a reducing agent. These cells were used for all hydrogen uptake experiments. Growth and collection of active cells of *Sulfolobus brierleyi*. Composition of growth medium (g/l) is given in Table 2. After addition of 10% inoculum the pH of the medium was continously adjusted between 1.7-2.0 by adding sodium carbonate solution. Cells were collected by centrifuging the broth and tested for oxygen uptake to check their activity. These active cells were used for all experiments conducted. Hydrogen uptake measurement using Warburg apparatus by Coal and Diphenyl methane Bacteria used in this experiment were *S. brierleyi* and *D. desulfuricans*. For this experiment, *S. brierleyi* was first grown aerobically, harvested, and the experiment was then performed under anaerobic conditions. The *D. desulfuricans*, being a strict anaerobe, was grown under anaerobic conditions and used for the experiment. The Warburg apparatus essentially consists of a manometer attached to a flask. The design of the flask and the manometer is such that it is possible to introduce a known gas into the system and then seal it from the surrounding air. A thermobarometer consisting of only the medium (at pH = 2) in a hydrogen atmosphere was used to follow the effect of temperature on the hydrogen pressure. The Methylene Blue

acted as an indicator of hydrogen uptake into the solution. The experimental flasks consisted of

- 0.1 % diphenyl methane in medium (pH = 2) + cells (10 % by vol.) in hydrogen atmosphere.
- 5 % coal slurry in medium (pH =2) + cells (10 % by vol.) in hydrogen atmosphere.

The total volume of liquid in all cases was 3 ml. Flasks with *S. brierleyi* and *D. desulfuricans* were immersed in a water bath maintained at 60°C and 30°C respectively. Any uptake of hydrogen would then be observed as a level change in the manometer. Experimental conditions for hydrogen uptake by different coals and coal-related substrates in presence of *D. desulfuricans*. The medium composition is given in Table 1. However, lactate and yeast extract were eliminated for these experiments . Coal samples were taken into serum vials before autoclaving them containing prereduced growth medium (50 ml per vial under zero grade H₂ atmosphere, whereas, DPM and MB were injected into vials using hypodermic syringe . All vials were incubated at 37°C with 100 RPM in a Psycrotherm™ Controlled Environment Incubator Shaker . After allowing 30 min. stabilization time 2ml of cell suspension (4.52 mg cell protein / vial) was added only to the test vials. Gas samples were taken periodically using Unimetrics gas tight syringe and analyzed by GC.

Experimental conditions for hydrogen uptake by different Coals and Coal-related substrates using *S. brierleyi*.

Medium composition is given in Table 2. However, yeast extract and vitamin mixture were excluded from the medium. The coal samples, asphaltene, DPM and MB were added to 50 ml of sterilized growth medium contained in serum vials. The head space of the vials was flushed with zero grade H₂ then sealed with rubber septum and aluminum cap. All vials were incubated at 60°C with 100 RPM in a Psycrotherm™ Controlled Environment Incubator Shaker. After allowing 30 min. stabilization time 2 ml of cell suspension (6.36 mg of cell protein / vial) was added to all test vials. Gas samples were taken periodically using Unimetrics gas tight syringe analyzed by GC. Culture conditions for the action of bacteria on Diphenyl Methane and Coal (KCER#91182) present in medium, medium-benzene mixture *Sulfolobus brierleyi*, *D. desulfuricans*, and Oil-2 isolate were used for this study. The bacteria were grown under anaerobic conditions in recommended growth media, harvested and resuspended in the medium. In all cases the liquid phase was 100 ml and the gas phase was 25 ml consisting of 80 % hydrogen and 20 % carbon dioxide. Table 6 shows the treatment steps used in this experiment. For experiment on coal in presence of *D. desulfuricans*, 100 grams of coal was suspended in a

liter of medium and pH was adjusted to 7.4. For the experiments with medium-benzene mixture, 0%, 20%, 50%, and 80%, of benzene (V/total Volume of medium) was added. Specific conditions for controls and tests are given in Table 7. The total volume in each case was 400ml. Twenty ml of bacterial suspension containing 1.8 mg protein was added to each flask. All the flasks with the conditions mentioned in Table 7 were flushed with hydrogen and sealed. The flasks were maintained at 35°C and agitated on an incubator shaker. Samples were taken at periodic intervals and the UV spectra of the aqueous phase was observed.

Experimental conditions for in-situ mixed-metal catalyst formation using *S. brierleyi*. These experiments containing 5% of Coal (KY#11) were conducted in 10 litre capacity Biostat E fermenter maintaining at a constant pH 2.5, temperature at 60°C and continuously sparged with air and CO₂. However, the amount of coal varied from 1 to 10% by weight in different runs. In addition, ammonium molybdate (200 ppm) was also added in one of the runs. Finally, cells of *S. brierleyi* containing 70 mg of cell protein was added per one liter of medium. periodically samples were taken for analytical purposes. Conditions for the activity of *D. desulfuricans* on coal with varying amounts of benzene to study variation in extent of liquefaction of coal The culture conditions are given in Table 8. This experiment was carried out under H₂ gas using different amounts of benzene. Suitable controls are also introduced. Experimental conditions for utilizing organic sulfur compounds added to coal-liquid and aqueous medium mixture by *S. brierleyi*. Composition of the medium is given in Table 2. However, vitamin solution was not added to the medium in this case. Different organic sulfur compounds (0.1%) namely Dibenzothiophene (DBT), Thiophene, Methyl disulfide, Ethyl disulfide, Ethane thiole were added separately into different vials containing 2.5 ml of coal-liquid and 50 ml of growth medium. Finally, *S. brierleyi* cells were added into the test vials and incubated in Psycrotherm™ Controlled Environment Incubator Shaker at 60°C with 100 RPM. One set of vials (one control + one test) were removed at regular intervals for analytical purposes. Analytical methods: Protein estimation was done using Goa Method. (Goa,1953) Quantitative and qualitative gas analysis was carried out by Shimadzu GC-9A attached with data processor Chromatopac C-R 1B Organic sulfur and metabolic products of it as well as products released from coal into medium were analyzed by Helwett & Packard GC-MS 5890 after extracting the aqueous phase with methylene chloride. All absorption spectra (UV & Visible) were obtained using Beckman DU-50 Spectrophotometer and Hp 8452 Spectrophotometer with appropriate blanks. Sulfate was

estimated as barium sulfate with the Spectrophotometer at 440 nm. Liquid phase iron was quantified by Varian 375 Atomic Absorption Spectrophotometer. Oxygen uptake by cells of *S. brierleyi* was done with an oxygen polarograph (Yellow Springs Instruments, Ohio) at 60°C. Presence of hydrogenase was studied with reduction of MB using Spectrophotometer. Coals used in this study and their identification numbers. The different coals used in this study are KCER# 71637 (WKY#9); KCER #4677 (FIRE CLAY); KCER #91182 (KY #11); KCER #91182P (Coal was subjected to partial liquefaction conditions for one hour at 200°C under hydrogen atmosphere as a pretreatment); Asphaltene (obtained at 450°C).

RESULTS AND DISCUSSION

Hydrogen uptake by different coals and coal-related substrates in presence of *D. desulfuricans* and *S. brierleyi*. It was discovered in 1931, the enzyme hydrogenase catalyzes the reversible activity of molecular hydrogen (Stephenson & Stickland, 1931). The enzyme was found to be widespread in bacteria of different taxonomic and physiological types (Gest 1954). Hydrogenase is involved in all biological reactions in which hydrogen is consumed and evolved (Schneider and Schlegel 1976). Hydrogen transfer reactions in microbial communities which showed production and use of hydrogen often represent a classical food chain and special feature of the food chain is that hydrogenotrophs (H₂ utilizing microorganisms), by using H₂, can cause hydrogenogens (H₂ producing microorganisms) to produce more H₂ than they would produce in absence of hydrogenotrophs. These systems are present in various ecosystems such as rumen, large intestine, anaerobic waste decomposition, natural aquatic environments (Wolin 1982). In fact, hydrogen transfer reactions including interspecies transfers is one of the latest and leading areas of research (Slater, 1981; Belaich et al., 1990). It had also been reported hydrogen cycling as a general mechanism for energy coupling within the sulfate reducing bacteria e.g. *Desulfovibrio* sp. containing cytoplasmic and periplasmic hydrogenases (Odom & Peck 1981, Pankhania et al., 1986). However, recent work on species of *Desulfovibrio* has demonstrated that members of this genus may contain three types of hydrogenases. These are classified by their metal reaction centers: (1) iron, (2) iron - nickel and (3) iron-nickel-selenium. These enzymes have been found in the cytoplasm, periplasmic space and attached to the membrane (Hardy 1983). But it has not been clearly determined if the utilization of a particular source of hydrogen is related to the type of hydrogenase or its location in bacterial cells.

Many species of sulfate-reducing bacteria (SRB) in the genus *Desulfovibrio* can use hydrogen as an energy source, with acetate and CO₂ as carbon and sulfate as terminal electron acceptor (Czechowski et al., 1990). It is also interesting to know that some species of *Desulfovibrio* can also use cathodically-generated hydrogen from metal as the sole electron source for the reduction of sulfate, as an energy source for limited growth, or as a supplementary energy source for increased reduction of sulfate. This removal of hydrogen by sulfate-reducers from the surface of a metal could be an essential step in the corrosion process, e.g. cathodic depolarization or alternative cathodic depolarization (Czechowski et al., 1990). Since the time of Wolzogen Kuhr and Van der Vlugt (1934), much of the considerable research into how the SRB actually promote corrosion shows that the products of SRB metabolism may singly, or in combination (i.e. iron sulfide, H₂S, elemental S, phosphorous compounds and organic acids) accelerate corrosion (Bryant & Laishley 1990). *Desulfovibrio vulgaris* (Hildenborough) and other *Desulfovibrio* species also showed their capacity to adapt to grow on H₂ as energy source. Therefore, SRB are capable of growth on a wider range of substrates are thus very flexible ecologically, (Pankhania et al. 1986). Although many of the SRB have the ability to utilize hydrogen, there are also many other non SRB that possess the enzyme hydrogenase and have the ability to produce sulfide from partially reduced inorganic sulfur compounds (Bryant & Laishley 1990). Keeping the reversible nature of the hydrogenase in view, we have taken *D. desulfuricans* and *S. brierleyi* to study any possibility of hydrogen uptake preferably for reductive depolymerization of different coals and coal related substrates.

Desulfovibrio vulgaris with a highly active Fe-containing periplasmic hydrogenase, *D. salexigens* with a Fe-Ni-Se periplasmic hydrogenase, and *D. multispirans* with Fe-Ni cytoplasmic hydrogenase utilized hydrogen gas. Hydrogen was utilized within 1 to 4 days. The periplasmic hydrogenase in anaerobic bacteria has been proposed to be a specific adaptation for utilization of low levels of hydrogen for activity and growth. Hydrogen utilization by *D. multispirans* was unexpected as this bacterium has so far been found to have only a cytoplasmic hydrogenase. Therefore utilization of hydrogen will indicate that the hydrogenase is bidirectional. This would necessitate a strict specialization of electron transfer proteins and carriers for the bidirectional regulation of the enzyme as proposed for *D. gigas* (Czechowski et al., 1990).

Our preliminary results on hydrogen uptake by DPM and Coal (KCER#91182) in presence of *S. brierleyi* (Fig. 1) and *D. desulfuricans* (Fig. 2) using Warburg apparatus are shown in

Figures 1 and 2 and Table 3. The hydrogen uptake for MB, Coal, and DPM in micro liters versus time is plotted in Figure 1 and Figure 2. Table 3 gives the calculated rate constants in terms of micro moles hydrogen / g substrate / hour and gives a comparison between the two bacteria in terms of hydrogen uptake. But to deduce that *S. brierleyi* is a better organism for hydrogenation on this basis may be wrong since the hydrogenase enzyme of the *D. desulfuricans* is very sensitive to oxygen and may have been inactivated during the transfer of bacteria.

The results of hydrogen uptake (measured by GC) by different coals and coal-related substrates in presence of *D. desulfuricans* are shown in Tables 4 and Figs. 3 to 9. The presence of hydrogenase of *D. desulfuricans* was shown by reduction of the MB. In case of *D. desulfuricans* hydrogen uptake was shown from 24 hours onwards and all substrates tested showed considerable uptake. The summarized hydrogen uptake values by different substrates in presence of *D. desulfuricans* is shown in Table 4. Maximum uptake (2370 5moles/gram substrate) was shown by the pretreated coal (Coal #91182P). Among the unprocessed coals, Coal #4677 showed the maximum hydrogen uptake (1109 5moles/gram substrate).

The summarized hydrogen uptake (measured by GC) values by different substrates in presence of *S. brierleyi* is given in Table 5 and Figures 10 and 11. Methylene Blue, Coal # 91182P and Coal#91182 showed uptake only at the end of 144 hours. This could be due to the adaptation time required by the organism. However, hydrogen uptake by asphaltene and DPM were shown right from 18 hours incubation. Maximum uptake was shown by asphaltene (1908 5moles / gram substrate). These studies were done under strictly anaerobic conditions and results of hydrogen uptake showed much improvement over the results obtained using Warburg apparatus. Moreover, *D. desulfuricans* showed more uptake values than that of *S. brierleyi*.

The nature and location of the enzyme hydrogenase present in *D. desulfuricans* and *S. brierleyi*, responsible for hydrogen uptake is not clearly understood to substantiate its precise role in hydrogenating coal substrates. It is also important to note that there was hydrogen uptake even in control runs which did not contain microorganisms, but uptake was less when compared to test runs.

Action of bacteria on DPM and coal present in medium, medium-benzene mixture:

These experiments were performed to see whether benzene influences bacteria in metabloizing DPM and coal under anaerobic conditions. Figure 12 shows the changes in the absorbance at 260 nm, when *S. brierleyi* was grown on benzene, benzene-aqueous medium mixture. It should

be noted that the X - axis represented as treatment # corresponds to that shown in table 6. Similar experiments were also conducted with *D. desulfuricans* and Oil-2. From all the figures it can be seen that the absorbance at 260 nm considerably diminished in the cases where benzene was present but the maximum growth was observed in the absence of benzene. In case of *D. desulfuricans* and Oil-2 also similar observations were noted (data not shown here). But the fact to be noted is that the bacteria showed good growth even in mixtures containing 80 % benzene. These results were obtained when the cultures were grown under a mixture of gases (80% H₂ and 20% CO₂).

Figures 13 and 14 show the UV spectra of the various runs after 0, 5 and 9 days. When the experiment was carried out under H₂ gas and without benzene (Fig. 13) showed large increase in the absorbance between 200 and 350 nm range. For the flasks containing benzene there was an increase in the absorbance values at 210 and 256 nm (characteristic absorbance of benzene) and also wavelengths in between.

A total organic carbon (TOC) analysis of the aqueous phase, obtained by treating the medium with *D. desulfuricans*, of the various runs was performed after 10 days (Table 7). As seen from Table #7, there was a large decrease in the TOC of the run containing no benzene as compared to the control, while the runs with benzene had significantly higher TOC. At the end of the run (15 days) the aqueous phase for the run with 50% benzene was extracted with methylene chloride and the methylene chloride phase was analyzed using GC-MS. Figures 15 and 16 show the results of the GC-MS analysis of the components extracted from the aqueous phase by methylene chloride. The GC-MS analysis of the runs with 50 % benzene showed a compound resembling phenol in its' mass fragments, the major fragment being 94 (m/z). Thus one could conclude that presence of an organic solvent could influence the metabolism of coal-related substrates by bacteria. Bioformation and optimization of in-situ mixed-metal catalysts containing active iron.

Previous studies (Bhattacharyya et al. 1990) with thermophilic *S. brierleyi* indicated significant changes in iron forms of biotreated coals. Depending on the operating conditions (such as pH, CO₂/air ratio, initial FeS₂ concentration), reprecipitation of iron compounds on coal particle surface occurred in different forms. Precipitation of iron was clearly influenced by pH, temperature and addition of iron compounds e.g. Fe₂(SO₄)₃ (Norton et al. 1990). There are also other catalysts based on molybdenum, cobalt and nickel compounds which enhance liquefaction

of coal (Besson et al. 1990). Fortunately, these metals are also required for the growth of microbes and thus allowing us to incorporate tolerable levels. Water soluble compounds such as ammonium molybdate, nickelous sulfate were used to study the possibility of enhancing the formation of FeOOH and mixed-metal fine crystals in the presence of *S. brierleyi*.

It was observed that the release and reprecipitation of liquid phase iron pattern (Figure 17) which was obtained by using 1% coal. However, the maximum amount of iron released into the liquid was only 67 PPM unlike our last report (Bhattacharyya et al. 1990) in which approximately 400 PPM (when 5% coal was used) was released. Therefore, the quantity of iron released varies with the amount of substrate taken. However the run with 10% coal did not support the growth of *S. brierleyi*. The presence of ammonium molybdate (200 ppm) clearly showed increase in cell protein. However, the amount of iron released into the aqueous phase was tremendously reduced to the level of 5 to 12 ppm (Figure 18). This could possibly due to precipitation of iron in the presence of molybdenum. The coal samples are given for EXAFS and Mössbauer analysis to know the nature of the metal precipitation on coal surface. Chemical liquefaction of coals obtained from different ways of microbial treatment. The results of liquefaction of different biotreated coals are given in Tables 9 and 10. In the presence of 20 and 50% benzene *D. desulfuricans* enhanced the liquefaction to the extent of 7%. However, 80% benzene did not result in any improvement of liquefaction (Table 9). But, *D. desulfuricans* when treated with Coal (KCER#4677) under strict anaerobic conditions with H₂ gas showed increase of liquefaction to the extent of 5%. In fact, we also have data to support this improvement in liquefaction of the biotreated Coal (KCER#4677) which showed 1109.5 moles H₂ uptake per gram of coal. Similarly, Coal (KCER#91182) treated with *S. brierleyi* in presence of molybdenum improved liquefaction by 2%. Therefore, benzene could probably play a vital role in further improving the percent of liquefaction under strict anaerobic conditions particularly in a H₂ atmosphere. Microbial upgrading of liquefied coal by organic sulfur reduction. Many microorganisms can use coal's inorganic sulfur as a source of energy (Kilbane & Bielaga 1990). Coal also contains organic sulfur compounds such as DBT, thiophene & benzothiophene etc. Reports describing DBT oxidation by *Pseudomonas* sp., *Beijerinckia* sp., *S. acidocaldarius* have appeared in literature (Monticello et al., 1985). However, attempts to use bacteria to remove organic sulfur from coal have not yet met with similar degree of success.

Sulfolobus sp. have been widely used for desulfurization of pyritic sulfur of coal

(Bhattacharyya et al. 1990). Recently *S. acidocaldarius* was also reported to oxidize DBT (Kargi 1984, 1985, 1986). Oil-2, which was isolated in our lab, was able to oxidize organic sulfur present in the oil phase (Khalid et al. 1989). Since, *S. brierleyi* is physiologically very similar to *S. acidocaldarius*. *S. brierleyi* was used in the present study to examine its ability to utilize organic sulfur compounds added to coal-liquid.

The results of organic sulfur utilization in presence of *S. brierleyi* are given in table 11. DBT and thiophene were utilized to the extent of 27 and 36% respectively. There is a concomitant increase of sulfate content in the aqueous phase and increase in cellular protein content. DBT and thiophene were oxidized with the supplement of yeast extract by the cells of *S. brierleyi*. However it is not clear whether yeast extract is necessary for the oxidation of DBT and thiophene. From the results, it also appears part of the carbon might have gone into cell mass. Accumulation of 3-hydroxy-2-formyl benzothiophene or other metabolic products were not seen in the GC-MS analysis of the aqueous medium extracted with methylene chloride.

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TABLE 1. Composition of medium used for growth of *Desulfovibrio desulfuricans*

Solution A		Solution B	
K ₂ HPO ₄	0.50	Ferric Amm.Citrate	0.50 grams
NH ₄ Cl	1.00	Distilled H ₂ O	10.0 ml
Na ₂ SO ₄	5.00		
CaCl ₂ .2H ₂ O	0.02		
MgSO ₄ .7H ₂ O	0.20	Solution C	
DL Sod. Lactate	5.00	Sod. thioglycollate	0.10 grams
Yeast extract	0.05	Ascorbic acid	0.10 grams
Resazurin	.001	Distilled H ₂ O	10.0 ml
Distilled water	1 liter	Adjust pH to 7.8	

TABLE 2. Composition of medium used for growth of *Sulfolobus brierleyi*

Medium Composition		Wolfe's Vitamin solution	
(NH ₄) ₂ SO ₄	1.30 grams	Biotin	2.00 mgrams
KH ₂ PO ₄	0.28 grams	Folic acid	2.00 mgrams
MgSO ₄ ·7H ₂ O	0.25 grams	Pyridoxin HCl	10.0 mgrams
COCl ₂ ·2H ₂ O	0.07 grams	Thiamine HCl	5.00 mgrams
FeCl ₃ ·6H ₂ O	0.02 grams	Riboflavin	5.00 mgrams
MnCl ₂ ·4H ₂ O	1.8 mgrams	Nicotinic acid	5.00 mgrams
Na ₂ B ₄ O ₇ ·10H ₂ O	4.5 mgrams	Ca-pantothenate	5.00 mgrams
Yeast extract	0.20 grams	Cyanacobalamine	100 mgrams
Wolfe's Vitamin Soln.	10.0 ml	p-aminobenzoic acid	5.00 mgrams
Distilled H ₂ O	1 liter	Thioctic acid	5.00 mgrams
Adjust pH to 2.0 with 10N H ₂ SO ₄ .		Distilled H ₂ O	1 liter

Table 3. Comparative rates of hydrogen uptake (measured by Warburg apparatus) catalyzed by *Sulfolobus brierleyi* and *Desulfovibrio desulfuricans*

Organism	Substrate	Hydrogen Uptake $\mu \text{ mole g}^{-1} \text{ coal h}^{-1}$
<i>S.brierleyi</i>	Coal ²	44.10
<i>D.desulfuricans</i>	Coal ²	4.63
<hr/>		
		$\mu \text{ mol} / \mu \text{ mol DPM}^* / \text{h}$
<i>S.brierleyi</i>	DPM	0.5357
<i>D.desulfuricans</i>	DPM	0.0701
<hr/>		
		$\mu \text{ mol} / \mu \text{ mol MB}^{**} / \text{h}$
<i>S.brierleyi</i>	MB	619
<i>D.desulfuricans</i>	MB	48

² - KCER # 91182

* - DPM - Diphenyl methane

** - MB - Methylene blue

**Table 4. Hydrogen uptake by different coal-related substrates
in the presence of *Desulfovibrio desulfuricans* measured by GC**

Substrate	Hydrogen Uptake (micromoles / g substrate)			
	24 hrs	36 hrs	48 hrs	144 hrs
Coal # 71637 ¹	---	288	373	192
Coal # 4677 ¹	349	---	801	1109
Coal # 91182 ¹	---	585	486	293
Coal# 91182P ^{*1}	634	---	2370	---
Asphaltene	263	---	1793	783
DPM ^{**}	0.025	---	0.539	1.117
MB ^{**}	5.972	---	58.922	56.437

¹ - Denotes KCER numbering of different coals

* - Pretreated coal (200°C and hydrogen atmosphere)

** - Hydrogen uptake for Diphenyl Methane (DPM) and Methylene Blue (MB) are expressed as micromoles / micromole substrate.

Table 5. Hydrogen uptake by different coal-related substrates in the presence of *Sulfolobus brierleyi* measured by GC

Substrate	Hydrogen Uptake (micromoles / g substrate)			
	18 hrs	48 hrs	72 hrs	144 hrs
Coal # 91182 ¹	---	---	---	111
Coal# 91182P ^{*1}	---	---	---	423
Asphaltene	401	1466	582	1908
DPM ^{**}	0.42463	0.17565	0.17474	0.27456
MB ^{**}	---	---	---	1.4851

¹ - Denotes KCER numbering of different coals.

* - Pretreated coal (200°C and hydrogen atmosphere)

** - Hydrogen uptake for Diphenyl Methane (DPM) and Methylene Blue (MB) are expressed as micromoles / micromole substrate.

Table 6. Different culture conditions used to test effect of various bacteria in Diphenyl Methane (DPM) and coal (KCER #91182)

Treatment #	Lactate	Coal	DPM 0.1 %	Benzene	Medium
1	+	-	in benzene	80 %	20 %
2	-	-	in benzene	80 %	20 %
3	-	-	in benzene	50 %	50 %
4	-	-	in water	-	100 %
5	-	+	in benzene	80 %	20 %
6	-	+	in water	80 %	20 %

Biotreatment conditions

Medium : Modified Starkey's medium C (ATCC # 207), .05 g/l yeast extract
 In all cases liquid phase was 100 ml in volume and gas phase was 25 ml consisting of 80% hydrogen and 20% carbondioxide

Table 7. Total organic carbon analysis of aqueous phase of the experiment with *Desulfovibrio desulfuricans* on coal (KCER # 91182) in benzene/medium mixtures

Sample #	Sample Description	TOC (ppm)
1	<i>D.desulfuricans</i> medium containing salt solution and 0.05 g/l yeast extract.	2.36
2	Control containing medium+10% coal. (No benzene, no bacteria)	110
3	Control containing 50/50 benzene/medium mixture + 10% coal (no bacteria)	310
4	<i>D.desulfuricans</i> on 10% coal in medium. (No benzene)	15.2
5	<i>D.desulfuricans</i> on 10% coal in 50/50 benzene/medium mixture.	582
6	<i>D.desulfuricans</i> on 10% coal in 20/80 benzene/medium mixture.	523

Biotreatment conditions.

Medium : Modified Starkey's medium C (ATCC #207) under hydrogen atmosphere, 0.05 g/l Yeast extract, no sodium lactate.

Table 8. Description of the various runs of *Desulfovibrio desulfuricans* on coal (KCER #91182) in the presence of varying amounts of benzene

Run #	Sample Description - Coal from :-
Control 1	Control containing medium+10% coal. (No benzene, no bacteria)
Control 2	Control containing 50/50 benzene/medium mixture + 10% coal (no bacteria)
Run 1	<i>Desulfovibrio desulfuricans</i> on 10% coal in medium. (No benzene)
Run 2	<i>Desulfovibrio desulfuricans</i> on 10% coal in 20/80 benzene/medium mixture
Run 3	<i>Desulfovibrio desulfuricans</i> on 10% coal in 50/50 benzene/medium mixture
Run 4	<i>Desulfovibrio desulfuricans</i> on 10 % coal in 80/20 benzene/medium mixture

Biotreatment conditions

Medium : Modified Starkey's medium C (ATCC #207), 0.05 g/l yeast extract, no sodium lactate.

Substrate : Coal (KCER # 91182) 10% by weight

Atmosphere : Hydrogen.

Table 9. Chemical liquefaction results of biotreated (KCER #91182) coal in the presence of varying amounts of benzene

Liquefaction Products Wt. % MAF*	Control 1	Control 2	Run 1	Run 2	Run 3	Run 4
Gas	1.19	1.11	1.09	1.16	1.08	1.29
Oils	11.19	13.62	13.32	11.94	14.08	10.39
Asphaltenes	38.01	22.43	20.35	23.92	23.08	27.81
Preasphaltenes	5.33	21.39	25.78	28.67	27.61	21.05
IOM**	44.28	41.45	39.46	34.31	34.15	39.46
Conversion	55.72	58.55	60.54	65.69	65.85	60.54

MAF* - Moisture and ash free basis.

IOM** - Insoluble organic matter.

Biotreatment conditions are given in table #8

Liquefaction Conditions.

Temperature	: 385°C
Atmosphere	: 800 p.s.i Hydrogen
Reaction Time	: 15 minutes
Solvent used	: Tetralin

Table 10. Chemical liquefaction results of different coals (5 %) treated with
Desulfovibrio desulfuricans and *Sulfolobus brierleyi*

Liquefaction Products Wt. %	Coal (KCER # 4677) ¹		Coal (KCER # 91182) ¹		Coal (KCER # 91182) ²	
	Control	Test	Control	Test	Control	Test
Gas			1.49	1.80	1.36	1.36
Oils	10.24	9.07	14.23	15.04	14.12	14.12
Asphaltenes	16.98	18.63	17.01	18.06	19.45	19.45
Preasphaltenes	22.00	26.83	14.51	11.93	11.75	11.75
IOM**	50.78	45.43	52.76	53.17	53.32	53.32
Conversion	49.22	54.57	47.24	46.83	43.41	46.68

- 1 - Test run was treated with *D.desulfuricans*. Liquefaction was carried out at the end of 144 hrs.
- 2 - Test run was treated with *S.brierleyi*. Liquefaction was conducted at the end of 18 days.
- IOM**- Insoluble organic matter.

Liquefaction conditions.

Temperature : 385°C
 Atmosphere : 800 p.s.i Hydrogen
 Reaction Time : 15 minutes
 Solvent used : Tetralin

**Table 11. Removal of organic sulfur added to coal-liquid mixed with aqueouss medium using
*Sulfolobus brierleyi***

Organic sulfur compound + coal-liquid	Protein in aqueous medium ($\mu\text{g/ml}$)		Organic sulfur utilized (%)	Sulfate in aqueous medium ($\mu\text{g/ml}$)	
	1st day	20th day		1st day	20th day
Dibenzothiophene	60	90	27	Nil	65
Thiophene	40	80	36	Nil	53
Coal-liquid (alone)	80	95	Nil	Nil	Nil
Methyl disulfide	38	28	Nil	Nil	Nil
Ethyl disulfide	58	54	Nil	Nil	Nil
Ethane thiole	56	65	Nil	Nil	Nil

Fig.1. Hydrogen uptake into Coal, Diphenyl Methane and Methlene Blue in the presence of *Sulfolobus brierleyi*

Fig.2. Hydrogen uptake into Coal, Diphenyl Methane and Methlene Blue in the presence of *Desulfovibrio desulfuricans*

Fig.3. Hydrogen uptake in the presence of *Desulfovibrio desulfuricans* on Coal # 4677.

Fig.4. Hydrogen uptake in the presence of *Desulfovibrio desulfuricans* on Coal # 91182.

Fig.5. Hydrogen uptake in the presence of *Desulfovibrio desulfuricans* on pretreated (200°C & hydrogen atm.) Coal # 91182P.

Fig.6. Hydrogen uptake in the presence of *Desulfovibrio desulfuricans* on Asphaltene

Fig.7. Hydrogen uptake in the presence of *Desulfovibrio desulfuricans* on Diphenyl Methane (DPM).

Fig.8. Hydrogen uptake in the presence of *Desulfovibrio desulfuricans* on Methylene Blue (MB).

Fig.9. Hydrogen uptake in the presence of *Desulfovibrio desulfuricans* on Coal # 71637.

Fig.10. Hydrogen uptake in the presence of *Sulfolobus brierleyi* on Diphenyl Methane (DPM).

Fig.11. Hydrogen uptake in the presence of *Sulfolobus brierleyi* on Asphaltene.

Fig.12. UV absorbance of the aqueous phase at 260nm when acted upon by *Sulfolobus brierleyi* under various treatments.

Fig.13. Action of *Desulfovibrio desulfuricans* on coal (10% slurry) in Desulfuricans medium. Absorbance of the aqueous phase after 0, 5, and 9 days.

Fig.14. Action of *Desulfovibrio desulfuricans* on coal (10% slurry) in 50% Benzene-medium mixture. Absorbance of the aqueous phase ater 0, 5, and 9 days.

Fig.15. GC-MS analysis of Methylene Chloride extract of the aqueous phase of the control blank containing 10% coal slurry in 50% Benzene-medium mixture.

Fig.16. Action of *Desulfovibrio desulfuricans* on coal (10% slurry) in 50% benzene-medium mixture. GC-MS analysis of Methylene Chloride extract of the aqueous phase after 10 days.

Fig.17. Variation of liquid phase iron concentration with time for 200 mesh coal (KCER#91182) of 1% slurry treated with *Sulfolobus brierleyi* in the presence of CO₂ at 60°C and pH 2.5.

Fig.18. Variation of liquid phase iron concentration and protein for coal plus ammonium molybdate medium treated with *S.brierleyi*

Project III.2 Chemical Routes to Breaking Bonds: New Approaches to Low Temperature

Liquefaction (John H. Penn)

INTRODUCTION

During the past year, we have completed our evaluation of 1,4-dihydroquinone (DHQ) as a coal hydrogenation source. DHQ yields larger amounts of THF-extractables with several given coals than standard hydrogen sources. The enhancement of THF-solubility occurs at very low temperatures (ca. 200°C).¹ Model compound studies show that DHQ functions by providing a source of hydrogen to quench radical chain processes.

RESULTS AND DISCUSSION

EXPERIMENTAL

Samples of coal were obtained from the Argonne Premium Coal Sample Bank. Bakerstown coal and Sewell coal were obtained from the West Virginia Coal Sample Bank.

A given weight of coal and a given weight of the added reagent were added to 5 mL of acetonitrile (CH_3CN , freshly distilled from NaH) in a 10 mm glass tube. Oxygen was removed from the solution *via* 3 freeze-pump-thaw degassing cycles and the sample tube was then sealed *in vacuo*. The sample tube was placed in a tubing bomb reactor to which excess CH_3CN was added to equalize the pressure on the outside and inside of the glass. The tube was then placed in an oil bath at the indicated temperature for the indicated length of time. After removal from the oil bath, the contents of the glass tube are placed in a Soxhlett extractor and refluxed with THF for 24 h. After evaporation of the THF *in vacuo*, the weight of the extract and the weight of the insolubles were determined.

COAL SOLUBILITY STUDIES

In order to evaluate the effect of a reagent on liquefaction of coal, control experiments were performed with no added reagent to establish the amount of extractables without reagent. In all cases, the coal was heated at 200°C for 48 h in the indicated solvent. Not surprisingly,

Table I. Coal Extractability Without Added Reagent

Coal	Coal Rank	Solvent	%THF Extractable
Bakerstown		CH ₃ CN	19.9
		THF	25.9
		C ₆ H ₆	21.7
		C ₆ H ₁₂	4.8
Sewell		CH ₃ CN	19.5
Pittsburgh #8	HV Bituminous	CH ₃ CN	34.4
Blind Canyon	HV Bituminous	CH ₃ CN	26.4
Upper Freeport		CH ₃ CN	12.7
Beulah-Zap	Lignite	CH ₃ CN	5.4

the choice of solvent does have an effect upon the amount of THF-extractables obtained in these experiments. The results of these experiments are given in Table I. As expected, there is a solvent dependence on the amount of THF-extractability as evidenced by the effects shown on the Bakerstown coal.

Following discussions at the CFFLS annual technical meeting in Utah during which our total recovery was questioned, we performed experiments to evaluate whether our experimental results could be explained by incomplete solvent evaporation during the work-up procedure. For all coals, acetonitrile seems to give somewhat higher yields than quantitative. This suggests that there is solvent incorporation into either the residue or the THF extract during the low temperature heating of coal with acetonitrile. This increased mass is observed for several different coals with 110-120% mass balance being obtained no matter how long the samples are evacuated to remove all traces of extraction or original solvent. However, when other solvents are used to run the reaction (e.g., THF or benzene), yields less than 100% are observed in all cases. Therefore, we believe that the increased mass balances in the acetonitrile experiments are due to solvent incorporation into the coal.

The results of adding a 1:1 weight ratio of dihydroquinone (DHQ) to the coal are shown in Table II. In these experiments, the coal and the DHQ have been heated together in

the indicated solvent for 48 h at 200°C. In this table, the effects of the reagent are given by a Liquefaction Enhancement (L.E.) which has been defined by eq (1). In this equation, THF_{coal} and THF_{DHQ} are the amounts of extractables when either the coal or DHQ are treated alone. Normalization to the starting amount of coal is performed to enable comparison of one coal to another coal.

$$L.E. = \frac{(Total\ THF\ extract) - (THF_{coal} + THF_{DHQ})}{starting\ weight\ coal} \times 100\% \quad (1)$$

Table II. Enhancements Using 1:1 Weight Ratio of DHQ

Coal	Coal Rank	Solvent	L.E.
Bakerstown		CH ₃ CN	20.5
		THF	1.0
		C ₆ H ₆	2.3
		C ₆ H ₁₂	10.0
Sewell		CH ₃ CN	-1.9
Pittsburgh #8	HV Bituminous	CH ₃ CN	41.7
Blind Canyon	HV Bituminous	CH ₃ CN	7.8
Upper Freeport		CH ₃ CN	3.4
Beulah Zap	Lignite	CH ₃ CN	45.4

As can be seen in Table II, reasonable enhancements in the liquid yields are obtained. These results are made more remarkable when one considers that these LEs were obtained for temperatures as low as 200°C. A solvent dependence is noted for this effect, with only CH₃CN and cyclohexane (C₆H₁₂) showing positive enhancements for Bakerstown coal.

Efforts to optimize the L.E. from the coals using DHQ have been accomplished. In Table III, the amount of enhancement for different DHQ/coal weight ratios is recorded. This clearly shows that DHQ itself does not act as a catalyst, since >1:1 weight ratios of DHQ/coal are required to give optimal enhancements.

A second variable which has been examined is that of temperature (Table IV). For

Table III. Effect of Different Ratios of DHQ to Coal

Coal	Liquid Enhancement (%)	DHQ/Coal Ratio
Bakerstown	57.9 (4.6)	2
	65.9 (3.2)	1
	9.5 (0.6)	0.3
Sewell	8.4 (0.4)	2
	32.3 (4.2)	1
	2.3 (2.1)	0.3

Table IV. Effect of Temperature on DHQ/Coal Reactions (Using Constant DHQ/Coal Ratio = 1)

Coal	Liquid Enhancement (%)	Temperature (°C)	Time (h)
Bakerstown	-5.6 (0.4)	150	72
	65.9 (3.2)	200	48
	155.8 (0.4)	245	48
Sewell	19.0 (0.4)	150	72
	32.3 (4.2)	200	48
	141.4 (5.2)	245	48

both Bakerstown and Sewell coals, decreased enhancements are seen at 150°C. However, dramatic improvements are noticed at 245°C. While these results would seem to indicate that higher temperatures achieve better enhancements, improper mass balances were observed in the high temperature experiments, suggesting that incorporation of solvent problems could be more severe at these higher temperatures.

Of general interest is the capability of DHQ to enhance liquefaction relative to other reagents which have been used previously. The standard for coal liquefaction in the past

Table V. Comparison of DHQ to Other Liquefaction Reagents

Coal	Liquid Enhancement (%)	Reagent
Bakerstown	-13.1 (2.0)	Tetralin
	11.8 (3.0)	DHA
	65.9 (3.2)	DHQ
Sewell	-2.5 (2.5)	Tetralin
	9.5 (0.9)	DHA
	32.3 (4.2)	DHQ

All experiments used 2.72 mmol of react, 200°C, and 48 h of time. DHA=9,10-dihydroanthracene

seems to be tetralin. In addition, a second material which has been used in this Consortium has been 9,10-dihydroanthracene (DHA). These materials have the advantage of being able to donate hydrogen readily to coals. Therefore a comparison of DHQ to these reagents was deemed to be in order. In order to carefully examine the effects and not bias the system for the amount of hydrogen added, we added the same number of moles of tetralin, DHQ, and DHA to the various coal samples. Thus, 2.72 mmoles of reactant was added to a given weight of coal. Therefore, the same number of hydrogen atoms were available. As seen in Table V, in all cases DHQ outperformed tetralin and DHA by a considerable extent for both Bakerstown and Sewell coals. Therefore, we conclude from this data that DHQ shows exceptional capabilities to enhance the amount of THF extractables.

MODEL COMPOUND STUDIES

Because of the success with DHQ in enhancing THF extractables, we turned to model compound studies to evaluate the ability of DHQ to cleave ethers. Two ethers were chosen to model the reactivity of coal, because of their similarity to known functional groups in coal. These compounds were benzyl phenyl ether (BPE) and diphenylmethyl phenyl ether (DPMPE). The experimental procedure is similar to our reactions utilizing coal in which the compounds are dissolved in freshly distilled CH₃CN, followed by removal of O₂ by three freeze-pump-thaw cycles, and sealed under vacuum. The sample is placed in an oil bath at

the indicated temperature for the indicated time.

The reactivity of **DPMPE** is shown in eq (2). The products of the reaction were

(2)

determined to be phenol (PhOH), diphenylmethane (PhCH₂Ph), benzophenone (PhCOPh), 2-hydroxytriphenylmethane, 4-hydroxytriphenylmethane, 2,5-dihydroxytriphenylmethane, and 1,1,2,2-tetraphenylethane (TPE). The identification of these compounds rests on standard organic chemistry methodology wherein sufficient melting point data, GC/MS, IR, and/or NMR data have been obtained to rigorously establish the identity of the compounds. When no **DHQ** is added to the solution, 45% conversion is obtained, while equimolar **DHQ** yields *ca.* 55% conversion.² The appearance of **TPE** in the experiments with no added **DHQ** gives strong evidence that **DPMPE** undergoes homolytic bond cleavage to yield a diphenylmethyl radical and a phenoxy radical as the primary reaction pathway. Without available hydrogen atoms for abstraction, the diphenylmethyl radicals couple to yield **TPE**. In contrast, a lesser quantity of **TPE** was observed in the **DHQ** experiments, with diphenylmethane and 2,5-dihydroxytriphenyl methane being a part of the reaction mixture. Since the product yields of all products are qualitatively similar with and without added **DHQ**, the same reaction pathway is likely occurring under both conditions. This observed reaction is simply the homolytic bond cleavage of **DPMPE**. The role of **DHQ** in this reaction is to provide a source of hydrogen and a reactive ring structure to terminate radical chain processes.

A similar situation is obtained in the pyrolysis of benzyl phenyl ether (**BPE**) in the presence and absence of **DHQ** as shown in eq (3). The first thing to notice about **BPE**

is that the same amount of conversion is obtained (*i.e.*, 14.5%), irregardless of whether **DHQ** is added to the solution or not.³ Second, this small amount of conversion is obtained at a temperature much higher than for **DPMPE**. At 200°C, no reaction of **BPE** is obtained in the presence of **DHQ** or in the absence of **DHQ**. Third, the product distributions are the same within experimental error. With this data, we are forced to conclude that **DHQ** has absolutely no influence in accelerating reaction rates of compounds within the coal. However, it does function to terminate radical chain processes as indicated above.

CONCLUSIONS

DHQ enhances the yields of THF-extractables from coal for a variety of coals under very low temperature conditions. **DHQ** functions better in this capacity than tetralin or 9,10-dihydroanthracene on a mole-to-mole basis. Model compound studies show that **DHQ** functions by providing chain termination capabilities, both by providing hydrogen and by providing a reactive ring structure.

REFERENCES

1. J.H. Penn, Y.-Q. Liu, and P. Yassini, ACS Fuel Div. Preprint Pap., 1991.
2. A previous quarterly report reported different conversion amounts and different yields. These numbers have been found to be in error.
3. Careful inspection of the data shows that the yield of diphenylmethanol is unknown when no DHQ is added to the solution, with a high amount of benzophenone being formed. This results from overlapping GC peaks. Since the results were qualitatively similar to those obtained with DPMPE, no further effort was made to resolve this ambiguity in exact yield determinations.

Project III.3 Cyclic Olefins: New Donors for Coal Liquefaction

(Christine W. Curtis and Michael W. Bedell)

INTRODUCTION

A new set of hydrogen donors known as cyclic olefins (CLO'S) has been evaluated to determine their effectiveness as hydrogen donors to coal. These CLO's, as well as their conventional donor analogues TET, OHA, and DHA, were reacted with the coals from the Argonne Premium Coal Sample Program under equivalent reaction conditions. The CLO'S and their analogues were also reacted with Pittsburgh No. 8 coal at reaction times of 5, 15, 30 and 60 minutes under equivalent conditions. Reactions with a combined HHA / DHA (1:1 ratio by weight) system were also performed. Reactions were also performed with process solvents derived from Pittsburgh No. 8 and Illinois No. 6 coals supplied from the liquefaction experiments of the Wilsonville coal liquefaction pilot plant.

EXPERIMENTAL

The reactions of both CLO's and three conventional hydroaromatic donor compounds with the coals from the Argonne Premium Coal Sample Bank and a Western Kentucky No. 9 coal were performed. For this study the following reaction conditions were employed: 30 minute reaction time, 1250 psig nitrogen atmosphere at ambient temperature, 380°C reaction temperature, 2.0 g coal, 4.0 g total solvent mixture including 0.1-0.5 weight percent donable hydrogen of the model compound with the balance being hexadecane as the diluent solvent, and 700 cpm vertical agitation rate using stainless steel tubing bomb reactors of approximately 50 cm³ volume. The reaction temperatures were limited to 380°C because of the high reactivity of the CLO's. At higher temperatures these CLO's react so quickly that their effect on liquefaction would be difficult to observe.

The hydrogen donor compounds and their products from the coal liquefaction reactions were analyzed by gas chromatography using a Varian 3400 gas chromatograph equipped with a HT-5 column from SGE and FID detection. The internal standard method was used for quantitation

with biphenyl as the internal standard. The peaks were identified by comparing retention times with authentic compounds and by GC mass spectral analysis using a VG 70EHF mass spectrometer. For this work coal conversion is defined as $\text{conversion} = \{1 - [\text{IOM (maf)} / \text{coal charge (maf)}]\} \times 100$ where IOM is the insoluble organic matter remaining after the reaction and maf means moisture and ash free. The moisture and ash content for the Argonne coals was provided by the supplier. The moisture content of Western Kentucky No. 9 coal was experimentally determined to be $4.5 \pm 0.6\%$ and the ash, $10.2 \pm 0.14\%$.

REACTION OF HYDROGEN DONORS WITH ARGONNE COALS.

The coal conversion to THF solubles for the eight Argonne Premium coals and a Western Kentucky No. 9 coal from the PSU/DOE sample bank obtained from reactions with CLO's and hydroaromatic donor is presented in Table 1. In Table 1 and in the discussion that follows all percents used are weight percents. One of the most striking features of the data in Table 1 is the differences in the inherent reactivity of the coals themselves. When the reactions with no added hydrogen donor were examined, the following reactivity ranking for coal conversion was obtained: Illinois No.6 > Western Kentucky No. 9 > Pittsburgh No. 8 > Blind Canyon > Wyodak-Anderson and Upper Freeport > Beulah-Zap and Lewiston-Stockton >> Pocahontas No. 3. The ranking of the reactivity of the coals became less distinct when the different hydrogen donors were added to the reaction system. The order of the more moderately reactive coals, e.g. Upper Freeport, Beulah-Zap, Lewiston-Stockton, and Wyodak-Anderson, varied depending upon the model hydrogen donor that was present. However, for all the added donors, Illinois No. 6, Western Kentucky No. 9, and Pittsburgh No. 8 were reactive coals while Pocahontas No. 3 was completely unreactive in the current reaction system, regardless of the donor present.

When the reactions involving the hydrogen donors were examined for the reaction systems involving the different coals, ISO always produced greater conversion than its conventional donor analogue, TET; ISO produced greater, or equivalent, coal conversion to the conventional donor OHA, except for the reactions with Western Kentucky No. 9. TET produced lower conversions to THF solubles than the reactions of Upper Freeport, Blind Canyon, or Beulah-Zap with no added hydrogen donor. DHA always produced more coal conversion than HHA; DHA produced much more conversion for the reactions involving Upper Freeport (31.3%), Lewiston-Stockton (16%), and Blind Canyon (23.2%). For the Blind Canyon reactions, HHA produced 13.7% more

conversion than was obtained with the other model donors.

As was shown in previous work of Bedell and Curtis (2), the cyclic olefins released their hydrogen rapidly. A possible explanation to the experimental observation of the low coal conversion produced by the CLO's with Upper Freeport, Lewiston-Stockton, and Blind Canyon coals, may be that the coals were not inherently reactive coals, and thus, the CLO's released their donable hydrogen before needed by these coals. Likewise, DHA, which was more stable, was able to remain in the reaction system for a longer period of time. DHA was able to retain its hydrogen over the reaction time period until it was needed to cap the free radicals that were formed in dissolving the coal matrix and, hence, resulted in more coal conversion.

Illinois No. 6 was determined to be an extremely reactive coal and produced 55% coal conversion to THF solubles with no added donor. Illinois No. 6, with no added donor, achieved more than twice the coal conversion of Western Kentucky No. 9, which was the second most reactive coal with no added donor. With Illinois No. 6, 15% more coal conversion was obtained with DHA compared to that with no added donor. This amount was the smallest differential from no donor present to the donor promoting the highest coal conversion (DHA) of any of the coals, except for Pocahontas No. 3, which was non-reactive. With Illinois No. 6, there was only ~7% more coal conversion obtained with DHA than was produced by TET, which had the lowest conversion with any of the added donors.

For the reactions involving Upper Freeport coal, ISO produced ~20% conversion, DHA produced more than 45% coal conversion to THF solubles, while HHA only produced ~15% conversion. ISO produced more than 2.5 times the coal conversion than was obtained with its conventional donor analogue TET. DHA produced more than four times the coal conversion than that which was obtained with no added donor. For the reactions involving Pittsburgh No. 8, 36.3% more coal conversion was obtained with DHA when compared to the reaction of the coal with no added donor. The cyclic olefin ISO produced nearly 12% more coal conversion than its analogue TET. HHA produced ~12% more conversion than OHA, and ~5% less than DHA. With the Lewiston-Stockton reactions, 35% more conversion was obtained with DHA than with no added donor. DHA produced nearly 16% more conversion than HHA; ISO produced approximately 2 times the conversion that was obtained with its analogue, TET. With Blind Canyon coal reactions, there was nearly 50% more conversion obtained with DHA compared to the reactions with no added donor. DHA produced over 23% more conversion than HHA, which

in turn produced ~13% more conversion than OHA.

The moisture content of Wyodak-Anderson coal was 28.1% as-received, while the Beulah-Zap coal had an as-received moisture content of 32.2%. These moisture contents were in contrast to those of the other coals studied, whose moisture content ranged from less than 1% to ~8%. Therefore, these two coals were dried to eliminate any possible effect the excess moisture might have on the reaction. Also, as a comparison to the conversions obtained with the dried coal, a pair of reactions was repeated for both Wyodak-Anderson and Beulah-Zap with the as-received coals. The reactions for Wyodak-Anderson coal were with ISO and TET, while that for Beulah-Zap were with HHA and DHA. For all four sets of reactions, no statistically meaningful differences in the conversions were obtained with the dried and as-received coals. Thus, it appeared that the additional moisture had no effect on the coal conversions obtained; however, the high water content would affect the amount of energy (and cost) to heat the as-received coals to reaction temperature. For Wyodak-Anderson, ~38% more conversion with DHA was obtained than was obtained with no added donor. HHA produced ~20% more coal conversion than OHA, while producing ~10% less conversion than DHA. For Beulah-Zap ~28% more conversion with DHA was obtained compared to that with no added donor. ISO produced more than 2.5 times the coal conversion than was obtained with TET; DHA produced ~15% more conversion than HHA.

GC ANALYSIS OF THE PRODUCTS FROM THE MODEL COMPOUNDS IN LIQUEFACTION REACTIONS

The THF soluble fraction for all the reactions with the model donors and the nine coals presented in Table 1 were further analyzed by gas chromatography (GC) to determine the effect the liquefaction reactions had on the model hydrogen donors present. The results of this analysis are presented in Table 2. OHA remained substantially unreacted for all the reactions in which it was initially present. The amount of OHA recovered ranged from more than 96% for the reactions with Upper Freeport to ~62% with Wyodak-Anderson coal. The primary reaction product from OHA in all the coal reactions was DHA; the only other reaction product was ANT.

HHA was completely converted to OHA, DHA, and ANT in all of the reactions that were performed. For the liquefaction reactions, the amount of DHA formed ranged from 81.1% in the Illinois No. 6 reactions to 38.0% with Beulah-Zap. DHA was produced in the largest amount

for all of the coal reactions, except those performed with Upper Freeport. For Upper Freeport, OHA was the primary reaction product at 52.2%, with 39.9% DHA and 8.0% ANT being formed.

The reactions with Pittsburgh No. 8 also produced a significant amount of OHA from HHA (43.1%).

For all of the coal reactions performed, DHA remained partially unconverted, being least reactive with Illinois No. 6 at 32.8% unconverted. DHA was most reactive with Beulah-Zap, where DHA was converted 86%. For the reactions with Western Kentucky No. 9, Illinois No. 6, Upper Freeport, Pocahontas No. 3, and Pittsburgh No. 8, the primary reaction product from DHA was OHA. In contrast, in the reactions with the Blind Canyon, Wyodak-Anderson, and Beulah-Zap coals where ANT was the primary reaction product, 44.3%, 56.0%, and 51.3%, respectively. Equivalent amounts of OHA and ANT at ~35% were produced in the reactions of Lewiston-Stockton coal with DHA. The reactions involving Western Kentucky No. 9 produced the largest amount of OHA in the reaction products at 61%.

ISO was completely converted to NAP and TET in all of the coal reactions performed. NAP was the primary reaction product which ranged from 84.6% formed with Beulah-Zap to 67.3% formed in the Pocahontas No. 3 reaction system. TET remained substantially unreacted for all of the liquefaction reactions performed, with NAP being the only product being formed. The most TET converted was ~25% in the reactions with Beulah-Zap coal. TET was completely unconverted for reactions with both Upper Freeport and Lewiston-Stockton coals.

NET HYDROGEN DONATED FROM THE MODEL COMPOUNDS DURING LIQUEFACTION.

The net amount of hydrogen released from the model compounds was calculated based upon the product slate determined by the GC analysis for each set of reactions performed. This amount was determined as the difference in the total amount of hydrogen released and the amount of hydrogen required to form other species of the same ring series. For example, when HHA reacted, hydrogen was released when DHA and ANT were formed, but hydrogen was consumed when OHA was produced. The amount of net hydrogen released to the system was dependent upon the amount of HHA converted and the relative amounts of each product produced. The results of these calculations are also presented in Table 2.

Some trends observed with the individual model hydrogen donors present, regardless of the

coal reacted, are 1) ISO always released more hydrogen than its conventional donor analogue TET; 2) ISO always released more hydrogen than the conventional donor OHA; 3) HHA released more hydrogen than its analogue OHA, except for those reactions with Upper Freeport coal. As was indicated by the negative value for the net hydrogen donated with the reactions of DHA for all the coal reactions performed, hydrogen was incorporated into the model donor products.

REACTIONS WITH PITTSBURGH NO. 8 COAL

To investigate more fully the hydrogen donating ability of the cyclic olefin HHA and its conventional hydrogen donor analogue DHA, a series of liquefaction reactions was performed that were comprised of varying amounts of DHA and HHA, based upon the amount of donable hydrogen per molecule. The reactions were configured to maintain a constant level of 0.5 wt% donable hydrogen. The relative amounts of DHA and HHA varied from 75% HHA (25% DHA) to 75% DHA (25% HHA). The results of these reactions, as well as those with 100 % DHA or HHA, and no added donor, are presented in Table 3.

As can be seen from Table I, the reaction that produced the highest coal conversion to THF solubles corresponded to the experiment containing equal levels of donable hydrogen from HHA and DHA. This liquefaction reaction produced 12% more coal conversion than the corresponding reaction with 100% HHA, while producing ~7% more conversion than the reaction with 100% DHA. The reaction with 75% HHA (25% DHA) produced ~4% more coal conversion than the reaction with only HHA, while producing ~0.9% less coal conversion than the reaction with DHA alone. The reaction with 75% DHA (25% HHA) produced ~9.0% more conversion than HHA alone and ~4.4% more conversion than the DHA reaction. These results, e.g., the increase in conversion of the combined HHA / DHA reaction system, suggest that there is a synergistic effect in the liquefaction reactions that combine the very reactive cyclic olefin HHA with the less reactive conventional donor DHA. There were two possible explanations for this experimentally observed synergistic phenomenon. One postulate was that the presence of DHA in the HHA reaction system shifted the equilibrium toward HHA, because DHA is a dehydrogenation product of HHA. This shifting of the equilibrium may have the effect of slowing the rate of hydrogen loss from the very reactive HHA, which in turn would allow HHA to remain in the reaction system for a longer period of time. The loss of hydrogen from HHA may then more closely

match the rate at which it is needed by the free radicals generated by the coal matrix. A second possible explanation was that the very reactive CLO, HHA, still released its hydrogen rapidly and produced the initial increase in coal conversion to THF solubles, thereby preventing early retrogressive reactions, while the remaining DHA sustained coal conversion over the lifetime of the reaction.

In order to determine which postulate is the correct one, additional experimental work was performed. First, short time liquefaction reactions of five minutes were performed. If the reactions involving 100% HHA produced greater coal conversion than either the reactions with 100% DHA or the combined HHA / DHA reaction, then the second postulate, (i.e. HHA was producing the initial increase in coal conversion), discussed above would be supported. The postulate would be substantiated in that if the CLO's were producing the initial coal conversion to THF solubles, greater coal conversions would be obtained in the five minute reactions containing the most HHA. If greater conversion was obtained in the combined HHA / DHA reactions then the first postulate would be supported in that the role of the DHA would be to slow the rate of hydrogen loss from HHA to more closely match the rate of hydrogen required by the coal. Table 4 presents the results of coal conversion to THF solubles for the liquefaction reactions involving Pittsburgh No. 8 coal at various reaction times. In examining the reactions of five minutes, the highest coal conversion was obtained with HHA. HHA produced ~1.4% more coal conversion to THF solubles than the combined HHA / DHA reactions. These experimental results help to substantiate the postulate that the CLO's produce the initial increase in coal conversion at short reaction times. Also, in the short time reactions of five minutes, HHA produced ~17% more coal conversion than its analogue OHA and ~25% more conversion than those reactions with no donor added.

Additional experimental work to determine which of the two postulates explains the observed experimental phenomena consisted of model compound reactions that were performed thermally at 380°C under both nitrogen and hydrogen with the combined 50% HHA and 50% DHA. The experimentally determined product slate for the corresponding reactions with pure HHA were recently reported by Bedell and Curtis (2). By analyzing the products obtained in the combined reaction system, and comparing them to the reaction with 100% HHA, inferences can be made to determine the effect of the addition of DHA to the HHA reaction system. If HHA were found in correspondingly greater amounts in the combined system than in the system containing only

HHA, then postulate one would be substantiated, i.e. the rate of hydrogen loss from HHA was retarded by the presence of DHA. However, if HHA were found in the same relative amounts in both the combined and 100% HHA reaction systems, then HHA was being dehydrogenated at the same rate, regardless of the presence or absence of DHA. If the model compound reactions do indeed show that the hydrogen is lost at nearly the same rate in the combined and 100% HHA reaction systems, then postulate one is invalidated. Therefore, postulate two would be the correct explanation of the role of DHA and HHA in the combined liquefaction reaction systems. Table 5 presents the results that were obtained in the model compound reactions, both for the combined HHA / DHA reactions and those with only HHA. As can be seen the rate of hydrogen lost from the combined HHA / DHA reactions was approximately the same as was lost in the 100% HHA reactions. The fact that the hydrogen was lost at nearly the same rate in both reaction systems refutes the postulate that the role of DHA in the combined system was to slow the rate of hydrogen loss from HHA. Therefore, postulate two is substantiated, e.g. the HHA produced the initial increase in coal conversion.

Both the results of the model compound reactions and the short time liquefaction experiments suggest that the increase in coal conversion with the combined HHA / DHA reaction system resulted from the reactive CLO's releasing their hydrogen rapidly, producing the initial coal conversion, and preventing retrogressive reactions, while the less reactive DHA sustained the coal conversion over the lifetime of the reaction.

To more fully explore the rate of hydrogen acceptance by Pittsburgh No. 8 coal, additional liquefaction reactions were performed at reaction times of 15, 30, and 60 minutes. The hydrogen acceptance is monitored via coal conversion to THF solubles, i.e. the more coal conversion that was obtained, the more hydrogen was utilized by the dissolving coal macromolecules. The results of these experiments, as well as the 5 minute liquefaction reactions are presented in Table 4.

In the short time liquefaction reactions of five minutes, the cyclic olefin ISO produced 13.1% more coal conversion than its analogue TET; TET produced ~2% less conversion than was obtained in the liquefaction reactions with no added donor. ISO also produced 3.6% more coal conversion than the conventional donor OHA. There was a 25% increase in coal conversion obtained in going from the reaction with no added donor, 7.9% conversion, to that obtained with HHA, 32.3% conversion.

For the liquefaction reactions of 15 minutes, the combined HHA / DHA reactions produced the greatest coal conversion, 58.0%. The coal conversion obtained was ~3% more conversion than was obtained with DHA, and ~13% more conversion than was obtained with HHA. DHA produced ~11% more conversion than HHA, while HHA in turn, produced ~18% more conversion than its analogue OHA. The cyclic olefin ISO produced ~20% more conversion than its analogue TET. ISO also produced 11.2% more coal conversion than the conventional donor OHA. TET produced ~3% less conversion than was obtained in the reactions with no added donor. There was a ~37% increase in coal conversion from the reaction with no added donor to the conversion obtained with the combined HHA / DHA reactions, 20.9% versus 58.0%, respectively.

For the liquefaction reactions of 30 minutes, the combined HHA / DHA reactions produced the most coal conversion, 63.1 %, which was ~6.7% more conversion than was obtained with DHA and ~12% more conversion than was obtained with HHA. In the combined HHA / DHA reactions, 43.2% more coal conversion was obtained when compared to the liquefaction reactions with no added donor. HHA produced ~12% more coal conversion than was obtained with OHA. The cyclic olefin ISO produced ~12% more coal conversion than its conventional donor analogue TET, while producing 2.5% more conversion than OHA. TET produced ~10% more coal conversion than was obtained in the reactions with no added donor.

With the liquefaction reactions at 60 min, DHA produced the most coal conversion, 67.7%, which was ~23.5% more coal conversion than was obtained in the reactions with no added donor. DHA produced 2.7% more conversion than HHA and 4.0% more conversion than the combined HHA / DHA reactions. The cyclic olefin ISO produced approximately the same conversion as OHA and ~2.0% more conversion than TET. TET produced ~12% more conversion than was obtained with no added donor. With a reaction time of 60 minutes, coal conversion in the presence of a hydrogen donor appears to have reached its maximum. The reactions with DHA, HHA, and the combined HHA / DHA system, all produced nearly equivalent coal conversions, ~65%, which is only ~10% more coal conversion than was obtained with the poorest donor TET.

For all of the reactions with a given hydrogen donor, coal conversion increased with increasing reaction times. However, for the combined HHA / DHA reactions nearly all the conversion to THF solubles occurred in the first 15 minutes, (58%). In increasing the reaction

time to 60 minutes, only 5.7% more coal conversion was obtained. The two cyclic olefins, ISO and HHA, produced ~20% more conversion in 60 minutes when compared to that obtained in 15 minutes. The conventional donor TET had the largest increase in coal conversion, nearly 40%, obtained in the reactions at 60 minutes when compared to that obtained in the 15 minute reactions. OHA produced nearly 33% more coal conversion at 60 minutes versus 15 minute reaction time. In analyzing the reactions with a given model hydrogen donor present, the poorer donors TET and OHA, as well as those reactions with no donor added, most benefitted from the longer reaction time of 60 minutes. However, for DHA and the combined HHA / DHA reactions nearly all the ultimate conversions obtained were produced in the first 15 minutes of the reaction. For the cyclic olefins ISO and HHA, they produced the initial increase in coal conversion, but also benefitted from the longer reaction times. The CLO's released their hydrogen rapidly and were converted to less reactive conventional donors which required the longer reaction times to lose their available hydrogen and promote more coal conversion to THF solubles.

Overall, it appears that the combined HHA / DHA system was the most effective at producing the highest coal conversion in the least amount of time. It seems that the CLO released its hydrogen rapidly to produce the initial coal conversion, followed by the conventional donor DHA releasing its hydrogen to sustain the coal conversion.

GC ANALYSIS OF PRODUCTS FROM THE MODEL COMPOUNDS IN REACTIONS WITH PITTSBURGH NO. 8 COAL.

Table 6 presents the gas chromatographic analysis (GC) of the THF soluble fraction of the reactions for the combined HHA / DHA liquefaction reactions with Pittsburgh No. 8 coal. The amount of OHA formed was essentially constant at 47% for those reactions with the combined HHA / DHA. The combined system reactions produced ~3.0% more OHA than was formed with either HHA or DHA. The amount of DHA recovered increased with an increase in the amount of HHA initially present; the amount of DHA ranged from 26.4% with pure DHA to 44.8% with 100% HHA. The amount of ANT recovered decreased from 29.4% with 100% DHA to 12.1% with 100% HHA.

Table 7 presents the results of the GC analysis of the products from the model compounds in the liquefaction reactions at varying reaction times. In the combined HHA / DHA reactions the only HHA that was recovered was in the five minute reactions, 1.2%. The amount of OHA

formed increased from 0% at five minutes to ~70% for the reactions at 60 minutes. The amount of DHA recovered decreased with increasing reaction time while the amount of ANT produced increased until reaching a maximum at 30 minutes reaction time before decreasing to 15.5% at 60 minutes.

At a reaction time of 5 minutes OHA was essentially unreacted, with 2.4% THA being the only product formed. OHA was less than 10% converted, primarily to DHA, at reaction times of 15 and 30 minutes. OHA was less than 25% converted at a reaction time of 60 minutes. The amount of DHA formed increased with increasing reaction time. HHA was completely converted at all reaction times except for the five minute reactions where 28.4% was recovered. The primary reaction product at the five minute reaction time was DHA at 55.7%. At the reaction times of 15 and 30 minutes nearly equivalent amounts of OHA and DHA were formed. The product slates at 15 minutes were identical, within experimental error, to that obtained at 30 minutes. With the reaction at 60 minutes, the amount of OHA formed decreased while the amount of DHA formed correspondingly increased. At the longer reaction time the OHA begins to dehydrogenate to DHA. At a reaction time of 60 minutes a minor amount of ANT (~2%) was rehydrogenated to DHA.

DHA was less than 25% converted in the reactions of five minutes; the primary product was ANT, with a minor amount of THA being produced and no OHA was formed. DHA was most reacted at 15 minutes, ~86% converted, and the most OHA was produced. As the reaction time increased to 30 and 60 minutes the amount of OHA formed decreased and produced a corresponding increase in the amount of DHA recovered. At a reaction time of 60 minutes the amount of ANT recovered decreased slightly. At the longer reaction time some of the OHA that was formed was in turn dehydrogenated to DHA with a minor amount of ANT being rehydrogenated to DHA.

The only reaction in which any ISO was recovered was the short time liquefaction reaction of five minutes, where 47.0% ISO was recovered. In the five minute reactions ~41% NAP was produced and ~12% 1,2-DHN formed. ISO was completely converted to TET and NAP at reaction times of 15, 30, and 60 minutes. As the reaction time increased, the amount of TET produced also increased. It appears that NAP, or 1,2-DHN, was being rehydrogenated to TET. TET was completely unreacted in the reaction times of five and 15 minutes, with only a trace of NAP being formed at 15 minutes. At longer reaction times of 30 and 60 minutes, TET

remained essentially unreacted, < 12% converted, with NAP being the only product formed.

REACTIONS WITH COAL DERIVED LIQUIDS

Two samples were obtained from SEI, Southern Clean Fuels Division, that were derived from liquefaction experiments with Pittsburgh No. 8 and Illinois No. 6 coals. The samples were from stream V131B, which was the recycle solvent stream to the first stage reactor. In addition to the coal derived liquids, the samples contained un-reacted coal and ash from the liquefaction process. The experimentally determined ash content for the sample derived from Pittsburgh No. 8 coal was 8.34 ± 0.01 weight percent, while the ash content for the sample derived from Illinois No. 6 coal was 7.15 ± 0.07 weight percent.

The THF soluble fraction of the raw recycle solvents was determined and is reported in Table 8. The insoluble fraction consisted of unreacted coal materials, which were potentially upgradable to THF solubles, and ash. To determine the effect of the thermal reaction on the recycle solvents, the solvents were reacted under liquefaction conditions in the absence of both coal and hydrogen donor compounds. The THF soluble and insoluble fractions were again determined, the results of which are also reported in Table 8. There were no statistically meaningful differences between the THF soluble fractions before and after the reactions were completed.

Because there were no significant differences in the amount of THF solubles before and after the reactions, it was initially felt that the THF insoluble fraction of the solvents would remain completely insoluble after liquefaction in the presence of coal. In order to more closely simulate an actual coal liquefaction process, the recycle solvent samples were reacted with the coals from which they were derived, i.e. the Pittsburgh No. 8 solvent was reacted with Pittsburgh No. 8 coal.

The initial calculations were performed using the assumption that there was no upgrading of the insoluble material from the solvent and, therefore, coal conversion was defined as $\text{Conversion} = \{1 - [(\text{IOM coal})_{\text{mar}} / (\text{COAL CHARGE})_{\text{mar}}]\} \cdot 100$. When the calculations were performed for the reactions of Pittsburgh No. 8 solvent and coal with no added donor, a coal conversion of nearly 100% was obtained. This is in comparison with a conversion of 20.1% for the same reaction in hexadecane. This high coal conversion suggested that the assumption of no upgrading of the THF insoluble fraction from the recycle solvent was incorrect. Indeed, some conversion of the insoluble fraction from the recycle solvent must have occurred in the presence of coal, where it did not under equivalent reaction conditions in the absence of coal. This is

analogous to the situation with DHA, which is very stable in model compound reactions containing only DHA, yet in the presence of coal produced a high coal conversion and released its hydrogen. (Bedell and Curtis, 1,2) Because some of the insoluble portion of the recycle solvent was converted to THF solubles, a new definition of conversion had to be developed on the basis of the total amount of potentially upgradable materials present (on a moisture and ash free basis). The potentially upgradable materials consisted of the unreacted coal from the recycle solvent and the additional coal that was added. Conversion is now defined as $\text{Conversion} = \{1 - [(\text{IOM total})_{\text{maf}} / (\text{PUM})_{\text{maf}}]\} * 100$ where $(\text{PUM})_{\text{maf}} = (\text{IOM solvent})_{\text{maf}} + (\text{Coal Charge})_{\text{maf}}$ and the (IOM solvent) was the amount of THF insolubles initially present in the recycle solvent minus the amount of ash that was present.

Using this new definition of conversion based upon the amount of potentially upgradable materials, the reactions with the two recycle solvents and their respective coals were analyzed. The results of PUM conversion to THF solubles is presented in Table 9. As can be seen for both series of reactions, the conversions obtained were constant, within experimental error. For the reactions with Pittsburgh No. 8 coal the mean conversion was $73.6 \pm 0.5\%$ and for the reactions with Illinois No. 6 coal the mean conversion was $69.9 \pm 0.5\%$. There was no observably increased effect on conversion by the addition of any hydrogen donor compound, be it CLO or a conventional donor. It appears that the process solvent itself is such a good dissolution medium that the overall conversion is not affected by hydrogen transfer reactions. This is analogous to the situation that was observed for the reactions of Western Kentucky No. 9 coal in fluorene, where coal conversion was constant in a hydrogen atmosphere with fluorene as the diluent solvent because of the dissolution power of fluorene. (Bedell and Curtis, 1)

CONCLUSIONS

In the course of examining the work that is presented in the section of this paper concerning the reactions of the Argonne coals, several important results needed to be re-emphasized. In all of the liquefaction reactions the cyclic olefin ISO always produced greater coal conversion to THF solubles and released more hydrogen than its conventional hydrogen donor analogue TET. The cyclic olefin HHA always produced greater coal conversion and released more hydrogen than its conventional donor analogue OHA. In the liquefaction reactions performed, ISO always produced more coal conversion than OHA, except for those reactions with Western Kentucky No.

9 coal. The conventional donor compound TET produced lower conversions to THF solubles than the reactions of Upper Freeport, Blind Canyon, or Beulah-Zap coals with no added donor. In all of the liquefaction DHA produced more coal conversion than HHA. For all the added donors in the liquefaction reactions, Illinois No. 6, Western Kentucky No. 9, and Pittsburgh No. 8 coals were reactive; Pocahontas No. 3 coal was completely unreactive in the reaction system used, regardless of the donor present. As was shown by the GC analysis of the reaction products, the cyclic olefins were completely converted in all of the liquefaction reactions that were performed. By contrast, their conventional hydrogen donor analogues all remained partially unreacted in every reaction system.

For all of the liquefaction with DHA, there was a net incorporation of hydrogen through its formation of OHA, which is a much poorer hydrogen donor compound for coal conversion.

For the reactions with Pittsburgh No. 8 coal, the 1:1 combined HHA / DHA system was the most effective at producing the highest coal conversion in the least amount of time. The cyclic olefin's release their hydrogen rapidly to produce an initial increase in coal conversion to THF solubles and the rate of hydrogen lost from HHA in the combined HHA / DHA reactions was nearly the same as in the 100% HHA reaction system. In general, coal conversion increased with increasing reaction time for all the reactions with a given hydrogen donor compound. In the liquefaction reactions, the cyclic olefin ISO always produced higher coal conversion than its conventional donor analogue TET; ISO also produced higher, or equivalent, conversion as the conventional hydrogen donor compound OHA. In the liquefaction reactions, the cyclic olefin HHA always produced higher coal conversion than its conventional donor analogue OHA.

REFERENCES

- 1) Bedell,M.; Curtis,C.; "The Liquefaction and Coprocessing Reactions of Cyclic Olefins With Western Kentucky No. 9 Coal."; in progress
- 2) Bedell,M.; Curtis,C.; "The Chemistry and Reactivity of Cyclic Olefins As Donors in Coal Liquefaction."; Energy and Fuels, for publication summer 1991

**TABLE 1 : COAL CONVERSION FOR THE LIQUEFACTION REACTIONS
WITH THE ARGONNE PREMIUM COALS.**

COAL REACTED	DHA	HHa	OHA	ISO	TET	NONE
KY #9	68.3(1.0)	65.0(3.3)	49.7(1.0)	37.2(0.4)	29.8(0.2)	25.6(1.8)
IL #6	69.6(2.0)	67.7(0.2)	66.1(2.8)	65.5(1.6)	62.1(2.0)	55.7(0.2)
UP FREE	47.1(2.0)	15.8(1.2)	13.0(1.7)	20.9(2.5)	8.3(0.7)	11.4(0.5)
POC #3	4.5(0.1)	-4.4(.01)	-6.1(2.0)	-6.7(1.5)	-3.1(1.0)	-5.7(1.7)
PITT #8	56.4(0.1)	51.8(0.6)	38.8(1.0)	42.3(5.3)	30.5(3.8)	20.1(3.3)
LEWIS	41.7(1.9)	25.2(2.1)	19.6(1.2)	20.9(1.1)	9.1(2.6)	6.0(3.1)
B. CANYON	64.8(3.9)	41.6(1.6)	27.9(0.7)	25.3(0.2)	15.2(2.0)	17.4(0.4)
WYODAK* (as recieved)	50.6(0.6)	40.5(1.3)	21.4(1.2)	21.1(2.9) 22.3(1.8)	14.9(1.5) 15.5(0.2)	11.7(1.5)
BEULAH* (as recieved)	35.6(3.0) 34.8(1.9)	20.8(3.0) 21.4(3.2)	13.3(1.0)	13.8(0.1)	5.0(2.5)	8.1(2.1)

Reaction Conditions : hexadecane, hydrogen, 30 minute reaction time, 380°C.

* dried to approximately 4% moisture content

**TABLE 2: GC ANALYSIS OF THE PRODUCTS FROM THE MODEL
COMPOUNDS IN LIQUEFACTION REACTIONS
WITH THE ARGONNE PREMIUM COALS.**

COMPOUND / COAL REACTED	WT% OHA	WT% DHA	WT% ANT	NET H DONATED
OHA				
KY #9	85.4(0.1)	14.6(0.1)	0.0	0.00324
IL #6	77.4(0.7)	13.1(0.9)	9.5(0.2)	0.00575
UP FREE	96.1(0.7)	3.9(0.7)	0.0	0.00086
POC #3	94.8(1.6)	4.5(1.1)	0.68(0.5)	0.00121
PITT #8	90.4(0.6)	9.6(0.6)	0.0	0.00213
LEWIS	86.6(0.3)	13.4(0.3)	0.0	0.00287
B. CANYON	76.0(0.8)	22.0(0.7)	2.0(0.1)	0.00548
WYODAK	62.0(0.9)	32.2(0.6)	5.8(0.4)	0.00888
BEULAH	67.8(0.3)	27.9(0.2)	4.2(0.1)	0.00748
HHA				
KY #9	47.5(0.3)	45.7(0.1)	6.8(0.3)	0.00659
IL #6	11.6(1.8)	81.1(1.5)	7.3(0.6)	0.01726
UP FREE	52.2(0.3)	39.9(0.3)	8.0(0.4)	0.00531
POC #3	15.8(0.6)	74.0(0.5)	10.1(0.3)	0.01631
PITT #8	43.1(1.0)	44.8(0.6)	12.1(0.5)	0.00843
LEWIS	38.9(0.9)	47.8(0.3)	13.3(0.6)	0.01568
B. CANYON	19.1(0.1)	50.8(0.6)	30.1(0.7)	0.01739
WYODAK	18.2(0.2)	39.0(1.4)	42.8(1.6)	0.01896
BEULAH	18.6(1.4)	38.0(1.1)	43.4(2.5)	0.01891
DHA				
KY #9	61.0(2.3)	24.6(2.4)	14.5(1.5)	-0.04970
IL #6	45.6(2.6)	32.8(0.3)	21.6(0.6)	-0.03378
UP FREE	55.4(0.5)	23.4(0.1)	20.2(0.5)	-0.05444
POC #3	60.7(1.4)	18.4(0.6)	20.8(1.1)	-0.04746
PITT #8	44.2(0.6)	26.4(0.1)	29.4(0.6)	-0.03013
LEWIS	35.3(0.9)	29.5(0.6)	35.2(1.4)	-0.02044
B. CANYON	34.8(0.3)	20.9(0.1)	44.3(0.3)	-0.01718
WYODAK	28.6(1.1)	15.4(0.4)	56.0(1.5)	-0.00806
BEULAH	35.2(3.9)	13.5(0.6)	51.3(4.5)	-0.01537

OHA = octahydroanthracene
DHA = dihydroanthracene
ANT = anthracene
HHA = hexahydroanthracene

**TABLE 2 CONTINUED : GC ANALYSIS OF THE PRODUCTS FROM THE
MODEL COMPOUNDS IN THE LIQUEFACTION
REACTIONS WITH THE ARGONNE PREMIUM COALS.**

COMPOUND / COAL REACTED	WT% TET	WT% NAP	NET H DONATED
ISO			
KY #9	17.8(1.3)	82.2(1.3)	0.01248
IL #6	23.5(0.6)	76.5(0.6)	0.01157
UP FREE	21.8(1.1)	78.2(1.1)	0.00296
POC #3	32.7(6.3)	67.3(6.3)	0.01018
PITT #8	20.5(0.7)	79.5(0.7)	0.01202
LEWIS	30.3(1.7)	69.7(1.7)	0.01054
B. CANYON	20.5(1.4)	79.5(1.4)	0.01202
WYODAK	18.6(0.1)	81.4(.01)	0.01231
BEULAH	15.4(0.6)	84.6(0.6)	0.01279
TET			
KY #9	79.8(0.7)	20.2(0.7)	0.00298
IL #6	94.0(1.5)	6.0(1.5)	0.00091
UP FREE	100.0	0.0	0.0
POC #3	97.4(0.5)	2.6(0.5)	0.00087
PITT #8	88.2(0.5)	11.8(0.5)	0.00178
LEWIS	100.0	trace	0.0
B. CANYON	85.7(0.6)	14.3(0.6)	0.00216
WYODAK	86.7(1.2)	13.3(1.2)	0.00201
BEULAH	74.5(5.0)	25.5(5.0)	0.00386

ISO = isotetralin

TET = tetralin

TABLE 3: COAL CONVERSION FOR THE LIQUEFACTION REACTIONS WITH PITTSBURGH NO. 8 COAL WITH VARYING RATIOS OF HHA AND DHA.

REACTION CONDITIONS	COAL CONVERSION
100% DHA	56.4(0.1)
75% DHA / 25% HHA	60.8(1.6)
50% DHA / 50% HHA	63.7(0.1)
25% DHA / 75% HHA	55.5(0.3)
100% HHA	51.8(0.6)
NONE	20.1(3.3)

DHA = dihydroanthracene

HHA = hexahydroanthracene

Standard conditions: Pittsburgh No. 8 coal, hexadecane, hydrogen, 380°C, 30 minute reaction time.

Note: all coal conversions are in percent, the numbers in the parentheses are the standard deviation for that point.

TABLE 4 : COAL CONVERSION FOR THE LIQUEFACTION REACTIONS WITH PITTSBURGH NO. 8 COAL AT VARYING REACTION TIMES.

RXN TIME	COMBINED DHA/HHA	DHA	HHA	OHA	ISO	TET	NONE
5 MIN	30.9(0.3)	27.5(1.1)	32.3(1.4)	15.5(1.2)	19.1(0.6)	6.0(0.4)	7.9(0.2)
15 MIN	58.0(0.5)	55.2(0.3)	44.6(4.0)	25.9(0.9)	37.1(1.6)	17.4(1.0)	20.9(0.1)
30 MIN	63.1(1.0)	56.4(0.1)	51.8(0.6)	38.8(1.0)	42.3(5.3)	30.5(3.8)	20.1(3.3)
60 MIN	63.7(0.1)	67.7(1.6)	65.0(0.7)	58.5(0.9)	58.8(0.2)	56.9(2.6)	44.2(3.1)

Standard Conditions : Pittsburg No. 8 coal, hexadecane, hydrogen, 380°C, combined DHA/HHA reaction were in a 1:1 ratio by weight.

DHA = dihydroanthracene
HHA = hexahydroanthracene
OHA = octahydroanthracene

ISO = isotetralin
TET = tetralin

Note: all coal conversions are in percent, the numbers in the parentheses are the standard deviation for that point.

TABLE 5: HHA RECOVERY IN 100% HHA AND COMBINED HHA / DHA SYSTEMS IN THE THERMAL REACTIONS AT 380°C UNDER BOTH HYDROGEN AND NITROGEN.

REACTION CONDITIONS	WEIGHT PERCENT OF HHA RECOVERED IN 100% HHA	WEIGHT PERCENT OF HHA RECOVERED IN COMBINED HHA/DHA**
NITROGEN		
2 MIN	47.0(4.3)	22.7(1.5)
10 MIN	10.8(2.6)	4.9(2.2)
15 MIN	2.0(0.1)	0.0
HYDROGEN		
2 MIN	60.9(0.7)	32.2(0.3)
10 MIN	14.4(1.7)	5.6(1.6)
15 MIN	10.3(5.3)	1.0(0.5)

** To compare the combined HHA / DHA reactions to the 100% HHA reactions on an equal weight basis of HHA, multiply the weight percent of HHA in the combined reactions by two.

**TABLE 6: GC ANALYSIS OF THE PRODUCTS FROM MODEL DONORS
IN REACTIONS WITH PITTSBURGH NO. 8 COAL WITH
VARYING RATIOS OF HHA AND DHA.**

COMPOUND / CONDITIONS	WT% OHA	WT% DHA	WT% ANT .
100% DHA	44.2(0.6)	26.4(0.1)	29.4(0.6)
75% DHA / 25% HHA	47.4(0.4)	26.0(0.1)	26.6(0.4)
50% DHA / 50% HHA	47.3(0.2)	29.6(0.1)	23.1(0.2)
25% DHA / 75% HHA	47.9(0.2)	32.9(0.2)	19.2(0.2)
100% HHA	43.1(1.0)	44.8(0.6)	12.1(0.5)

OHA = octahydroanthracene

DHA = dihydroanthracene

ANT = anthracene

HHA = hexahydroanthracene

THA = tetrahydroanthracene

Standard Conditions : Pittsburgh No. 8 coal, hydrogen, hexadecane, 380°C.

**TABLE 7: GC ANALYSIS OF THE PRODUCTS FROM MODEL DONORS
IN REACTIONS WITH PITTSBURGH NO. 8 COAL AT
VARYING REACTION TIMES.**

COMPOUND / CONDITIONS	WT% OHA	WT% HHA	WT% THA	WT% DHA	WT% ANT
DHA / HHA:					
5 MIN	0.0	1.2(0.1)	0.0	91.9(0.1)	6.9(0.1)
15 MIN	41.6(2.1)	0.0	0.0	41.2(0.8)	17.2(1.3)
30 MIN	47.3(0.2)	0.0	0.0	29.6(0.1)	23.1(0.2)
60 MIN	70.6(0.9)	0.0	0.0	13.9(0.2)	15.5(0.7)
OHA:					
5 MIN	97.6(0.2)	0.0	2.4(0.2)	0.0	0.0
15 MIN	92.5(0.4)	0.0	0.0	7.1(0.3)	0.3(0.03)
30 MIN	90.4(0.6)	0.0	0.0	9.6(0.6)	0.0
60 MIN	75.3(0.4)	0.0	0.0	21.8(2.4)	2.9(2.3)
HHA:					
5 MIN	7.9(0.9)	28.4(0.8)	3.1(0.3)	57.7(0.4)	2.9(0.2)
15 MIN	43.3(0.7)	0.0	0.0	44.6(0.7)	12.1(0.2)
30 MIN	43.1(1.0)	0.0	0.0	44.8(0.6)	12.1(0.5)
60 MIN	32.3(1.0)	0.0	0.0	57.9(0.4)	9.8(0.6)
DHA:					
5 MIN	0.0	0.0	3.5(0.2)	76.9(1.3)	19.6(1.2)
15 MIN	56.7(0.8)	0.0	0.0	13.9(0.3)	29.4(0.7)
30 MIN	44.2(0.6)	0.0	0.0	26.4(0.1)	29.4(0.6)
60 MIN	34.7(0.8)	0.0	0.0	41.2(0.5)	24.1(1.2)

OHA = octahydroanthracene

DHA = dihydroanthracene

ANT = anthracene

HHA = hexahydroanthracene

THA = tetrahydroanthracene

Standard Conditions : Pittsburgh No. 8 coal, hydrogen, hexadecane, 380°C.

**TABLE 7 CONTINUED: G.C. ANALYSIS OF THE PRODUCTS FROM MODEL
DONORS IN REACTIONS WITH PITTSBURG NO. 8 COAL AT
VARYING REACTION TIMES.**

COMPOUND / CONDITIONS	WT% TET	WT% 1,2-DHN	WT% ISO	WT% NAP
ISO				
5 MIN	0.0	11.7(0.5)	47.0(0.4)	41.3(0.7)
15 MIN	19.5(1.5)	0.0	0.0	80.5(1.5)
30 MIN	20.5(0.7)	0.0	0.0	79.5(0.7)
60 MIN	24.9(0.80)	0.0	0.0	75.2(0.8)
NAP				
5 MIN	100.0	0.0	0.0	0.0
15 MIN	100.0	0.0	0.0	trace
30 MIN	88.2(0.5)	0.0	0.0	11.8(0.5)
60 MIN	87.8(0.4)	0.0	0.0	12.2(0.4)

TET = tetralin

1,2-DHN = 1,2-dihydronaphthalene

ISO = isotetralin

NAP = naphthalene

Standard Conditions : Pittsburg No. 8 coal, hydrogen, hexadecane, 380°C.

TABLE 8: THF SOLUBLE AND INSOLUBLES FRACTIONS FOR THE PITTSBURGH NO. 8 AND ILLINOIS NO. 6 LIQUEFACTION RECYCLE SOLVENTS.

RECYCLE SOLVENT	THF SOLUBLE	THF INSOLUBLE
PITTSBURGH NO. 8		
BEFORE REACTION	83.6(1.4)	16.4(1.4)
AFTER REACTION	84.7(0.1)	15.3(0.1)
ILLINOIS NO. 6		
BEFORE REACTION	76.9(0.3)	23.1(0.3)
AFTER REACTION	78.7(2.1)	21.3(2.1)

Reaction conditions: hydrogen, 30 minutes reaction time, 380°C.

TABLE 9: CONVERSION FOR THE REACTIONS WITH PITTSBURGH NO. 8 AND ILLINOIS NO. 6 LIQUEFACTION RECYCLE SOLVENTS.

MODEL COMPOUND ADDED	CONVERSION WITH PITTSBURGH NO. 8 COAL	CONVERSION WITH ILLINOIS NO.6 COAL
NONE	73.4(0.04)	69.7(0.9)
TET	73.3(1.1)	69.8(0.5)
ISO	74.4(0.5)	69.8(0.5)
OHA	74.0(0.9)	70.4(1.4)
HHA	73.3(1.6)	70.4(0.9)
DHA	73.1(0.9)	69.0(0.4)

Reaction conditions: hydrogen, 30 minutes reaction time, 380°C.

Project III.4 Better Hydrogen Mass Transfer in Coal Liquefaction (A. R. Tarrer, J. A. Guin and C. W. Curtis)

SUMMARY

Coal liquefaction is similar to other catalytic gas-liquid slurry-type reactions that are free-radical driven. In Task 1 of this work, a simple kinetic model was used to demonstrate the important role that hydrogen mass transfer plays during the initial stages of coal liquefaction. The model was shown to predict observed profiles for the H:C ratio of liquefaction products versus reaction time curves.

Task 2 of the work involved the development of more effective gas-liquid contactors. Two basic parameters were identified as important to effective mass transfer: initial bubble-size distribution and effective bubble pathlength. Gas-liquid mass transfer coefficients were experimentally determined for different combinations of gas-liquid contactors and columns by utilizing a catalyzed sodium sulfite reaction system. It was found that the most critical factor in the gas-liquid contactors studied was the shear stress at the point of gas introduction.

Two model reactions, known to be mass transfer limited, were used to test equipment designs for their potential use in coal liquefaction. The model reactions studied were naphthalene hydrogenation and tetralin oxidation. Injector nozzles were fabricated, tested, and installed in a pilot reactor system. Also, different packing sizes and pumps were evaluated in the pilot reactor system using the naphthalene hydrogenation reaction. Optimization of this reaction was carried out to the point where the free radical generation rate, not gas-liquid mass transfer, was limiting the reaction.

The tetralin oxidation (TO) reaction was studied to gain experience with a more complex reaction mechanism. A kinetic study was conducted in the reactor system and a novel reaction mechanism, based on this study, is proposed. Data analysis showed that the pilot reactor system was gas-liquid mass transfer limited at catalyst concentrations greater than 0.0769 M. Small concentrations of acetic acid and N,N-dimethylacetamide were added in the reaction as catalyst dispersants and found to significantly improve conversion. Based on experimental observations, the active state of the catalyst is an organometallic complex formed during the reaction. One role of these dispersants was thought to be in facilitating the formation of this

highly catalytic organometallic complex.

The TO reaction was observed to model coal liquefaction in that inhibitors were observed to terminate free-radical generation and completely halt reaction once they were present above a certain threshold concentration. This aspect of the TO reaction, as with coal liquefaction, represents a challenge that must be further addressed in future research.

Task 3 of the work had to do with developing means of applying techniques observed to be effective for improving mass transfer in commercial-scale systems and to microreactor methods used in exploratory laboratory studies. As has been discussed in past reports, one technique observed to improve mass transfer is to control the free-radical generation rate by switching temperature from a high to a low level at a sufficiently high frequency. By cyclic switching temperature, the rate of free-radical generation, and thus reactant (H_2 or O_2) demand, will also shift between high and low levels. Because of this switching, reactant demand (kinetics) can be kept in balance with reactant supply (mass transfer capabilities). This concept was tested using the pilot reactor system and the TO reaction. A doubling of the frequency via a simple design alteration appears to have improved the mass transfer rate significantly.

In preparation for doing exploratory coal liquefaction studies, attempts were made to develop a methodology for evaluating the effect of switching frequency on liquefaction product distribution. To this end: a series of microreactor studies were performed using the model naphthalene hydrogenation reaction. Reaction conditions were identified at which mass transfer was controlling (i.e. reaction rate was limited by hydrogen supply). Responses in the rate of conversion and loss of catalyst activity in relation to changes in switching frequency were measured. It was observed that a high switching frequency, of the order of less than one switch every ten seconds, was required. The necessity of using this high of a frequency made it very difficult to use a standard microreactor to study the effect of this parameter.

Continued development of the techniques being studied in this work will eventually require pilot studies on a significant scale. For this reason, a concerted effort has been made to gain the interest of an industrial participant in the research. Eastman Chemical Company has expressed an interest in the research and efforts are now underway to establish cooperative agreements necessary for their future participation in this research program.

I. BACKGROUND AND RATIONALE (MATHEMATICAL MODEL : COAL LIQUEFACTION)

Coal Liquefaction

The major goal of most coal conversion processes is the removal of sulfur and minerals from the coal by conversion of the coal into a clean solid or liquid fuel. The two major problems in coal liquefaction are the difference in the hydrogen content between the raw materials and the desired products and the need for removal of heteroatoms, such as oxygen, sulfur, and nitrogen.

Chemistry

The chemical structure of coal has been identified as a combination of multi-benzene ring structures (1). The number of rings can vary from one to as many as six or seven rings condensed together, with an average size unit of about three rings. Conversion of such a multi-ring structure to materials, which would be gaseous or liquid at room temperature, has been shown (2, 3) to involve two steps. First, free radical fragments are formed by thermal cleavage or pyrolysis. These ring fragments, in turn, must either be stabilized by the addition of hydrogen to the unsaturated bond of the free radical or repolymerized. The amount of hydrogen required is dependent on the hydrogen content of the coal. The atomic hydrogen content of a typical coal (1) is on the order of 0.82 hydrogen atom for each carbon atom, while typical transportation fuels show hydrogen to carbon ratios of 2:1. Thus, liquefaction of a typical coal without the addition of hydrogen would theoretically allow only 42 percent of the carbon present to be converted into transportation fuels.

In addition, hydrogen combines with heteroatomic sulfur and oxygen in the coal to form hydrogen sulfide and water (1). These by-products can then be removed as gases. Therefore, most liquefaction processes require the addition of large quantities of hydrogen to the coal, usually by a combination of donor solvent and molecular hydrogen, to increase the hydrogen-to-carbon ratio and remove impurities. The resulting liquid products can then be used as transportation fuels.

Kinetics

Conversion of coal to a soluble form has been shown to consist of a series of very fast reactions followed by slower reactions (4). The fast initial reactions have been proposed to involve the thermal disruption of the coal structure to produce free radical fragments. This similarity between coal liquefaction and coal pyrolysis has been previously demonstrated (2).

Earlier research by Petrakis (5) has shown that large quantities of free radicals (~0.1 molar solutions) are produced when suspensions of coal in various solvents are heated to 450°C.

For the purpose of this discussion, a kinetic model is assumed and the validity of the model is then checked with available data on coal liquefaction. The basic assumption of this kinetic model is that the thermal formation of free radicals in coal is an autocatalytic reaction. Therefore, the reaction can be represented as follows:

where A equals the concentration of coal and $R\cdot$ is the concentration of free radicals. In such a reaction scheme, the reaction rate is slow at first because few free radicals will be present. However, the rate increases to a maximum as free radicals are formed, and then drops to a low value as the reactant is consumed.

The reaction rate for an autocatalytic reaction (6) is:

$$r = k [A][R] = \frac{d[R]}{dt} \quad [2]$$

where $k = k_0 e^{-E/RT}$. A frequency factor and activation energy for free radical formation is needed to estimate reaction rates. A frequency factor, 10^{11} min^{-1} , for coal pyrolysis was previously determined by Juntgen and van Heek (7). Activation energies for coal pyrolysis have been estimated by Juntgen and van Heek (7) and Wiser (2) to be 42.1 and 35.6 kilocalories per mole, respectively. These estimates are in agreement with energies calculated by Petrakis and Grandy (5) using dissociation energies for carbon-carbon bonds.

Free radical formation does not occur until the reaction mixture is above a threshold temperature. Petrakis (5) determined that this threshold temperature is about 400°C. It is assumed that the free radical concentration will equal zero below the threshold temperature. If hydrogen is available to the free radicals, product formation occurs. The rate of this reaction is dependent on the amount of hydrogen available in the bulk liquid. The concentration of products from this reaction will be designated P_1 . If hydrogen is unavailable, the radicals are not stabilized and undergo a variety of undesirable reactions where high molecular weight solids are formed. The concentration of products from these undesirable reactions will be designated P_2 .

These reactions can be represented by:

The product mixture from the conversion of coal will contain products from both reactions and unreacted coal. The concentration of unreacted coal will be designated A. The H:C ratio of the overall product mixture will be equal to:

$$\frac{(H:C)_1(\text{moles } P_1)}{(\text{moles } P_1 + P_2 + A)} + \frac{(H:C)_2(\text{moles } P_2)}{(\text{moles } P_1 + P_2 + A)} + \frac{(H:C)_A(\text{moles } A)}{(\text{moles } P_1 + P_2 + A)} = \text{H:C of coal products} \quad [5]$$

Therefore, the H:C ratio of the coal product mixture is a measure of the number of desirable reactions and an indication of the amount of hydrogen available.

The kinetics are complicated by a competing reaction which also utilizes hydrogen: the removal of heteroatoms. There is evidence that this reaction is a preferential one and that hydrogen used for heteroatom removal is at the expense of product formation. As a result, longer residence times at reaction temperature will allow more removal of heteroatoms at the expense of the H:C ratio of the products. This effect has been confirmed. Whitehurst (4) concluded that "long contact time thermal processes have the intrinsic disadvantage of poor selectivity for light hydrocarbon gas formation relative to heteroatom removal".

Free radical formation is independent of heteroatom removal but the formation of P_1 will compete with the heteroatom removal reaction for the available hydrogen. The effects of the catalyst on both free radical formation and hydrogenation are not well understood. Recognizing that these effects exist, the overall shape of plots predicting free radical concentration and H:C ratio of coal products should still be similar if the basic assumption of an autocatalytic reaction is true.

For the purpose of this discussion, it is assumed that the hydrogen demand rate is dependent only on the conversion of free radicals to product and no additional reactant is fed after time equals zero. In this scenario, the hydrogen demand will be proportional to the formation of free radicals with time, where the hydrogen requirements for heteroatom removal and the effects of the catalyst on reaction rate have been ignored.

The demand for hydrogen will be proportional to the rate of formation of free radicals, using the aforementioned assumptions. Therefore, $Q_{\text{demand}} \propto d[R]/dt$.

As shown in Figure 1, the demand rate reaches a maximum and then drops to zero as the reactant is consumed. Hydrogen supply rates with time were calculated for various types of equipment and are shown superimposed over the previously determined free radical formation rate (Q_{demand}) in Figure 1. The mass transfer coefficients (kla' values) were determined in an

Figure 1: Rate Comparison under Reactor Conditions of Constant Temperature and Pressure

Figure 2: Test Data from SRC Process (4)

earlier work (11) and are 0.3, 0.73, and 2.4 min⁻¹ for a bubble column, motionless mixer, and high shear device, respectively. A value for t_1 of 0.2 hour was arbitrarily chosen for illustration. The difference in the hydrogen demand and supply at any residence time is equal to the hydrogen deficit.

As discussed earlier, the H:C ratio of the coal products is a measure of the number of undesirable reactions and an indication of the magnitude of the hydrogen deficit.

The hydrogen supply will determine the number of moles of product 1 formed. It is assumed that at the end of each residence time in the reactor, the reaction mixture temperature is lowered to quench the reaction. Where a hydrogen deficit exists, the moles of free radicals at each residence time will convert to product 2.

Whitehurst (4) performed tests where the H:C ratio of the coal products was determined with residence time. This data is represented in Figure 2. The H:C ratio of the coal products in this reactor system reached a minimum at a residence time of approximately 95 minutes and then increased. Therefore, the autocatalytic free radical kinetics and the relative importance of gas-liquid mass transfer for coal liquefaction could be confirmed if the aforementioned model predicted a similar dependence of the H:C ratio of the product with time.

The following table summarizes the assumptions used in the model to predict the H:C ratio for the product with time.

Table 1
Coal Liquefaction Model Assumptions

Reaction Temperature = 460°C (8)
Reaction Pressure = 1200 psig (8)
Molecular Weight of Coal = 385
Activation Energy = 35.6 kcal/mole (2)
Frequency Factor = 10 ¹¹ min ⁻¹ (7)
Coal Concentration in Tetralin = 50 wt% (8)
Initial Coal H:C Ratio = 0.88 (4)
Mass Transfer Coefficient = 0.3 min ⁻¹

It should be noted that the Whitehurst H:C ratio data (4) did not include specific reaction conditions, so reaction conditions from the same process published in the same year from another source (8) were used. The molecular weight is an average of molecular weights published for

Figure 3: Dependence of Product H:C Ratio on t_1

Figure 4: Dependence of H:C Product Ratio on $(H:C)_1/(H:C)_2$

several types of coal (8).

There are only three adjustable parameters in the model once the above assumptions are made. These parameters are the H:C ratios of product mix 1 and product mix 2 and time, t_1 . First, $(H:C)_1$ and $(H:C)_2$ were assumed equal to 2 and 0.7, respectively, and t_1 was varied. The predicted H:C ratio with time is shown in Figure 3.

Secondly, t_1 was set equal to 0.025 hour and the ratio of $(H:C)_1/(H:C)_2$ was varied to determine the effect on the H:C product ratio. Figure 4 predicts that the H:C ratio of the overall coal products for this type of reactor system will increase with residence time until the maximum hydrogen supply rate is reached at t_1 . At this point, the H:C ratio of the coal products will start to decrease as more free radicals are formed and reaches a minimum when the concentration of free radicals reaches a maximum. Then, the ratio will again increase as the free radical concentration decreases as the concentration of coal decreases to zero. This figure closely correlates to Figure 2 and therefore it is concluded that the mathematical model is representative of kinetics in coal liquefaction.

Tubing Bomb Reactor

The other data that exists to confirm the autocatalytic nature of coal liquefaction involves tubing bomb reactors. The tubing bomb reactor is a batch-type reactor. Reactants are charged and then pressurized with hydrogen before placement into a constant temperature bath. If it is assumed that the concentration of hydrogen in the reactant liquid phase, c_1 , equals the saturation concentration at the initial pressure, c_{s0} , at time equal zero as before, then $Q_{[supply]}$ will again equal zero initially. As time increases the pressure in the reactor and c_s will decrease until both reach zero. Therefore, $Q_{[supply]}$ will also approach zero.

And again at t_1 , c_1 will become zero because all the hydrogen entering the bulk liquid solution through the liquid film is immediately consumed by the reaction. This would occur when the reaction rate is very fast and is the expected outcome when a large concentration of free radicals exists.

If it is assumed that c_1 reaches zero before the initial pressure in the reactor, and c_{s0} decreases significantly, then the following equation will apply:

$$Q_{[supply]} = k_1 a'(c_{s0}) \quad [6]$$

So, at times between zero and t_1 , it is assumed that c_1 will decrease linearly with time and therefore $Q_{[supply]}$ will increase linearly until c_1 reaches zero. After t_1 , $Q_{[supply]}$ will equal $k_1 a'(c_s)$.

Figure 5: Predicted Free Radical Concentration in Tubing Bomb Reactor

Figure 6: Free Radical Concentration from Tubing Bomb Reactor Tests (5)

Figure 5 is a plot of the hydrogen deficit or predicted free radical concentration with time.

Petrakis (5) conducted experiments into free radical concentrations in coal liquefaction with time using tubing bomb reactors. The data was obtained in tubing bomb reactors with Powhatan #5 coal and tetralin at 460°C and 1200 psig hydrogen. Figure 6 indicates the number of spins (free radical concentration) with time. Electron spin response (ESR) was used to determine the free radical concentration. In this technique, the sample is exposed to magnetic fields followed by electromagnetic radiation. The observed spectra is obtained at a fixed frequency while the field is varied. Each g-value from the spectra identifies the type of species and the number of spins is related to the intensity or concentration of the species. A comparison of Figure 5 with 6 indicates that the actual data does mirror the predicted free radical concentration for short times.

Conclusions

It is concluded that free radical formation is an autocatalytic reaction. Then residence time determines the concentration of free radicals (maximum conversion) and hydrogen concentration determines the conversion of these free radicals into the desired product (product selectivity).

Figure 1 predicts that the magnitude of the hydrogen deficit is related to the reactor design. The hydrogen demand is related to residence time in the reactor and the reaction temperature. The hydrogen supply is dependent on the mass transfer coefficient, reaction temperature, and residence time.

II. PILOT REACTOR SYSTEM

Introduction

The above modelling studies indicate that while hydrogenation at a constant temperature for long residence times will predict high conversion, it will not provide the product selectivity needed. One option is to slow the formation of free radicals by controlling residence time when the temperature is above the threshold for free radical formation. A very short reaction time combined with good mass transfer (high hydrogen supply rate) will allow operation of the reactor in a zone at the left side of Figure 1, where the hydrogen deficit is minimized. In addition, by limiting the time the reaction mixture is exposed to a hydrogen deficit, catalyst deactivation is prevented and product selectivity is obtained.

So, one is left with the dilemma that short contact thermal time is desired from the

standpoint of product selectivity and controlling heteroatom removal, but product conversion with short residence times is small and therefore not viable economically. The reactor system design must balance these competing forces.

Figure 7 illustrates the general concept envisioned for coal liquefaction. Cyclic switching between a reaction zone (high temperature) and quench zone (low temperature) is used to control the reaction rate. This reactor flow arrangement is commonly used with jet-type reactors, where reaction rates are very high. This type of system provides flexibility by allowing modification of two control parameters: 1) reaction zone temperature, and 2) the frequency of cyclic switching. These parameters can be adjusted to limit the mass transfer requirements per reaction cycle.

The pilot scale reactor system used in the current work is based on the same general concept. The chief difference is the use of the concept in a batch system rather than in a continuous one. The current reactor system (Figure 8) contains one high reactivity zone and one low reactivity zone. The reaction mixture is recycled through the system at a rate to produce very short residence times in the high reactivity zone.

A packed column-type reactor with its small liquid hold-up volume and high mass transfer was concluded to be preferred for hydrogenation. Even though conversion (free radical formation) can be optimized in an agitated reactor, a packed column is better for product selectivity. It was concluded that product selectivity was the more important criteria for reactor selection and therefore a packed column design was used. In addition, heat transfer for plug flow through a packed column with metal rings is highly efficient because there is a large surface area per unit volume of liquid.

Selectivity is dependent on hydrogen supply (mass transfer) to consecutive reactions after free radical formation. The principal factors affecting selectivity are:

- Solubility of gas in liquid
- Relation between the reaction rate and mass transfer rate
- Temperature of the reaction mixture
- Gas pressure
- Interfacial area related to unit volume of liquid
- Intensity of axial mixing in both phases
- Arrangement of the flows of gas and liquid in the reactor (co-or counter-current)

Figure 7: Proposed Concept for Coal Liquefaction

Figure 8: Current Reactor System Design Concept

The hydrogen supply to the reaction can be increased through modifications to equipment and/or reaction conditions. The maximum value of gas-liquid interfacial concentration, c_1^* , is equal to the solubility of the gas in the reaction mixture. The solubility is dependent on pressure and temperature. For example, the solubility of hydrogen in tetralin increases with increasing temperature (13). Therefore, an increase in temperature will increase c_1^* and result in a higher hydrogen supply rate. Dilution of reactant in the bulk liquid will also increase c_1 . However, the magnitude of these changes is too small to completely eliminate the deficit.

- The gas concentration at the gas-liquid interface, c_1^* , is determined by the gas transfer rate. Factors which affect the average gas transfer rate include power input per unit volume, gross flow patterns in the reactor, coalescence and redispersion rates of bubbles, bubble size distribution, total bubble surface area, holdup (gas volume fraction), and gas and liquid residence time distributions, and characteristics and intensity of flow (turbulence). These factors, in turn, are dependent on equipment design.

The desired goal in the system is to create the largest number of small bubbles economically achievable and maintain them throughout the reaction zone. The average gas-liquid mass transfer rate is affected by two parameters: (1) effective path length and (2) initial bubble formation. The effective path length is the residence time in the reactor system before significant coalescence occurs. This parameter is determined by the chemical characteristics of the reaction mixture. Initial bubble formation is determined by the gas-liquid contactor used for introduction of the gas.

III. GAS-LIQUID MASS TRANSFER STUDIES

Introduction

The objective of this facet of the research was to investigate different approaches to improving mass transfer (MT) rates directly through design. It was theorized that three parameters, the liquid and gas velocities at the initial gas-liquid contact point and the liquid velocity in additional distributors, were the most important factors affecting the mass transfer rate.

Gas Velocity

The gas velocity was not varied in the current work so that the nozzle-type contactor (discussed later) could be operated under optimum conditions at the upper flowrate and all test

results compared. The gas velocity used in the cold flow bench tests was 9.2 feet per second. the oxygen source for the current work was compressed air.

Previous investigators (10, 11) have studied the effect of gas velocity on the mass transfer coefficient. They concluded that the gas velocity can have an effect on the mass transfer coefficient. However, the dependence of the coefficient on the gas velocity does not follow a consistent pattern among different studies. Horak and Pasek (10) determined the mass transfer coefficient in a packed column with low gas velocities. Wang and Fan (11) investigated the effect of gas velocity, over a range of 5.4 to 42 feet per second, on the mass transfer coefficient in bubble columns and columns packed with motionless mixers. The results indicate that the k_1a' is more dependent on the type of column than it is on gas velocity. Oxygen was used in these tests.

Cold Flow Bench Tests

The initial gas-liquid contact device affects the number and initial size of the bubbles for the system and therefore affects the initial interfacial area for mass transfer. Additional saturators (packed columns, motionless mixers, etc.) redistribute the gas into smaller bubbles and thereby extend the effective path length and increase gas holdup and therefore, the overall mass transfer rate. A standard O_2 - Na_2SO_3 reaction system was used to determine mass transfer coefficients in cold-flow bench tests.

Experiments were conducted with five types of gas-liquid contactors and two types of columns. The gas-liquid contactors included mixing tees of various sizes, an injector nozzle, and centrifugal pump. The results of testing with the nozzle are discussed later. The columns included a 1" O.D. packed column and a 1/2" O.D. empty column (equivalent volume). The equivalent volumes assured a constant residence time in the column at comparable flowrates. The objective of the testing was to determine the effect of superficial liquid velocity at the initial gas-liquid contact point and in the column on the gas-liquid mass transfer coefficient.

Results

In general, cold-flow bench tests were conducted by lowering the dissolved oxygen content of distilled water with the addition of sodium sulfite in the presence of a catalyst (cobalt sulfate). Three tests were performed at each set of operating conditions and the values averaged.

The residence time in these tests is defined differently from previous investigators. Since it was discovered that the gas-liquid contactor had a significant effect on the mass transfer

coefficient, the combined volume of the gas-liquid contactor and the packed column was used to determine residence time. The liquid volume for the packed column used in the tests was determined to be 60 ml. The calculated volumes, after point of gas introduction, of the gas-liquid contactors were 0.4 ml, 2 ml, 21.24 ml, 18.6 ml, and 17.2 ml for the 1/4", 1/2", and 1" tees, nozzle, and pump, respectively.

The calculation of the test results is based on the film penetration theory. A packed column was used in a series of tests where the size of the gas-liquid contactor was varied. The objective was to determine the effect of the liquid velocity at the gas-liquid contactor on the mass transfer coefficient. Three tees were used as gas-liquid contactors and included 1/4" and 1/2" tubing tees and a 1" polyvinyl chloride piping tee. A short length of 1/4" tubing was installed in the gas side of the 1/2" and 1" tees to ensure that the initial gas-liquid contact would occur at the wall of the tee and at the same gas velocity for consistency in the tests. The data from these tests is tabulized below.

Table 2

**Effect of Liquid Velocity at the Gas-Liquid Mixing Tee
With Liquid Flowrate of 1.57 gpm**

Air Flowrate = 0.138 scfm

Test	Tee Size (in.)	Stable DO Conc. (ppm)	Temperature (°C)	Residence Time (secs)
34	1/4	6.205	30.2	0.61
35	1/4	6.21	31.3	0.61
36	1/4	6.4	30.9	0.61
26	1/2	4.5	27.5	0.626
27	1/2	4.4	29	0.626
28	1/2	4.3	23	0.626
30	1	4.8	28.3	0.82
31	1	4.8	29.7	0.82
40	1	4.8	31.1	0.82

Table 3

**Effect of Liquid Velocity at the Gas-Liquid Mixing Tee
With Liquid Flowrate of 3.614 gpm**

Air Flowrate = 0.138 scfm

Test	Tee Size (in.)	Stable DO Conc. (ppm)	Temperature (°C)	Residence Time (secs)
37	1/4	6.63	30.7	0.265
38	1/4	6.69	31.8	0.265
39	1/4	6.8	31.1	0.265
23	1/2	6.6	24	0.272
24	1/2	6.4	23.3	0.272
25	1/2	5.7	23.5	0.272
41	1	6.4	30.3	0.356
42	1	6.1	28.2	0.356
43	1	6.3	30.2	0.356

As can be seen from the tables, the tests were performed at two flowrates. An equivalent diameter was calculated for the packed column by using the actual length of the column and the measured liquid volume (60 ml). This equivalent diameter was used to calculate an average velocity within the packed column for comparison purposes. As can be seen (Figure 9), the superficial liquid velocity at the gas-liquid contactor is more important at lower column velocities. At both packed column velocities, there is a region where the liquid velocity at the contactor has little effect. However, after a point, a transition occurs and the liquid velocity at the gas-liquid contactor has a significant impact upon the mass transfer coefficient. As can be seen, this transition effect does not occur until a higher velocity with higher packed column velocity.

A similar effect has been observed in sodium sulfite tests with venturis (12). In these tests, the fraction of gas absorbed was not affected by an increase in the Reynolds number in the laminar region. However, a rapid increase in absorption was noted in both the transition and turbulent flow regions.

Effect of Packing and Column Velocity

The previously described packed column and a 1/2" cocurrent bubble column (equivalent

Figure 9: Effect of Liquid Velocity in Mixing Tee on Mass Transfer Coefficient

Figure 10: Diagram of Typical Nozzle

volume) were used in a series of tests where residence time in the column was held constant. The liquid velocity was varied between 0.58 and 13.99 feet per second at the gas-liquid contactor by using the 1/4" and 1" tees. The results are included in Tables 4 and 5.

The mass transfer coefficient with the packed column was higher at both gas-liquid contactor velocities. However, the cocurrent bubble column mass transfer coefficient more closely approaches that of the packed column when the velocity at the gas-liquid contactor is at the upper value.

Table 4

**Test Results from 1/2" Cocurrent Bubble Column at
Liquid Flowrate of 1.57 gpm**

Air Flowrate = 0.138 scfm

Test	Tee Size (in.)	Stable DO Conc. (ppm)	Temperature (°C)	Residence Time (secs)
47	1/4	6.9	22.0	0.61
48	1/4	6.75	23.9	0.61
49	1/4	6.8	24.8	0.61
44	1	4.3	23.2	0.82
45	1	4.5	23.0	0.82
46	1	4.4	20.8	0.82

Table 5

**Test Results from 1" Cocurrent Packed Column at
Liquid Flowrate of 1.57 gpm**

Air Flowrate = 0.138 scfm

Test	Tee Size (in.)	Stable DO Conc. (ppm)	Temperature (°C)	Residence Time (secs)
34	1/4	6.205	30.2	0.61
35	1/4	6.21	31.3	0.61
36	1/4	6.4	30.9	0.61
30	1	4.8	28.3	0.82
31	1	4.8	29.7	0.82
40	1	4.8	31.1	0.82

Nozzle-type Contactor

The nozzle is a Bernoulli device similar to an orifice or venturi. Figure 10 illustrates the essential elements of a nozzle. The device converts the potential energy of the drive fluid into kinetic energy. The resulting high speed jet entrains the slow speed fluid in a mixing chamber. The combined fluid flows into a diffuser and passes out of the device through a gradual enlargement. The angle of enlargement is maintained at an angle of 8 degrees or less, as in venturi design, to prevent phase separation. The air is entrained by the jet and the mixture compressed in the diffuser. The air compression is assumed to take place isothermally due to the relative heat capacities of gas and liquid. The action is simple and no moving parts are required. However, theoretical equations for the design of nozzles have not yet been fully developed for situations where one of the fluids is a gas. Development has been hampered by problems with compressibility, variations in volume and density, and the unsteady state conditions which exist within the interior of the nozzle. Therefore, the design of the nozzle must be based on parameters which are experimentally determined.

The ratio of the flowrate of air to the flowrate of water determines the location of mixing within the interior of the nozzle. Earlier investigations have identified three regions of operation for water jet air pumps. These regions are illustrated in Figure 10 and are dependent on the flowrate ratio. It is desirable to design the nozzle such that mixing occurs in the mixing

chamber. Under these circumstances, the pressure increase that occurs in the diffuser is then advantageously used to compress the bubbles previously formed. If the mixing occurs downstream of the mixing chamber, the efficiency of the nozzle is decreased. As shown in Figure 10, high gas rates cause a cavitated region to form throughout the diverging cone and into the discharge section. It has been experimentally determined (13) that the volumetric flowrate ratio of gas to liquid must be 0.33 or less to maintain a nozzle within region A.

As discussed earlier, the location of the gas introduction point is a critical parameter in the design of any gas-liquid contactor. It is the shear stress that breaks up the air and disperses it into a fine stream of bubbles. The shear stress at the wall is at a maximum and therefore it is desirable to introduce the gas at the wall of the nozzle .

The modified slot injector nozzle was evaluated at flowrates which were sufficient to produce a Reynolds number in excess of 4000 at the gas introduction point and therefore were in the turbulent flow region. Table 6 contains the results.

Table 6
Test Results From Nozzle as Gas-Liquid Contactor
Air Flowrate = 0.138 scfm

Test	Liquid Flow (gpm)	Stable DO Conc (ppm)	Temperature (°C)	Residence Time (secs)
17	1.57	4.6	24.0	0.79
18	1.57	4.4	23.0	0.79
19	1.57	5.5	23.0	0.79
20	2.425	6.0	23.0	0.51
21	2.425	6.4	22.5	0.51
22	2.425	6.0	23.0	0.51
11	3.1	6.0	27.0	0.40
12	3.1	5.8	28.0	0.40
13	3.1	5.5	29.5	0.40
14	3.614	4.9	40.0	0.34
15	3.614	6.5	24.0	0.34
16	3.614	6.0	24.0	0.34

Figure 11: Effect of Gas-Liquid Contactor on Mass Transfer Coefficient

The mass transfer coefficient for the nozzle/packed column system is compared in Figure 11 with the coefficients determined previously for tee/packed column combinations. As can be seen, the mass transfer coefficient for the nozzle falls between the 1/2" and 1" tees. The nozzle used had an outer diameter of 3/4" at the point of gas introduction. It can be concluded that the shear stress at the point of gas introduction is extremely important in determining the mass transfer coefficient, regardless of the design of the gas-liquid contact device.

Conclusions

It was concluded that the method of initial gas-liquid contact is a key parameter in improving the mass transfer coefficient. The gas-liquid contactor should be designed to introduce the gas at the point of highest shear stress. The impact of additional redistributors on the mass transfer coefficient is dependent on the efficiency of gas dispersion at the initial gas-liquid contact point. If the gas is not dispersed well initially, the role of the redistributor becomes more important.

The goal in a gas-liquid reaction system, therefore, should be to maximize shear stress at the initial gas-liquid contact point. The coalescence of the reaction mixture will then determine the number of additional redistributors required. The overall goal in design of the system should be to optimize the gas-liquid mass transfer with the minimum number of redistributors so that the pressure drop is limited.

IV. NAPHTHALENE HYDROGENATION

Introduction

Coal liquefaction, as discussed earlier, involves a complex set of reactions. Major reactions known to occur (1) include decarboxylation, desulfurization, denitrogenation, deoxygenation, and hydrogenation of aromatic rings. The complexity of the reaction mechanism does not lend itself to experimental testing of equipment designs. Therefore, several model reactions, known to be limited by gas-liquid mass transfer, were used to evaluate equipment designs for their potential to improve mass transfer. The hydrogenation of naphthalene to tetralin was one of the model reactions selected for study.

Hydrogenation of Naphthalene

In the hydrogenation of naphthalene to tetralin, free radicals will be formed if the reaction mixture is at temperature ($>90^{\circ}\text{C}$). Product formation will occur only if hydrogen is available with sufficient catalyst. It has been reported (10) that catalytic liquid phase hydrogenation of naphthalene with suspended powder catalysts is first order with respect to naphthalene and zero order with respect to the hydrogenated product.

The current work concentrated on maximizing mass transfer continually through the high activity zone of the reactor. The free radical reaction rate is controlled by sequential heating and cooling of the reactant so as to not allow the hydrogen demand rate to exceed the hydrogen supply rate. The demand is slowed, or partially quenched, by cooling below 90°C to prevent a hydrogen deficit. The primary operational variables used to control reaction rate are the heating and cooling temperatures and reactant recycle flow rate, F_1 .

The hydrogenation of naphthalene has been shown in previous tests (14) to be gas-liquid mass transfer limited when sufficient catalyst is present. In gas-liquid mass transfer, improvements in yield or reaction time would indicate that the reactor design provided better gas-liquid mass transfer. Different equipment designs were investigated and evaluated for mass transfer improvements in the current work.

The hydrogenation reactor system can be divided into three interrelated subsystems. These are: (1) the basic system consisting of packed column reactors and a liquid pump, (2) a gas recirculation unit, and (3) a liquid heating and temperature control system.

A piston pump was used to recycle the slurry in the first equipment configuration of the

reaction system tested. The reactor columns were packed with 5/8" diameter stainless steel rings. The free liquid volume of one of the packed columns was measured and found to be 67.5 milliliters. A 1/4" tubing tee was used as the gas-liquid contactor. The liquid flowrate through the system was varied from 0.291 to 1.356 gallons per minute in a series of tests. The catalyst charge (13 ± 0.1 grams 5% palladium on carbon) was maintained at a constant ratio to the tetralin (0.017) and naphthalene (0.1).

As shown in Figure 12, increasing the flowrate did produce an increase in the conversion rate below 1.2 gallons per minute. However, the reaction rate did not appreciably change above this flowrate. It would be expected that the kinetics of free radical generation would limit the maximum flowrate. At some specific flowrate, the residence time in the reactors would be so short that the hydrogen demand decreases below the hydrogen supply. Therefore, no increase in conversion rate would be observed with higher flowrate because the demand is limited. Table 7 compares the reactor residence times, flowrates, and conversion rates for the tests illustrated in Figure 12.

Table 7
Effect of Flowrate on Reactor residence Time and Reaction Rate

Liquid Flowrate (gpm)	Conversion Rate (% conversion/min)	Residence Time (secs)
0.291	0.692	25.74
0.728	0.751	10.29
1.165	0.856	6.43
1.456	0.848	5.14

The piston pump produced a pulsing flow, whose average flowrate was the indicated rate. The flowrate over half the reaction time, however, was below this rate. The effect of a consistently higher flowrate was tested by replacing the piston pump with a gear pump.

The reactor system was then operated under the same conditions as those used for the piston pump. The conversion rate with the gear pump was lower than that found with the piston pump, at comparable calculated flowrates.

This effect can be explained by one of two observations. First, there were mechanical difficulties with the gear pump. The pump was subject to overheating during the tests and appeared to have difficulty with pumping the reaction slurry. It is suspected that the actual flowrate may have been below the calculated rate shown on the graphs. The second explanation lies in the fact that during half the reaction time with the piston pump, the flowrate was higher than the calculated rate. This higher velocity could be producing the higher conversion rate.

The piston pump was reinstalled in the system and the reactor columns packed with 0.4" diameter stainless steel rings. The free liquid volume of a packed column was determined and found to be 60 milliliters. A comparison of the free volumes of the columns (60 ml versus 67.5 ml) reveals that the packing density is increased by using smaller packing rings. Packing density, in turn, will affect the mass transfer coefficient by increasing the gas holdup and hindering action of the packing and increasing the average liquid velocity in the reactor. In addition, the residence time in the reactors is decreased. The objective of the test was to determine if this equipment configuration would provide a closer match of hydrogen demand and supply rates.

The operating conditions were maintained, as in previous experiments, and the flowrate (1.165 gpm) which produced the highest conversion rate used. A comparison of the conversion rates for the two ring sizes is shown in Table 8.

The reduction in packing ring size increased the packing density and decreased the free liquid volume in the reactor columns by 11%. An increase of 5.5% in the conversion rate was produced by the smaller packing. Residence time in the reactors was calculated to be 5.71 seconds with the smaller packing. This residence time is between the times previously calculated for the flowrates of 1.165 gpm (6.43 seconds) and 1.456 gpm (5.14 seconds), where no change in conversion rate was observed. The results indicate that the operating conditions are close to optimization. Theoretically, there is a maximum conversion rate for the system. This maximum would occur where the hydrogen demand rate (free radical generation) is perfectly matched to the hydrogen supply rate.

Table 8
Effect of Packing Rings on Naphthalene Hydrogenation

Packing Ring Diameter (inches)	Conversion Rate (% conversion/min)
0.400	0.903
0.625	0.856

The reaction was carried out at constant operating conditions with different catalyst loadings. Two equipment configurations were tested in the catalyst study. The equipment in the first series included 5/8" packing rings and the piston pump set at a liquid flowrate of 0.291 gallons per minute. The pump was set at a liquid flowrate of 1.165 gallons per minute and 0.4" packing rings were used in the second configuration.

Graphs of the reciprocal rate versus reciprocal catalyst loading have been used to determine the relative importance of gas-liquid mass transfer. The hydrogen transfer rate can be calculated from the naphthalene conversion rate. In addition, the catalyst surface area is proportional to the catalyst loading. So, a plot of the reciprocal of the catalyst loading versus the reciprocal of the hydrogenation rate will indicate the relative importance. The reciprocal of the reaction rate should be linear with a positive slope. The magnitudes of the slope and intercept provide insight into the transfer resistances. If the intercept is larger in magnitude than the slope, then the gas-liquid mass transfer rate is controlling. If the slope is larger than the intercept, solid-liquid mass transfer rate is controlling.

The catalyst weight was varied from 6.49 to 19.49 grams. The plot (Figure 13) of the reciprocal rate versus the reciprocal loading indicates that for both equipment configurations, the gas-liquid mass transfer rate was controlling. The 5/8" ring and 0.291 gallons per minute flowrate is more dependent with a slope of 33.4 and intercept of 2420.8 (ratio of 72.6). The ratio of intercept to slope is 10.5 with the smaller rings and higher flowrate. The change in ratio indicates an improvement in the transfer rate. It can be concluded that the smaller packing rings and higher liquid flowrate did increase the gas-liquid mass transfer coefficient, thereby increasing the conversion rate.

Conclusions

Piston pump flowrate tests indicated that between a flowrate of 1.2 and 1.5 gallons per

Figure 12: Effect of Piston Pump on Naphthalene Hydrogenation

Figure 13: Effect of Catalyst Loading on Naphthalene Hydrogenation

minute, the hydrogen supply rate in the reactor exceeded the demand rate due to the short residence time in the reactors. An increase in packing density produced a higher conversion rate by more closely matching hydrogen supply and demand. It was concluded with catalyst loading studies that the gas-liquid mass transfer rate is controlling the reaction with both types of packing and over the range of flowrates tested.

V. TETRALIN OXIDATION

Introduction

The oxidation of tetralin is a free-radical, slurry-phase catalytic type reaction. Previous work performed by other investigators with the reaction has resulted in low tetralin conversion and low selectivity for alpha-tetralone. It was theorized that the previous problems were caused by catalyst deactivation due to a low oxygen mass transfer rate. Catalyst deactivation has been reported by a number of investigators (15-17) in reaction times as short as 20 minutes. The objective of the current work was to determine if the improved gas-liquid mass transfer provided by the current reactor system could produce higher conversions and better selectivity for alpha-tetralone.

The literature review revealed that no consensus on the kinetics of tetralin oxidation exists. For example, investigators (15-17, 20) have concluded that the conversion rate is independent of catalyst concentration, as well as, half, first and second order. The commonly accepted reaction scheme for tetralin oxidation is shown in Equation 7.

Equation 7

The tetralin oxidation reaction was carried out in the same equipment as that used for naphthalene hydrogenation, except for a few changes. Modifications to the equipment included enlargement of the preheater and chiller, disconnection of the gas compressor, and installation of a nozzle-type contactor as the gas-liquid contactor. The reactors were packed with 5/8" stainless steel packing rings for all oxidation tests.

The charging of the materials to the reactor and operation of the system was consistent in all tests. A predetermined quantity of tetralin and catalyst (copper hydroxide), and in some cases toluene or hydrogen peroxide, were charged to a beaker. The slurry was sonicated for about 10 minutes and charged to the system when the desired reactor temperature was reached. Tetralin (100 milliliters) was then used to flush the charge line. The system pressure was increased to 215 psig with oxygen. The pressure of the system was monitored and the pressure maintained at 215 psig by addition of oxygen. The reaction time was started when continuous usage of oxygen was obtained. Samples were removed from the system at ten minute intervals in the pilot scale tests. When the desired reaction time was reached, the reactor was cooled and vented. The reactor contents were drained, the final product mixture filtered twice, and a sample removed. The reactor system was charged with tetralin, recycled, and drained to flush the system after each test. The samples were analyzed by gas chromatography using 1-methylnaphthalene as the internal standard.

Smaller scale tests were conducted in a stainless steel tubing bomb microreactor. The outer diameter of the reactor was 0.75 inches. The oxygen was charged to the reactor via a regulating valve through 1/4" tubing. The reaction temperature was maintained by immersing the reactor in a fluidized sand bath equipped with a temperature controller. The reactor was agitated at 400 cycles per minute for 2.5 minutes in the bath. After the reaction time, the reactor was removed from the bath, quickly cooled in a water bath, and dried. The reactor was then vented and recharged with oxygen before return to the sand bath. This process was repeated until the total time in the bath equalled the desired reaction time. The contents of the reactor were filtered twice and a sample analyzed by gas chromatography.

Figure 14: Tetralin Oxidation with
 0.0384 M Cu in Preliminary Tests

Figure 15: Tetralin Oxidation with
 0.0096 M Cu in Preliminary Tests

Since no consensus on reaction kinetics was discovered in the literature review, an exploratory kinetic study was conducted in the pilot reactor system. The results of this study revealed that the reaction rate appears to be dependent on catalyst concentration and that conversion and product formation are higher at the upper temperature. These results would be expected for this type of reaction.

Further observations can be made when the data is plotted as illustrated in Figures 14 and 15. First, the THP concentration reached a maximum during the reaction at both temperatures. In addition, unknowns 1 and 2 form late in the reaction and the tetralol reaches a steady state concentration relatively early in the reaction. Also, THP concentration was observed to vary inversely with catalyst concentration. Tetralone production was found to be more strongly dependent on catalyst concentration than on temperature. The catalyst concentration had a much smaller effect on tetralol production.

Correlation of these observations with equation 7 can provide insight into the reaction kinetics. The generation of free radicals from tetralin is a function of temperature and time only. Therefore, an increase in the temperature would increase the free radical generation rate. The data indicates that the catalyst is participating in the tetralone formation reaction. The oxygen supply is crucial only in THP formation and in secondary oxidation of the products. Therefore, if tetralone formation is more dependent on catalyst loading than on temperature the reaction is not limited by the free radical generation rate but by either the THP formation rate or the catalyst concentration.

Tetralol formation also showed dependence on catalyst loading and so it is concluded that the catalyst is participating in this reaction. In addition, the tetralol concentration profile with time suggests that it is an intermediate in a reaction to tetralone. This indicates that a reaction step is missing from equation 7.

Unknowns 1 and 2 are related to the tetralone and tetralol concentrations and therefore are suspected to be the secondary oxidation products, 1,4-dihydronaphthoquinone and 1,2,3,4-tetrahydro-1-hydroxy-keto-naphthalene. Hydroquinones, as a general class, are known inhibitors of oxidation reactions. Alpha-naphthol and 1,4-naphthoquinone are commonly used as antioxidants (35) to stabilize tetralin and prevent oxidation during storage. Alpha-naphthol has also been isolated as a higher product of tetralin oxidation by Martan et al. (19). The mechanism for the inhibition is known (22). The inhibitor molecules react with free radicals generated in

the reaction. The effect of the inhibitor is magnified beyond its concentration because each inhibitor molecule reacts with two radicals (21).

Further reactor tests were conducted to obtain more complete kinetic data for tetralin oxidation in the pilot reactor system. Samples were withdrawn from the reactor at 10 minute intervals in these tests. The reaction condition chosen were based on the preliminary test results. The catalyst concentration was progressively increased to determine its effect on product formation while other reaction conditions were kept constant. Since free radical generation did not appear to be limiting the reaction, the temperature was maintained at 100°C. It was theorized, then, that the products of the secondary oxidation of tetralone were responsible for autoinhibition in tetralin oxidation. Another interesting observation made was that the conversion rate after the initial rate is higher with higher catalyst loadings.

Tetralin concentration variance with time reveals that tetralin conversion proceeds at a constant rate only at short reaction times. This constant rate was labeled the initial rate. A linear regression analysis was performed on the early tetralin concentration variation with time and the conversion rate determined from the slope for each test. The determination coefficient (r^2) was 0.98 or greater in all regression analyses. The values are shown in Table 9.

Table 9
Initial Reaction Rate

Catalyst Concentration (mols/lit)	Initial Reaction Rate (mols/lit-min)
0.0190	0.0593
0.0383	0.5231
0.0769	0.5307
0.0769	0.0909
0.0942	0.0583
0.1154	0.7198

These initial reaction rates were used to derive an empirical rate expression. The derived expression is:

$$-[\text{dTet}]/[\text{dt}] = k[\text{Tet}][\text{Cu}]^{1/2} [\text{THP}]^{1/2} \text{mol/lit-min} \quad [8]$$

where k equals 0.18 min^{-1} . Since the reaction rate is half order with respect to copper and THP, it suggests that a THP-copper complex is the active form of the catalyst and that the initiation reaction is first order in copper and THP and catalyst deactivation is occurring. A complex as the active catalyst would explain the slower drop off in conversion rate with higher catalyst loadings. More THP would be complexed with higher catalyst loading at which significant inhibition and shutdown of THP formation occurs. So, the reservoir of THP is higher and conversion can continue for a longer period of time.

Catalyst Complex

Initiation by metal-peroxide complexes is not unknown. Chain initiation via the unimolecular decomposition of an iron-hydroperoxide complex has been proposed by Sheldon and Kochi (23). Their mechanism would be as follows for the current system:

In low polarity media, the copper is tied up as the complex with the alkyl hydroperoxide in excess. As the concentration of alkyl hydroperoxide decreases, a point is reached at which $[\text{Cu}] \gg [\text{THP}]$ and the equilibrium concentration of the uncomplexed Cu^{I} increases to the point that oxidation of the copper occurs. The formation of Cu_2O produces an insoluble catalyst which precipitates, decreasing the available catalyst concentration. It was observed in the current work that a catalyst color change to brown corresponds with the reaction rate slowdown. It is theorized that the brown color is indicative of the formation of copper oxide (Cu_2O). The copper oxide is insoluble in the reaction mixture and precipitates the copper out of solution.

A simple test was conducted to determine if THP concentration was affected by catalyst addition. Copper hydroxide in two different amounts was added to aliquots of product solution from an experimental product high in THP concentration. An immediate color change from gold/light brown to green was associated with the dissolution of the catalyst. A solution of copper hydroxide in tetralin is turquoise blue. Only in the presence of THP was the distinctive green color observed with catalyst addition. The green color appears to be indicative of the copper-THP complex.

The apparent THP concentration was found to decrease after addition of copper hydroxide. The results of this simple test have broad implications. It can be concluded that 1) the complex

is soluble in the reaction mixture, 2) when the complex still exists in a sample, product concentrations are increased, and 3) selectivity, when the complex is present, is falsely skewed high. Based on previous results, the complex concentration will decrease with reaction time as inhibition occurs. So, the analytical results will approach the real concentrations at longer reaction times and only early samples are significantly skewed.

THP formation is one of the key parameters critical to understanding the kinetics of the reaction. THP concentration data from the pilot reactor study is plotted as a function of catalyst concentration and reaction time in Figure 16. Several interesting observations can be made from this graph. First, the observed THP concentration reaches a maximum during the reaction and the maximum is inversely related to the catalyst concentration. Second, the reaction time at maximum concentration is shifted later in time, with a decrease in catalyst concentration.

Mizukami and Imamura (18) also observed that THP formation decreases rapidly with increasing catalyst concentration and upon decreasing initial tetralin concentration. Martan et al. (33) and Kamiya et al. (20) both proposed that the maximum THP concentration is proportional to the catalyst concentration as follows:

$$[\text{THP}]_{\text{max}} = 1/[\text{metal}]^n \quad [13]$$

However, Martan (19) found that n equalled 1 while Kamiya's data (20) fit a value of 2 for n . Martan conducted his tests at 80°C with an initial tetralin concentration of 3.79M in acetic acid with cobalt acetate (0.0027-0.008M). The Kamiya data was generated by tetralin (1.22M) oxidation at 50°C in acetic acid with cobalt acetate (0.001-0.004M).

The following kinetic expression was derived for $[\text{THP}]_{\text{max}}$:

$$[\text{THP}]_{\text{max}} = k_1 [\text{R}\cdot][\text{O}_2]/k_2 [\text{Cu}]^n \quad [14]$$

So, a plot of $[\text{THP}]_{\text{max}}$ against the reciprocal of catalyst concentration would produce a graph whose slope is proportional to the product of free radical and oxygen concentrations. It can be concluded, then, that n is equal to 2 at all catalyst concentrations and that a calculation of 1 for n from equation 13 is related to limitation of the reaction by the catalyst concentration. The reciprocal of the square of catalyst concentration against the maximum THP concentration is shown in Figure 17. The slope is constant at the higher catalyst loadings in this graph. A constant slope indicates that the numerator in equation 14 is not changing and is indicative of rate limitation caused by either oxygen supply or free radical generation. Where the slope is decreasing with lower catalyst loadings, the numerator in equation 14 is changing proportionally

Figure 16: THP Concentration

Figure 17: Dependence of Steady State THP Concentration on Reciprocal Square of Catalyst Loading

to the denominator and indicates that the catalyst concentration is limiting.

It can be concluded, then, that the Martan et al. data (19) at 80°C was limited by catalyst concentration. The Kamiya et al. data (20), on the other hand, was limited by either oxygen supply or free radical generation. The limitation can be determined by companion data (16) published by Kamiya et al. in similar equipment at 50°C.

Conclusions

Tetralin oxidation is not limited by the free radical generation rate at 100°C. The addition of hydrogen peroxide to the reaction mixture proved not to have a lasting effect on yield or conversion. An empirical rate expression was developed for initial tetralin conversion and used to predict catalyst deactivation.

The active catalyst in the reaction is not the catalyst as charged, but a metal-alkyl hydroperoxide complex. The complex was shown to be composed of two molecules of copper and one molecule of THP. The presence of the complex can be detected by its distinctive green color. A subtle form of catalyst deactivation is occurring in the reaction. The deactivation is caused by decreasing THP formation and the inability of the copper to complex. A color change accompanies the deactivation.

Product formation is via a reaction of 2 molecules of complex with 1 molecule of tetralin to produce equal amounts of tetralol and tetralone. Selectivity is more strongly dependent on reaction time than catalyst loading because it is a function of tetralol oxidation.

Secondary oxidation products are responsible for the observed autoinhibition. The mechanism of inhibition involves reaction of the free radicals with these secondary products in a ratio of 2:1.

In the pilot reactor system, it was shown that the reaction was gas-liquid mass transfer limited with catalyst concentrations in the range of 0.0769 to 0.1154 M and catalyst limited in the range of 0.019 to 0.0769 M.

Small quantities of either acetic acid or DMA added in tetralin oxidation improve both catalyst dispersion and conversion. DMA, however, is preferred as the additive because it provides higher tetralone yields while suppressing the tetralol yield. The optimum molar ratio of DMA to copper is 3.

It can be concluded from the analysis in this section that the reaction mechanism for tetralin oxidation is as shown in equation 15.

Equation 15: General Reaction Mechanism

FIGURE 18: EFFECT OF REACTION FREQUENCY ON THP PROFILE

A key to controlling free-radical generation rates as proposed herein in commercial-scale systems will be the frequency and amplitude ranges required for the cyclic switching of reaction temperature. To evaluate the sensitivity of the effective mass-transfer rate to changes in switching frequency, the reactor was divided evenly by volume and a heat exchanger was added between the reactor sections to cool the reactant. In effect, this doubled the switching frequency. In response, as shown in Figure 18, the $[THP]_{max}$ occurred at a much sooner time which is consistent with the proposed mechanism given by Equation 15. This observation is most important in that it implies that mass transfer can be improved simply by changing the switching frequency.

IV. MICROREACTOR STUDIES

Attempts have been made throughout the year to develop a methodology for using microreactors to evaluate the importance of cyclic switching frequency and amplitude. This has proven to be a difficult task in that since the frequency range is rather high (one switch per 5 to 10 seconds or less), it is difficult to cool the reactor in a controlled manner.

Initially, reaction conditions were identified at which mass transfer was clearly controlling: when hydrogen pressure was doubled the reaction rate increased significantly (almost doubled). Also, when reaction temperature was increased further by 20°C, the reaction rate changed only slightly. Under these reaction conditions, switching frequency was crudely varied by sequentially heating the reactor to the specified temperature for set times followed by cooling to room temperature via water quenching. In one series of experiments, each reaction (model naphthalene hydrogenation) was carried to a set degree (>95% conversion), and the activity of the spent catalyst was then measured at base reaction conditions. In another series of experiments, the response in conversion for a set reaction time to changes in switching frequency was measured. The results will be presented in a future report.

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Project III.5 Catalytic Hydropyrolysis and Energized

Extraction of Coals (L. L. Anderson, W.H. Yuen and

J. Jaturapitpornsakul)

Three high volatile bituminous coals were used in this catalytic hydropyrolysis study; namely, Pittsburgh #8, Hiawatha and Blind Canyon, (Utah). Pittsburgh #8 (PA) was one of the Argonne Premium Samples. Hiawatha (UT) was obtained freshly from a mine and Blind Canyon was from the Penn State Coal Bank (sample DECS-6).

Pittsburgh #8

In addition to ferrophos reported earlier (annual report May 1989 - April 1991), two additional iron-based compounds were used in this catalytic hydropyrolysis study. Ferrocene (di(cyclopentadienyl) iron, $(C_5H_5)_2Fe$) which is soluble in organic solvent and ferric citrate which is soluble in water were chosen to investigate the effect of impregnating solvent on the catalytic hydropyrolysis of coal. Each catalyst was used in each set of experiments. Both catalysts were introduced to coal by incipient wetness impregnation. THF was used as solvent for ferrocene impregnation whereas water was used for ferric citrate impregnation. Hydropyrolysis experiments were conducted in tubing bombs heated by a fluidized sand bath with shaking. The reaction temperature was either 350°C or 450°C and the pressure was 1050 psi H_2 (cold) for 350°C and 900 psi H_2 (cold) for 450°C. The reaction time for all experiments was one hour. The product yields are shown in Table 1.

TABLE 1
Yields from Catalytic Hydropyrolysis of Pittsburgh #8 Coal

Run No.	Catalyst	Temp. °C	<u>% of maf coal</u>	
			THF Insol.	THF Soluble (Liquefaction %)
FP-PT #5	- none -	450	65	14
FRC-PT #1	Ferrocene	450	53	28
FRC-PT #2	Ferrocene	350	67	33
FCT-PT #1	Ferric Citrate	450	42	33
FCT-PT #2	Ferric Citrate	350	62	38

When hydrolyzed in the presence of ferrocene, Pittsburgh #8 coal converted to a higher amount of THF soluble products. The liquid yield increased from 14% (no catalyst) to 28% at 450°C. In the presence of ferric citrate the amount of THF soluble products increased to 33% at 450°C. The amounts of char in both cases were lower than when no catalyst was used. Not only the char yields of hydrolysis runs at 350–400° C were higher than those of runs at 450°C, the THF soluble yields were also higher at 350°C than at 450°C. This is due to the fact that much lower amounts of gases were formed at 350°C. From a comparison of the data from runs with ferrocene and runs with ferric citrate, no apparent advantage of THF as impregnation solvent was found relative to water. However, this could be the result of the differences of the catalysts used.

Hiawatha

Pyrolysis of Hiawatha coal with and without catalyst was studied. In the absence of catalyst, coal was pyrolysed either in nitrogen or in hydrogen atmosphere. Ferric citrate or molybdenum sulfide or both were used as catalysts for the catalytic hydrolysis runs. The catalyst was introduced to the coal by incipient wetness impregnation from an aqueous solution of the catalyst. Ammonium tetrathiomolybdate was used as a precursor of molybdenum sulfide. All experiments were conducted in tubing bombs heated by a fluidized sand bath to 350°C. The THF insoluble and THF soluble yields are shown in Table 2.

TABLE 2
Yields from Catalytic Hydropyrolysis of Hiawatha Coal

run		atm.*	(% of maf coal)	
			THF Insol.	THF Soluble
#1	Solvent Extraction	-	90	14
#2	Pyrolysis of Dried Coal	N ₂	83	20
#3	Pyrolysis of Dried Coal (3 hr.)	N ₂	76	21
#4	Pyrolysis of Undried Coal	N ₂	78	25
#5	Pyrolysis of Undried Coal	H ₂	76	22
#6	Catalyst - 1.0% Fe (FCT)	H ₂	73	25
#7	Catalyst - 0.2% Mo (ATM)	H ₂	37	54
#8	Catalyst - 0.2% Mo (ATM) +.04% Fe (FCT)	H ₂	55	40

Reaction time - 1 hour (except run# 3)
Hydrogen Pressure - about 2000 psig at reaction temperature
FCT - Ferric citrate
ATM - Ammonium tetrathiomolybdate

Hiawatha coal, when extracted with THF, gave 14% maf THF soluble products. When pyrolysed at 350°C in the absence of catalyst, in either nitrogen or hydrogen atmosphere, Hiawatha coal yielded about 20 to 25% maf THF solubles. In the presence of molybdenum sulfide, pyrolysis of Hiawatha coal produced 54% maf THF solubles. Ferric citrate did not appear to increase the amount of THF soluble products from pyrolysis of Hiawatha coal at this reaction condition. The soluble yield obtained from the ferric citrate/molybdenum sulfide run was also less than that obtained from the molybdenum sulfide-only run.

Blind Canyon

Three sets of experiment were conducted to investigate the effect of iron catalysts from different precursors--solid superacid catalyst, iron (III) nitrate (with ammonium sulfate), and ammonium iron (III) sulfate. Superacid catalyst, SO₄²⁻/Fe₂O₃ obtained from Irving Wender's group, was physically mixed with the coal. Iron (III) nitrate nonahydrate was introduced to coal by incipient wetness impregnation in aqueous solution. In some experiments ammonium sulfate was added in attempt to promote the activity of iron nitrate by co-impregnated with iron nitrate on coal. Ammonium iron(III) sulfate dodecahydrate was used as iron catalyst which might be promoted by sulfate produced in situ. Ammonium tetrathiomolybdate which was a precursor of molybdenum sulfide was also used in a couple of experiments. Ammonium iron (III) sulfate and ammonium tetrathiomolybdate were used as co-catalyst to study the promoter effect, if any, of

iron and molybdenum. All the experiments were conducted in tubing bomb reactors heated by a fluidized sand bath. The reaction time was 1 hour and the reaction pressure was about 2000 psig. The THF soluble and insoluble yields are shown in Table 3.

When pyrolysed without catalyst, Blind Canyon coal yielded 24 wt% at 350°C and 30 wt% at 400°C (THF solubles). Although solid superacid iron catalyst was reported to be an active catalyst in coal liquefaction, THF soluble yields from hydrolypyrolysis of Blind Canyon coal with this catalyst were only slightly higher than those obtained from blank runs. This is possible due to the lack of availability of surface contact between coal and the catalyst because the catalyst was only physically mixed with coal and there is no solvent to help facilitate reactions.

Iron(III) nitrate with or without ammonium sulfate caused decreases in the amount of THF soluble produced at 350°C. Coal hydrolypyrolysis with ammonium iron (III) sulfate as catalyst precursor produced significantly higher amounts of liquid than those from blank runs, especially at 400°C.

Ammonium iron(III) sulfate was an active catalyst for hydrolypyrolysis of this coal, especially at 400°C. Ammonium tetrathiomolybdate was a precursor of a very active catalyst which helped reduce char yields to 60% at 350°C and 8% at 400°C. Best results of each temperature group were obtained when ammonium iron (III) sulfate and ammonium tetrathiomolybdate were used together as co-catalyst.

TABLE 3
Yields from Catalytic Hydropyrolysis of Blind Canyon Coal

run		T (C)	(% of maf coal)	
			THF Insol.	THF Soluble (Liquefaction %)
#1	blank (no catalyst used)	350	74	24
#2	blank (no catalyst used)	400	59	30
#3	2 wt % Fe (IN)	350	84	16
#4	2 wt% Fe (IN) + 0.2 wt% AS	350	82	17
#5	2 wt% Fe (IN) + 4.7% wt% AS	350	89	12
#6	2 wt% Fe (solid $\text{SO}_4=\text{Fe}_2\text{O}_3$)	350	72	26
#7	2 wt% Fe (solid $\text{SO}_4=\text{Fe}_2\text{O}_3$)	400	56	38
#8	2 wt% Fe (AFS)	350	76	27
#9	2 wt% Fe (AFS)	400	40	50
#10	2 wt% Fe (AFS)	425	39	43
#11	0.2 wt% Mo (ATM)	350	59	43
#12	0.2 wt% Mo (ATM) + wt% Fe (AFS)	350	40	(50)
#13	0.2 wt% Mo (ATM)	400	08	(74)
#14	0.2 wt% Mo (ATM) + 2 wt% Fe (AFS)	400	06	(57)

Coal - Blind Canyon (DECS - 6 Penn. State)

Reaction Time - 1 hour

Hydrogen Pressure - about 2000 psig at reaction temperature

IN - Iron (III) nitrate

AS - Ammonium sulfate

AFS - Ammonium iron (III) sulfate

ATM - Ammonium tetrathiomolybdate

Catalytic hydropyrolysis has shown to be a viable way to produce liquids from coal. With proper catalyst only a small amount of coal was unconverted or crosslinked to become insoluble products. Ammonium iron(III) sulfate showed high activity for this reaction. Although molybdenum is moderately expensive (per unit mass), molybdenum sulfide from ammonium tetrathiomolybdate exhibited extremely high activity even at low concentration (0.2%). Hence, molybdenum might prove to be a justified catalyst for coal hydropyrolysis. Co-catalyst of iron and molybdenum sulfide were shown to be very active and was better than iron or molybdenum alone. Future study will be concentrated on finding the best catalyst for catalytic hydropyrolysis of coal. This includes searching for a new catalyst, trying to reduce the amount of molybdenum, and exploring the promoter/synergistic effect of molybdenum and iron.

ABSTRACT

Laboratory experiments were performed to investigate the effect of ultrasound on coal liquefaction in different solvent extraction conditions. In this research project, ultrasonic waves were generated by a Fischer-Sonic Dismembrator with a titanium tip. These generate an ultrasonic wave at a frequency of 21 KHz and give a 300-watt maximum power output. When the output power is at a maximum, this means a maximum tip intensity of 98.4 W/cm^2 can be generated by this equipment.

Under the ultrasonic environment, experiments were done to reveal the relation between the coal liquid yield and other parameters such as: the tip intensity, reaction time, solvent and catalyst. From a series of experiments, the best ultrasonic tip intensity generated by this dismembrator for coal extraction was 88.6 W/cm^2 .

Coal samples used in this project were Blind Canyon Coal (PSOC-1503) and Argonne high-volatile bituminous coal (ID 601:00065). Solvents such as THF, THF-water and pyridine-methanol were used with catalysts such as FeCl_3 , KOH, and TBAH.

It was shown that pyridine-methanol-water mixture with a small amount of tetrabutyl-n-ammonium hydroxide could give a high yield of coal liquid when applied on Blind Canyon Coal (PSOC-1503). After 2 hours ultrasonic extraction, the yield was 44.07%--29.71% higher than the THF Soxhlet extraction.

INTRODUCTION

Long term studies on the effects of ultrasound to those of sonochemical reactions show that ultrasound has a remarkable effect on the following sonochemical reactions: polymerization, depolymerization and heterogeneous catalytic reactions [1].

Although the coal structure is not well-defined as yet, with the help of modern coal characterization technologies, coal is usually considered as a crosslinked-macromolecule derived from lignin [2]. That means some properties of coal are similar to those of polymers. Hence, sonochemically enhanced coal degradation (sometimes referred to as coal depolymerization) becomes a recent topic in field of direct coal liquefaction research.

Several studies have been done to determine if significant increases in yield and/or quality of products can be achieved in solvent extraction if ultrasonic energy is implemented in coal extraction [3-5]. Most of these studies have used typical commercial ultrasonic cleaners with

ultrasonic energy fields less than 1 watt/cm². Higher ultrasonic energy fields are also used with a collimated beam generated from an amplifying horn and with acoustic intensities as high as 300 watt/cm².

Because of the evidence of random C-C bond cleavage and water decomposition, ultrasound should have a positive effect on coal extraction and under certain circumstances can greatly improve the solvent extraction yields of coal.

EXPERIMENTAL SECTION

- Coal Samples:

Blind Canyon coal samples used in this research are:

Coal A: Argonne premium coal, -20 mesh, ID 601#00065 (HVBC)

Coal B: PSOC-1503, -20 mesh, HVBC

Coal C: Coal B after 48 hours THF Soxhlet Extraction (14.36% extracted). All the samples have to be dried in a desiccator at 110°C overnight before ultrasonic extraction take place.

- Ultrasonic Intensities:

A Fischer-Sonic Dismembrator with a standard titanium tip was used (tip intensity adjustable from 0 to 100 W/cm²) and generates a ultrasound with a frequency of 21 KHz.

- General Ultrasonic Extraction Condition:

A 100-ml beaker was used for coal extraction, the weight of coal sample was usually from 1.0 g to 2.0 g and the solvent/coal ratios were usually 30 to 50. Although it depends on the completeness of the reaction and the solvent properties, the reaction time was usually less than 4 hours.

RESULTS

Figure III.5.1. The best tip intensity for THF coal extraction is close to 90 watt/cm².

Figure III.5.2. The rate of ultrasonically enhanced coal extraction is very fast, after 10 minutes extraction the percent of coal extracted is 11.94% and after 60 minutes extraction the coal extracted is 12.67%.

Batch	Coal	Catalyst	Solvents	Time (Min)	Temp (C)	% of Coal Extracted	
2	A	---	THF	10	55	11.94	
2	A	---	THF	60	55	12.67	
3	C	---	THF	60	55	3.8	(+14.36)
3	C	KOH (1%)	THF	60	55	3.10	(+14.36)
3	C	KOH (5%)	THF	60	55	0	(+14.36)
4	C	---	THF/H ₂ O=1/1	60	55	5.97	(+14.36)
4	C	FeCl ₃ (1%)	THF/H ₂ O=1/1	60	55	6.70	(+14.36)
4	C	FeCl ₃ (5%)	THF/H ₂ O=1/1	60	55	4.80	(+14.36)
4	C	---	THF	60	55	3.80	(+14.36)
4	C	FeCl ₃ (1%)	THF	60	55	3.26	(+14.36)
4	C	FeCl ₃ (5%)	THF	60	55	0	(+14.36)
6	B	KOH (1.4%)	Pyridine/MeOH =3/1	105	63	20.39	
7	B	Pyridine/MeOH/TBAH -70.1/23.4/6.5		120	72	73.58	
9	B	Pyridine/H ₂ /MeOH/TBAH =67.5/8.5/17.5/6.5		30	63	37.65	
9	B	Pyridine/H ₂ O/MeOH/TBAH =67.5/8.5/17.5/6.5		60	63	44.07	
9	B	Pyridine/H ₂ O/MeOH/TBAH =67.5/8.5/17.5/6.5		90	63	44.07	

Tip m(#ity: 88.57 W/cm²

Coal A: Argonne Coal, Blind Canyon, -20M, ID.601#00065 (HVBC).

Coal B: PSOC - 1503, -20M, Blind Canyon Coal (HVC).

Coal C: Coal B after Soxhlet Extraction (14.36% Extracted).

Figure III.5.3. The extraction yield when FeCl_3 was used as catalyst, it is obvious water could improve the activity of this catalyst.

CONCLUSIONS

From Table 1, we know pyridine/methanol/tetrabutyl-n-ammonium hydroxide solvent system combined with ultrasound could improve the yield of coal extraction to a great extent. That might be due to the combined effects of ultrasound and the coal swollen ability of TBAH. More research should be done in the future, such as temperature influence, TBAH concentration influence, product analysis and best ultrasonic tip intensity in these kind of solvents.

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Task IV

Novel Catalysts for Coal Liquefaction

Program Coordinators: Christine Curtis and Dady Dadyburjor

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Novel Catalysts for Coal Liquefaction

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Report Period: May 1, 1990 - April 30, 1991

**Project IV.1 Gallium Catalysts in Mild Coal Liquefaction.
Potential of High Temperature-High Pressure
Microscope in Coal Liquefaction (I. Wender and
J.W. Tierney)**

A look at the Periodic Table shows that gallium is surrounded by elements which, as chlorides, are active as direct coal liquefaction catalysts. Zinc is to the left, germanium and tin are to the right, and aluminum is directly above gallium in the Table. Yet, as far as we know, gallium chloride(s), or other forms of gallium, have never been tested as coal liquefaction catalysts.

We decided to test a chloride of gallium as a catalyst for the conversion of coal to liquids. The best-known chlorides of gallium are GaCl_3 and GaCl_2 . The actual composition of the dihalide is $(\text{GaCl}_2)_2$ or $\text{Ga}^+(\text{Ga}^{3+}\text{Cl}_4)^-$. GaCl_3 fumes excessively on exposure to moisture in air and is therefore difficult to use. However, GaCl_2 , with minimal fuming in air, is much easier to handle and was therefore chosen as a catalyst in all our coal liquefaction experiments. It is important to note, however, that GaCl_2 disproportionates into GaCl_3 and metallic gallium above 200°C :

GaCl_2 is soluble in benzene and in water. It has a low melting point (about 164°C) which could

be beneficial from the standpoint of making good contact between the liquid catalyst and coal.

A rapid screening test of the activity of GaCl_2 as a catalyst for liquefaction of a Pittsburgh Seam bituminous coal was made using a high pressure, high temperature polarized microscope under a stream of hydrogen at 1000 psig. The catalyst and coal particles were placed on the microscope stage in a fused silica sample pan inside a stainless steel reaction cell. Hydrogen was maintained at a constant flow (2cc/min) of H_2 gas and heated at about 20°C per minute. Changes in reflectance of the surface of the reaction mixture were recorded on a video screen. Between 50 and 75°C , the catalyst particles liquefied due to absorption of moisture from the coal and appeared to penetrate the coal particle. Significant changes were not observed until a temperature of about 250°C was reached. At about 255°C , some plastication or viscous movement on the coal surface was observed, but the first droplets or bubble formation was seen at about 270°C , which may have been the onset of coal liquefaction. Swelling of the coal surface was observed at about 280°C and vigorous bubbling occurred at 310°C . At about 320°C , clear formation of a viscous liquid was seen.

The catalytic activity of GaCl_2 with Pittsburgh Seam coal, as observed in the microscope, was significant enough at low temperatures to warrant further investigation of this catalyst. To determine the general applicability of GaCl_2 as a coal liquefaction catalyst, a survey was first made, in tubing bomb reactors, of the liquefaction of three different coals from the Argonne Sample Bank: Illinois #6 (high volatile bituminous, -100 mesh), Pittsburgh Seam (bituminous, -100 mesh), and Wyodak (subbituminous, -20 mesh). All but a few special runs were carried out under the following conditions: 2 g. of coal, 8 g. of tetralin, 5 wt% of Ga^0 (as GaCl_2) based on coal, 350°C and 1000 psig of H_2 (cold) for one hour. As shown in Figure 1, conversion of the coals to methylene chloride soluble material was almost twice that obtained in the absence of GaCl_2 . Increases in asphaltenes and in oils (pentane solubles) were obtained with each coal under the same conditions. The Wyodak coal gave the largest increase in pentane soluble material.

Illinois #6 coal and tetralin were used in all further experiments. Parameters studied were: reaction time, temperature, catalyst (GaCl_2) concentration and initial hydrogen pressure. Catalyst activity was also tested in the absence of hydrogen, i.e., in an atmosphere of helium. Gallium metal and a number of gallium compounds were tested for coal liquefaction activity but only the chloride(s) of gallium were active. Overall conversions and yields are expressed on a moisture, ash-free basis with respect to coal.

Effects of varying reaction temperature in the 300 to 400°C range on the GaCl_2 catalyzed conversion of the Illinois coal are shown in Table 1. Overall conversions rose sharply from 300°C ($\approx 34\%$) to 350°C ($\approx 71\%$) and then rose slightly at 400°C (75%). The yield of oils showed a steady increase from 300°C ($\approx 11\%$) to 400°C ($\approx 38\%$) with the asphaltene yield peaking at 350°C. After two hours at 350°C, overall conversions rose to $\approx 77\%$ from 71%, asphaltenes dropped to 30% from 38% and the yield of oils rose to $\approx 40\%$ from 27%. After two hours at 400°C, overall conversions reached 82%, asphaltenes fell dramatically to 15% and oil yields rose sharply to 57%.

GaCl_2 seems to be a good catalyst for converting asphaltenes to oils at the higher temperatures. Increasing reaction severity in terms of both temperature and time evidently leads to greater hydrocracking and hydrogenation, resulting in improved selectivity to oils.

The halides of boron, aluminum, gallium all form adducts with nitrogen-containing compounds. The stability order for this adduction is $\text{B} > \text{Al} > \text{Ga}$. It is possible that GaCl_2 or GaCl_3 formed such adducts with nitrogen species in coal; these adducts may dissociate at about 300°C, making more of the gallium chloride available for catalytic action.

The effect of varying GaCl_2 concentration on liquefaction activity at 350°C in the presence of hydrogen is seen from Figure 2. Catalyst concentrations were such that the weight percent of gallium with respect to the initial weight of coal varied from 2.5 to 7.5%, beyond which the conversion approached a limiting value. The yield of oils increased over the range of catalyst concentrations studied. Increased retrogressive reactions may limit overall conversions at higher catalyst concentrations but a breakdown of asphaltenes to lighter products does occur.

Unexpected results were obtained when the initial hydrogen pressure was decreased from the usual 1000 psig to 500 psig and then, when the hydrogen was completely replaced by helium at 1000 psig initial pressures (Figure 3). Overall conversion as well as yield of oils increased significantly and almost linearly with reduction in the initial pressure or amount of hydrogen, while the yield of asphaltenes decreased. The amount of hydrogen used may affect catalyst activity by influencing the decomposition of GaCl_2 to GaCl_3 which could be the catalytic species most responsible for the coal liquefaction activity. It is possible that catalyst activity could be inhibited due to increased formation of hydrogen sulfide at high hydrogen pressures.

In the absence of hydrogen, the large excess of tetralin provides an ample supply of donor hydrogen. Analyses of the residue and of the oils, which would shed light on the reactions which

occur in the absence of hydrogen, are not available at this time. Gallium dichloride must be an effective catalyst for the transfer of hydrogen from tetralin to coal. Experiments at lower tetralin to coal ratios will be run in the next year. Experiments with hydrogen in the absence of a hydrogen donor will also be carried out.

Another interesting result was the effect of varying catalyst concentration at 350°C in the presence of 1000 psig of helium (initial) (Figure 4). A pronounced catalytic effect of GaCl₂ was seen only above a concentration of 2.5% Ga by weight of coal, where a sharp increase in overall conversion and yield of oils was observed. It is possible that the GaCl₂ is neutralized by adduction with the basic sites in coal, mostly due to the presence of nitrogen-containing species. The ratios of the gallium chlorides to the nitrogen in the Illinois #6 coal, on a mole basis, are given below:

<u>Ga⁰/Coal</u> <u>wt %</u>	<u>GaCl₂/N</u>	<u>GaCl₃/N</u>
2.5	0.44	0.29
3.75	0.66	0.44
5.0	0.87	0.59

While the mole ratios of the chlorides to nitrogen are less than one in all cases, only part of the nitrogen is basic. In any case, it is likely that any such adducts would fall apart at elevated temperatures, freeing the catalytic species.

Obviously, experiments of the catalytic effects of gallium chlorides with model compounds should be carried out. Work with gallium chloride will be continued in the next year, with termination of the work in about six months.

Table 1. Effect of Reaction Temperature on Conversion of Illinois No. 6 Coal. Reaction Conditions: 2 g Coal, 8 g Tetralin; 1000 psig H₂ initial; Catalyst GaCl₃, 5% wt. Ga/coal; Time 1 h.

Expt. Number	Temp. °C	Percent Conver.	Percent Asphal.	Percent Oils	Percent Gases
CR-1*	300	18	10	6	2
CR-2*	350	37	21	12	4
CR-3*	400	65	36	22	7
CR-4	300	33	20	10	3
CR-4R**	300	35	21	11	3
CR-5	325	47	28	14	5
CR-6	350	70	37	27	6
CR-6R**	350	72	39	26	7
CR-7	400	75	26	38	11
* Thermal runs. ** Repeat runs.

Figure 1. Effect of coal rank on conversion. Tetralin/coal ratio: 4; 350°C; 1 hour; GaCl₂ catalyst; 5 wt% Ga/coal; 1000 psig H₂ cold.

Figure 2. Effect of Catalyst Concentration on Conversion of Illinois No. 6 Coal. Tetralin:Coal, 4:1; Catalyst: GaCl_2 ; Temperature: 350°C ; Time: 1 hour; 1000 psig H_2 cold.

Figure 3. Effect of Initial Hydrogen Pressure on Conversion of Illinois #6 Coal. Tetralin:Coal, 4:1; Catalyst: GaCl_3 ; Ga:Coal, 1:20; Temperature: 350°C ; Time: 1 hour.

Figure 4. Effect of Catalyst Concentration on Conversion of Illinois #6 Coal. Tetralin:Coal, 4:1; Catalyst: GaCl_2 ; Temperature: 350°C ; Time: 1 hour; 100 psig Helium (cold).

Project IV.2 Evaluation of Nitride Catalysts for Hydrotreatment and Coal Liquefaction

(Dady B. Dadyburjor and John H. Penn)

INTRODUCTION

The goal of the overall coal liquefaction process is to obtain a liquid fuel product that can be subjected to processes in a conventional refinery to produce motor fuels indistinguishable from those based on petroleum. Formation of the liquid fuel products involves two steps: liquefaction (or dissolution) and hydrotreatment (or upgrading). These steps may occur simultaneously or sequentially. Liquefaction consists of C-C bond cleavage and C-H bond formation to produce liquids (preferred) and gases. Hydrotreatment (HT) refers to the removal of S-, N-, and O-containing (heteroatom) constituents from the liquid product. HT consists of simultaneous hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO), when the offending constituents are hydrogenated at high pressures to H_2S , NH_3 and H_2O respectively. For coal liquids, HDN is the major problem. Ideally, no additional C-H bonds are to be formed in HT (other than those required to produce the liquid phase in liquefaction); this minimizes hydrogen consumption and maximizes product value, particularly as a motor fuel. The use of catalysts in coal liquefaction has led to increased conversions, increased selectivity and improved liquid quality; all these improvements have occurred at lower temperatures and much lower pressures [1].

While the use of catalysts in coal liquefaction is not in question, the catalysts used presently are unsatisfactory. HT catalysts used (sulfided $\text{NiMo}/\text{Al}_2\text{O}_3$) are closely related to those used in petroleum-based processes, where HDS, rather than HDN, is the major problem. In coal liquefaction, the catalyst lifetime is an order of magnitude shorter than in petroleum processes, and the deactivated catalysts cannot be readily and completely regenerated [2]. A recent review of catalysis in coal liquefaction [3] points out the lack of effort devoted to the development of catalysts specifically meant for coal liquefaction. The present research is one attempt to remedy this situation.

BACKGROUND

We seek to develop a family of catalysts for HT and perhaps dissolution as well. Specifically, we are investigating the catalytic properties of boron nitride for the HDN of a model compound, quinoline.

To the best of our knowledge, other similar uses of these materials as catalysts have not been reported in the open literature. Borides of sodium, nickel and cobalt have been used for HDS reactions [4]. Nitrides of molybdenum have recently been prepared in the form of high-surface area porous solids, and their properties are currently under investigation [5]. Other transition metal nitrides can be prepared as conventional low-surface-area powders. Reaction networks for HDN, HDS and HDO reactions have been reported and reviewed [6,7].

BRIEF DESCRIPTION OF EXPERIMENTAL METHOD

Operating Procedure and Materials

The HDN reactions were carried out in batch mode in an autoclave. The reaction system is shown in Figure 1. The reactor used is a 300 ml Parr autoclave. The quinoline and hexadecane are from Fisher Scientific. The boiling range for quinoline is 237.1 - 237.5°C. The purity of hexadecane is 99.3 Mol%. The BN is from Aldrich with a purity of 99% and BET surface area of 2.83 m²/g. The commercial catalyst used for comparison is a 1/16" Co-Mo catalyst (HR-801) from Houdry, with a BET surface area of 293 m²/g. The commercial catalyst was ground and sieved to 37-53 μ before use. For the standard operation, 5 g of the catalyst was first loaded into the reactor and dried at 400°C overnight under flowing nitrogen. If pretreatment was needed, a pretreatment gas was then fed into the reactor at about 40 psig for 2 hrs. The pretreatment temperature was 350°C for H₂S and 400°C for NH₃. The reactor was then cooled overnight to room temperature under flowing nitrogen.

Before reaction, the reactor was filled with 200 psig H₂ and then evacuated; this was repeated 2 more times. The technique removes excess pretreatment gas. The reaction solution (70 ml of 2 wt% of quinoline in hexadecane) was introduced into the reactor from the liquid reservoir. This procedure prevents air from being introduced into the reactor. The reactor was then pressurized with H₂ to 600 psig at room temperature, and heated up. The stirrer was turned on (800 rpm) when reaction temperature was reached. After a certain period of time (usually 3 hours), the reactor was rapidly cooled to room temperature.

The reactor gas phase was then released through a metering valve, a GC sampling loop for gas analysis and a HBO_2 solution trap for overall NH_3 analysis. As recommended by Skoog and West [8] a 4% solution of HBO_2 was used in the trap. The liquid in the reactor was then removed and separated from the solid catalyst using a centrifuge. The liquid samples before and after the reaction were analyzed with a Varian 3400 GC with FID and TSD. The column was DB5 (30M x 0.53 mm, J & W Scientific). The sample separated by the column splits into two streams entering both FID and TSD. This GC configuration allows a component to have the same retention time on both FID and TSD chromatograms.

Identification of Nitrogen-Containing-Compounds (NCCs)

Liquid analysis after the reaction showed many products resulting either from HDN of quinoline or cracking of hexadecane. NCCs were determined by comparing peak areas of the same retention time from FID and TSD. A preliminary study showed that the area ratios (FID to TSD) are about 0.3 for quinoline, tetrahydroquinolines and decahydroquinolines. The area ratios of hexadecane, benzene, propylbenzene and C7 hydrocarbons are in the range of 1000. If the area ratio (FID/TSD) is less than 1, therefore, the component is identified as NCC. If the area ratio is in the range of 1000, the component is identified as a hydrocarbon compound. However, some minor peaks (about 3% of overall) cannot be identified according to the above rule because their peak ratios are around 10. Satterfield and co-workers [9] reported that a large variety of higher-molecular-weight compounds were observed in their HDN study. The higher molecular weight NCC may very possibly give peak ratios higher than that of quinoline. For conservative reasons, these compounds are labelled as NCC in this study.

RESULTS AND DISCUSSION

Drying the Catalyst

Boron nitride (BN) was used as the catalyst. BN is hygroscopic. The test runs, which used BN as received, showed large H_2O peaks in the gas analysis. Since the H_2O content of BN can not be controlled and the presence of water may affect BN's catalytic activity on HDN, removal of H_2O is necessary. In a test run, 1 gram of BN was heated in the reactor under flowing nitrogen at 350°C . It is found that a minimum of 5 hours is needed to remove most of H_2O , as shown in Figure 2. Although the peak disappeared after 5 hours of drying, a trace

amount of H₂O was found in the products after 3 hours reaction. This may indicate a strong bonding of H₂O with BN, and/or presence of H₂O in the reaction solution (quinoline and/or hexadecane). This suggests that a higher drying temperature and a longer time are preferred. As a standard, overnight drying (not less than 12 hours) and 400°C was chosen for catalyst study.

Product Distribution

As mentioned earlier, many products were observed after reaction. The major products were identified by GC/MS. They are 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, decahydroquinolin (cis and trans), aniline, propylcyclohexane, cyclohexane, propylbenzene and NH₃. The nitrogen balances for the reactions are normally between 85 to 99%. According to the reaction mechanism proposed in the literature [9,10], the moles of NH₃ formed should equal the moles of nitrogen removed from the liquid. However, only a small fraction of the theoretical NH₃ was found in our analysis. Satterfield et al. also report a similar observation [9], and attribute it to different reaction mechanisms and NCCs other than NH₃ which are not identified.

Effect of Temperature

In order to evaluate catalysts and the effect of pretreatment on the catalyst activity and selectivity, standard reaction conditions need to be set. Among operating conditions, temperature is probably most important. The reaction temperatures reported in the literature for HDN of quinoline are in the range of 330 to 460°C [10-14]. Three reaction temperatures (300, 350 and 400°C) were tested in this study. Temperatures higher than 400°C were not tested because of temperature limitations of the reactor. The results are listed in Table 1, along with drying temperature.

Table 1. Effect of Temperature on HDN of Quinoline

Drying Temp. (°xC)	Reaction Temp. (°C)	1-(A _Q /A _Q ^o) (%)
300	300	4.4
350	350	13.4
400	400	43.5
400	350	24.0

* estimated conversion, where
A_Q is GC area of quinoline after reaction
A_Q^o is GC area of quinoline before reaction

The reaction temperature of 300 and 350°C gives a small estimated conversion, and indicates that the catalyst is not active. For the following study, 400°C was then selected. It is important to note that the conversions are also dependent on drying temperature. For 350°C reactions, drying at 400°C gives a conversion 79% higher than drying at 350°C. This confirms the suggestion made earlier, that H₂O may affect the HDN activity of BN.

Effect of Catalyst Pretreatment

To evaluate the effect of catalyst pretreatment on catalyst activity, effect of materials other than the catalyst should be isolated. Oyama and co-workers [11] reported that the reactor they used had catalytic activity after being repeatedly treated with H₂S. The reactions carried out in our lab showed that the reactor, even when not treated with H₂S, also has significant catalytic activity (Table 2). This suggests that a parallel reaction scheme should be used in evaluation of catalytic activity. As has been suggested by many others [10,11], the HDN of quinoline goes through a series of reactions. These reactions can be simplified as the conversion of quinoline to NCC and then HDN of NCC to hydrocarbons (HC) and NH₃, as shown below:

In order to evaluate these k 's, experiments were carried out in six categories, as shown in Table 2. Two to six repeated runs were made in each category. The reaction rate constants obtained are also listed in Table 2, where k_1 and k_1' , represent rate constants for Q conversion and k_2 and k_2' for HDN of NCC. The values of k_1 and k_2 are given on a surface-area basis.

It is interesting to note that the BN pretreated with either H_2S or NH_3 gives k_1 values lower than that of the commercial Co-Mo catalyst, but k_2 values are 6-25 times larger than the commercial catalyst. This shows superior catalytic effect of BN towards HDN. It is also important to point out that the relatively higher catalytic effect of the empty reactor results from BN having a low surface area. If BN can be highly dispersed to give a surface area similar to that of the commercial catalyst, then the effect of the reactor would be very small.

Equilibrium Consideration

Reversible reactions or equilibrium have been reported for NCCs involved in HDN of quinoline. If equilibrium is reached, reaction schemes more complicated than Equations 1 and 2 should be used in evaluation of catalyst performance. In order to check this, mole ratios of major NCCs in the products were evaluated, assuming that the partial pressure of H_2 is constant in all the cases. No constancy of mole ratios could be found under any category, which suggests that equilibrium is not reached under the reaction conditions we used. This is further supported by noting that a near-equilibrium mole 1,2,3,4-tetrahydroquinoline/quinoline equal to 4 is reported by Satterfield et al. [9]; this is much greater than the value of less than 2 obtained in our case.

CONCLUSIONS

BN shows better catalytic activity for HDN (k_2) than a commercial Co-Mo catalyst, based

on surface area of the catalysts. Pretreatment with H_2S improves the activity (k_1) but decreases the HDN. Pretreatment with NH_3 improves k_1 less than H_2S does, but HDN is decreased less for NH_3 than for H_2S . The BN is not very active at 300 and 350°C. The presence of H_2O deactivates BN.

Future work will evaluate simultaneous HDS and HDN for this catalyst and other similar catalysts. The role of these catalysts in changing the products of coal liquefaction should also be considered.

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Table 2. Rate Constants for Quinoline Conversion and HDN

Catalyst	Pretreatment	Rate Constants			
		$\times 10^3 \text{ [min}^{-1}\text{]}$		$\times 10^6 \text{ [m} \cdot \text{min}^{-1}\text{]}$	
		k_1'	k_2'	k_1	k_2
No	No	2.08	1.72	---	---
No	H ₂ S	2.88	2.61	---	---
BN	No	---	---	0.32	15.96
BN	NH ₃	---	---	1.77	14.28
BN	H ₂ S	---	---	4.66	3.29
Co-Mo	H ₂ S	---	---	6.23	0.56

Figure 1. Experimental Apparatus

Figure 2. Removal of H₂O from BN

Project IV.3 Coprocessing and Coal Liquefaction With Novel Catalysts (James W. Guin)

SUMMARY OF RESULTS

This past year's work was performed in three areas as proposed: (1) macroporous catalyst studies (2) fundamental diffusion studies and (3) slurry phase catalyst studies. The details of these experiments are given below and in the references cited at the end of this section. Future work is to be performed only in area (3).

Macroporous Catalyst Studies

The objective of this part of our work was to determine the effect of alkali metal impregnation on the rate of deactivation of several catalysts used in our study last year [1]. Last year we showed that the bimodal macroporous catalysts had longer lifetimes and higher activities in both coal and model compound reactions. The primary mode of deactivation of the catalysts was due to heavy coke deposition. Other investigators [2, 3, 4] had found that by adding alkali metal promoters, e.g. Ca, Na, that the coke formation was often considerably reduced. Thus, we decided to try this approach with our own laboratory catalysts to see if it would lessen the coke accumulation and increase catalyst lifetime. The catalysts used and their properties are described by Wang [1] and Guin and Wang [5]. These catalysts, as shown in Table 1, were impregnated with Ca by Dr. Henry Haynes, Jr. at the University of Wyoming. Other properties of the catalysts are shown in Table 1 as well. The basic equipment and methodology used to test the Ca promoted catalysts was the same as used by Wang and Guin [5]. A summary of the experimental design is given in Table 2, and complete details are given by Chang [6]. The CDS continuous reactor system was the same as used by Wang [1]. The model compound reactions used to evaluate catalyst activity were hydrogenation of naphthalene (A_H) and demetallation of a vanadium porphyrin (A_{HDM}). The detailed reaction procedures and activity measurements are given by Chang [6] and Wang [1]. The effect of Ca promotion on the rate of deactivation as evidenced by hydrogenation (A_H) and hydrodemetallation (A_{HDM}) activities is shown in Figures 1 to 3. Figure 1 shows that the activity is extended for the Ca promoted unimodal F-00 catalyst, i.e. the deactivation time is increased from 200 to 400 hours. A similar effect is found for the

same catalyst in Figure 2, where the Ca promoted F-00 run was stopped at the same time (200 h) and has significantly higher activity. On the other hand, Figure 3 shows that the Ca promotion was not effective in lengthening the lifetime of the macroporous catalyst F-40, and in fact the Ca promoted catalyst declined in activity slightly faster than the original F-40 catalyst. It may be that since coke is not as detrimental to the activity of the macroporous catalyst (F-40) as compared to the F-00 catalyst, that the effects of Ca promotion are not as apparent with the macroporous catalyst. The coke contents of the spent catalysts are shown in Table 3. Although the coke contents of the macroporous catalysts were greater, a t-test showed that there was no significant difference in the coke contents of the Ca promoted catalysts vs. the unpromoted catalysts, in contrast to observations of previous investigators. An analysis, and C/H ratio of the coke on the spent catalyst, as shown in Table 4 did however show a less refractory coke on the promoted catalyst, perhaps accounting for the activity improvement. Thus, in summary, the Ca impregnation was effective in extending the lifetime of the unimodal catalyst, although it was not effective with the bimodal catalyst. In addition both promoted and unpromoted catalysts has similar total coke contents, although the Ca promoted catalyst had a somewhat less aromatic coke.

Fundamental Diffusion Studies

Catalyst pore diffusion is known to be an important factor in coal liquefaction. As a catalyst ages, accumulation of metals and coke can cause significant changes in catalyst pore diameter and tortuosity due to pore plugging and/or blockage. These changes in catalyst pore geometry have been observed to affect the magnitude of the intraparticle diffusivity of the reacting species. It has been suggested that the diffusivity can be restored by controlled oxidative regeneration of catalyst. In order to investigate this hypothesis for the catalysts used in the hydrotreatment of model compounds as discussed in the previous section, the magnitude of diffusivities for fresh, aged, and regenerated catalysts was determined. To determine the diffusivity, a constant volume cell was used to conduct the diffusion experiment which monitored the diffusion of undecane from catalyst pellet to a bath of toluene. A least square fit of the experimental data to an analytical solution curve was used to determine the diffusivity. The methods and experimental set-up are described in detail by Tsai [7], Rhee [8], and Chang [6]. The catalyst used in these experiments were the same ones which were aged in the preceding

section using the CDS reactor with model hydrogenation and demetallation experiments. The Ca promoted catalysts were also compared with regard to diffusivity changes during deactivation.

The results of the diffusion experiments are shown in Table 5. The catalysts were withdrawn from the runs concluded at the times shown in Table 2. The diffusivity of the aged macroporous catalyst (F-40) is decreased relative to the fresh catalyst, but is restored by oxidative regeneration. The Ca impregnated F-40 behaved in about the same manner as did the original F-40. The diffusivity for the aged catalysts was generally reduced by ca. one order of magnitude relative to the fresh catalyst, in general; however, it could be completely restored by oxidative regeneration. Statistical t-tests revealed no significant differences in the behavior of the Ca impregnated catalysts relative to the unpromoted ones, or in the regenerated catalysts as compared to the fresh catalysts at the one percent significance level.

Slurry Phase Catalyst Studies

In recent years, the use of highly dispersed catalysts has interested many investigators as a development in coal liquefaction technology. Highly dispersed iron catalysts are particularly of interest from the economic point of view. In our work, the tubing bomb microreactor (TBMR) was employed to directly determine coal liquefaction with three modes of iron addition. Iron sulfate heptahydrate powder ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was used as a dispersed catalyst precursor. Direct addition of iron sulfate heptahydrate, impregnation of iron sulfate on coal, and impregnation of iron sulfate on an alumina microsupport were examined in this study. Several runs were conducted to investigate the effects of the slurry phase dispersed iron-based catalyst on coal liquefaction. The percentage of pentane soluble fraction was used as an indicator of coal conversion in our study.

Experimental

Materials

The chemicals were used as received: tetrahydrofuran (Fisher, histological grade) tetrahydronaphthalene (Fisher, purified grade), n-pentane (Fisher, HPLC grade), iron(II) sulfate heptahydrate (Aldrich, 99% purity). Tetrahydronaphthalene (tetralin) served as a hydrogen donor solvent. Ultra high purity hydrogen was supplied by Air Products and Chemicals. Catapal alumina, a high purity boehmite alumina from Vista Chemical Company, was an acid-dispersible

, spray-dried powder used as a microsupport. Illinois No. 6 coal was used in the coal liquefaction reactions.

Methods

Three methods of catalyst precursor addition were investigated in this work. The first method was to directly add 1.5 grams of sulfate heptahydrate powder when the coal and tetralin were loaded. The 1.5 grams of sulfate heptahydrate powder was equivalent to adding 10 wt% iron based on mf coal for liquefaction. The second method was to dissolve 1.5 grams of iron sulfate heptahydrate in 2.26 grams distilled water and then to impregnate the solution on the coal at incipient wetness. The impregnated coal was then dried and loaded with tetralin into a TBMR for reaction. The third method was to dissolve 1.5 grams of iron sulfate heptahydrate in 2.26 grams of distilled water and then to impregnate the solution on Catapal alumina powder at incipient wetness. The dried microsupported catalyst precursor was then loaded with coal and tetralin for reaction. Complete details are given by Chang [6].

RESULTS AND DISCUSSION

The pentane soluble percentage (P.S. %) was the total percentage of pentane soluble oil from coal liquefaction and is defined in Equation 1.

$$P.S.\% = \frac{W_{\text{original organic material}} - W_{\text{pentane insoluble organic material}}}{W_{\text{original organic material}}} * 100\% \quad (1)$$

The operating conditions, and P.S. % for each run are shown in Table 6. The results for each run were provided by replicated reactions. A higher percentage of pentane soluble fraction indicated more conversion to oil and gases in coal liquefaction and a statistical t-test was used to investigate significance of the differences. From this test, it was found that neither catalyst run exhibited a significant difference in P.S. % at 1 % significance level as compared to the thermal run. To investigate the two alternate methods for catalyst impregnation, another t-test was conducted for the two impregnation runs, and no significant difference was found at the 1 % significance level. These results should be viewed as preliminary and further work needs to be done to evaluate the effectiveness of the microsupported catalyst. In addition, it appeared that uniform distribution of the iron compound was not achieved during the impregnation on coal and a better impregnation method is needed.

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Table 1 Properties of Catalysts

Catalyst	F00	CaF00^a	F40	CaF40^b
Type^c	U	U	B	B
Chemical Composition, wt%				
Ni	2.47^d	2.35^e	2.65^d	2.53^e
Mo	13.49^d	12.84^e	12.99^d	12.38^e
Ca	0	4.85^e	0	4.67^e
Pore Volume, cm³/g				
V_{micropore}	0.378	f	0.308	f
V_{macropore}	0		0.475	

^a F00 Catalyst Promoted with Calcium

^b F40 Catalyst Promoted with Calcium

^c U stands for unimodal and B stands for bimodal

^d Galbraith Laboratories, Inc.

^e The Weight Percent Based on Promoted Catalyst

^f Not Measured

Note: See Ref. [1] for more complete catalyst properties.

**Table 2 Experimental Design of the Deactivation Runs
to Investigate the Effect of Calcium Impregnation**

Run No.	F00	CaF00-1	CaF00-2	F40	CaF40
Catalyst Name	F00	CaF00		F40	CaF40
Weight of Fresh Catalyst Packed g	11.22	12.36	11.57	6.83	7.20
Run Time hour	216	408	216	696	648
Deactivation Temperature °C	450	450	450	450	450
Reaction Temperature °C	400	400	400	400	400
Operating Pressure Psi	1000	1000	1000	1000	1000

Table 3 Coke Contents of Aged Catalyst^a

Run No.	Analysis A %	Analysis B %	Analysis C %	Average
F00	23.13	24.11	24.27	23.84
CaF00-1	25.40	24.30	25.09	24.93
F40	35.51	31.87	32.37	33.25
CaF40	30.01	30.14	30.17	30.11
CaF00-2	23.54	24.05	24.06	23.88

^a Percent Weight Loss on Combustion at 600 °C in Air

Table 4 Analysis of Aged F00 and CaF00 Catalysts

Catalyst	F00	CaF00^a	CaF00
Run Time (hr)	200	200	400
wt% C^b	22.82 22.62	14.31 14.56	22.06 22.74
wt% H^b	1.03 1.04	1.34 1.25	1.16 0.90
Mean C_xH_y	C_{1.89}H_{1.03}	C_{1.20}H_{1.29}	C_{1.88}H_{1.02}
Mean x/y	1.83	0.93	1.82

^a From the CaF00-2 Run

^b Analyzed by Galbraith Laboratories, Inc..

Table 5 Results of Diffusivity Measurements

Diffusion		Diffusivity x 10 ⁸ , cm ² /s		
Run No.	Catalyst	Fresh	Aged	Regenerated
F40	F40	4.47	0.20	5.90
		2.98	0.27	5.02
		3.96	0.31	
		3.88		
CaF40	CaF40		0.28	6.96
			0.38	5.25
			0.38	5.40
F00	F00	3.13	0.00	3.93
		3.50		3.85
		2.65		
		3.52		
CaF00-1	CaF00	3.15		4.13
		3.06		4.11
CaF00-2	CaF00		0.11	
			0.14	

Table 6 Results of Coal Liquefaction Runs

Run	mf coal g	tetralin g	iron sulfate heptahydrate g	Total P.I. g	boehmite g	P.S. %
Without Catalyst:						
1 - A	3.0687	10.1641		1.7287		48.86
1 - B	3.2450	10.5735		1.8758		47.21
2 - A	3.1085	10.0238		1.7223		49.89
2 - B	3.0132	10.1486		1.6226		51.63
3 - A	3.0389	10.0216		1.5216		55.86
3 - B	3.0570	10.0393		1.5871		53.80
4 - A	3.0107	10.1235		1.5291		55.06
4 - B	3.0010	9.9725		1.6613		49.95
With Catalyst:						
5 - A	3.0127	9.9501	1.5049	2.1101		51.21
5 - B	2.9984	9.9804	1.5004	2.1083		50.94
6 - A	3.0011	9.8546	1.5001	2.2183		46.89
6 - B	3.0018	9.7978	1.5009	2.3341		42.59
7 - A	3.0105	10.0536	1.5319	2.9828	1.0515	50.31
7 - B	2.9994	10.0345	1.4962	2.9484	1.0166	49.91

Note:

1. A and B represent replicate runs.
2. Run 5 used direct addition of catalyst.
3. Run 6 used impregnation of catalyst on coal.
4. Run 7 used impregnation of catalyst on boehmite.
5. Weight of catalyst after reaction is the weight of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \times (88/278)$.
6. Weight of boehmite after reaction equals original weight $\times 0.8$

Figure 1 Effect of Calcium Impregnation on F-00 Deactivation

Figure 2 Effect of Calcium Impregnation on F-00 Deactivation (Based on the Same Run Time)

Figure 3 Effect of Calcium Impregnation on F-40 Deactivation

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