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Cooperative Research in Coal Liquefaction

**Final Report on DOE Contract
No. DE-FC22-90PC90029
Period: May 1, 1991 to April 30, 1992**

Submitted to
U.S. Department of Energy

On Behalf of the
Consortium for Fossil Fuel Liquefaction Science

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

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February, 1993

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

Consortium for Fossil Fuel Liquefaction Science

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

on DOE Contract #DE-FC22-90PC90029

Period: May 1, 1991 - April 30, 1992

**G. P. Huffman, Director
Consortium for Fossil Fuel Liquefaction Science**

SUMMARY

Iron-Based Catalysts for Coal Liquefaction

Extensive research continued on catalysts based on novel anion-treated (mainly sulfated) oxides and oxyhydroxides of iron $[\text{Fe}_x\text{O}_y/\text{SO}_4]$. In addition, sulfated oxides of tin as well as molybdenum promoted iron oxides were used. Incorporation of small amounts of sulfate, molybdate, or tungstate anions by wet precipitation/impregnation methods was found to increase the surface acidic character of iron oxides; more importantly, it reduced the grain sizes significantly with corresponding increases in specific surface areas. These anion-treated iron and tin oxides were more active for direct coal liquefaction and coal-heavy oil coprocessing than their untreated counterparts. With these catalyst systems, higher conversion levels are obtained as compared to the soluble precursors of iron and molybdenum at the same catalyst metalloading (3500 ppm iron and 50 ppm molybdenum with respect to coal). Sulfated iron oxides and oxyhydroxides were equally active as coal liquefaction catalysts. The sulfate, molybdate, and tungstate anions were found to have similar promotional effects on the properties and activities of iron oxides.

One step in the synthesis of anion-treated iron and tin oxides is precipitation as hydroxides using either urea or ammonium hydroxide. The catalysts prepared using urea as a precipitation agent were more reproducible than those using ammonium hydroxide in terms of activities and properties. These catalysts/catalyst precursors were characterized by several techniques to determine their physical (size and structure related) and chemical (acidity) properties. Sulfated and molybdated iron oxides were found to have grain sizes as small as 10-20 nm. An attempt was made to correlate the physicochemical properties of these catalysts with their activity for coal liquefaction.

Direct coal liquefaction and coal-oil coprocessing reactions were carried out at temperatures between 375-425°C and 1000 psig (cold) H₂ in a well stirred 300 cc stainless steel autoclave to assess the activity of sulfated catalysts. Coal conversions as high as 90% maf (for the Argonne Illinois No. 6 and Wyodak coals) with over 50% yield of light oils (n-pentane soluble products) were obtained. Substantial heteroatom (N, S, O) removal was also observed. Incorporation of small amounts of molybdenum (20-100 ppm relative to coal) in sulfated iron oxides/oxyhydroxides resulted in improved conversions. The system Mo/Fe₂O₃/SO₄ resulted, for example, in 80 + % total conversion and 40 + % yield of oil for direct liquefaction of the low pyrite high volatile bituminous Blind Canyon coal at 400°C when 2500 ppm iron and 50 ppm molybdenum were used relative to coal.

Sulfated iron oxide catalysts, with or without molybdenum, were also active for coal-oil coprocessing reactions. Pure compound reactions carried out so far indicate that surface acidity of these catalysts has an influence on the product distribution, although the role of acidity in reactions involving coal has not yet been studied because of our inability to ascertain product distribution. The activity of sulfated and other anion-treated iron oxides for coal liquefaction seems to bear a strong relationship to their small initial grain sizes (< 20 nm) and their somewhat surprising ability of preserving their grain size under reaction conditions without much agglomeration.

From kinetic modeling studies^[1], it is apparent that sulfated iron oxides are catalysts for conversion of the intermediate coal asphaltenes to lighter oils in direct liquefaction of a subbituminous Wyodak coal. Reaction rate constants for sulfated iron oxides as catalysts were almost an order of magnitude higher than those with unsulfated iron oxide. This correlated well with the ratio of their specific surface areas.

Studies of the catalysts after reaction were carried out to quantify the composition and the extent of dispersion (grain sizes) of the inorganic sulfided phases formed during coal liquefaction. Anionic modification of iron oxide precursors prevents their sintering at high temperature. It takes about five minutes at 400°C

for the conversion of initially added $\text{Fe}_2\text{O}_3/\text{SO}_4$ to finely dispersed pyrrhotites. A very thin layer of carbonaceous material (wt% C by elemental analysis = 2-3%) forms on the surface of iron-containing particles in the liquefaction reactor; it is likely that this keeps the particles of pyrrhotite from agglomerating during the course of the reaction. An investigation of catalytic reactions of model compounds would help improve our understanding of the mode of action and reaction pathways with sulfated and other anion-treated iron oxides in coal liquefaction.

The multistep coal liquefaction treatment developed by Shabtai and coworkers[1,2] continued to be developed and improved. Several iron-based catalysts were tested using coal-simulating model compounds for comparative hydrogenolysis activity. Information was obtained for bond cleavage rates for several model compounds using a $\text{Fe}(\text{H}_2\text{O})_6\text{Cl}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst. A comparative hydrogenolysis study was initiated of the activity of soluble iron salts supported on SiO_2 to that of $\text{Fe}_2\text{O}_3/\text{SO}_4$. Systematic studies were carried out to determine optimum conditions for the HT-BCD(hydrotreatment - base catalyzed depolymerization) treatment for a Lewiston-Stockton coal from the Argonne premium coal sample bank. Following HT at 275°C, 1500 psig H_2 pressure, the yield of depolymerized products in the BCD step were found to increase markedly with an increase of the BCD temperature from 250 to 305°C. Finally, development of a flow reactor system was completed for a feasibility study of a two-stage HT-BCD, HPR(hydroprocessing) coal liquefaction process.

An improved model was developed for Mossbauer spectroscopic characterization of ultrafine iron oxide catalysts that exhibit superparamagnetic(spm) relaxation effects. The model involves fitting the spectra with a mixture of magnetic hyperfine, quadrupole doublet, and spm relaxation components. Improved size distributions result from such fits of spectra obtained at a number of temperatures. The size and structure of such catalysts has also been investigated by scanning transmission electron microscopy(STEM) and by SQUID magnetometry. In the STEM work, mean particle diameters are measured directly for several hundred particles and structure is determined by electron microdiffraction. The SQUID magnetometer measurement

determines a distribution function, $f(r)$, by assuming a log normal distribution and Langevin paramagnetism of spm particles. Comparison of the size distributions determined by these three methods for selected catalysts gave reasonably good agreement[3].

A 30 Å FeOOH oxide catalyst (NANOCAT, manufactured by Mach I) was found to exhibit a number of interesting properties. Mossbauer spectroscopy, in addition to showing spm properties, also exhibited a very low recoilless fraction, which vanished completely with increasing temperature at about 50 K. The recoilless fraction could be restored to nearly the value observed for bulk FeOOH by subjecting the sample to hydrostatic pressure or by freezing the sample in caruba wax. This established that most of the loss of recoilless fraction was due to particle recoil necessary to conserve momentum when gamma rays are emitted by the ^{57}Fe nucleus. XAFS spectroscopy established that Lewis acid sites exist at the surface of the 30 Å FeOOH particles, at which iron ions may have 3-5 oxygen/hydroxyl nearest neighbors. Radial distribution functions derived from the XAFS spectra established the structure to be FeOOH, with depleted coordination numbers for iron neighbor shells due to the large percentage of surface atoms.

Techniques were developed for characterizing the structure and size of ultrafine catalysts by scanning transmission electron microscopy (STEM). Size distributions and electron microdiffraction data were obtained for a number of iron-based catalysts, including the 30 Å FeOOH catalyst, an $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst, and iron oxide particles produced by cation-exchange of iron into a lignite. A study of the growth and transformation of iron oxide particles during annealing in air was initiated for the 30 Å catalysts.

Iron ion-exchanged into lignite from an iron acetate solution showed excellent activity for direct coal liquefaction. Two lignites were studied, and both exhibited significant increases in both total conversion and oil yields when from 1 to 7% of iron was incorporated into the coal by cation-exchange. Mossbauer spectroscopy and other characterization methods indicated that a substantial percentage of the iron was present in particles or molecular complexes less than 30 Å in diameter.

An investigation of catalyst dispersion has been made using electron probe microanalysis (EPMA) following impregnation of Wyodak coal with FeCl_3 and $(\text{NH}_4)_2\text{MoS}_4$ in aqueous solutions. Before hydrotreatment, the iron and molybdenum are found coating the coal particles. After hydrotreatment at 350°C and 1500 psig H_2 , both the Fe and Mo are dispersed throughout the interior of the coal particles.

Design, construction and testing of a batch-type tubing bomb microreactor has been completed in the liquefaction laboratory at West Virginia University. Tests of the variation in liquefaction yields for Blind Canyon coal as a function of time, temperature, and agitation speed have been completed. A second system, which is similar in design, but incorporates a hydrogen purge, associated gas preheat and downstream product analysis, has also been designed and constructed. Testing of this system is now in progress.

Reaction of ferric chloride at 5°C with sodium sulfide in aqueous solution yielded a black colloid of Fe_2S_3 . On heating to $100 - 200^\circ\text{C}$, the ferric sulfide disproportionates to pyrite, pyrrhotite, and elemental sulfur. Particle sizes of the iron sulfides produced by this method are typically around $200 \text{ \AA}$. These iron sulfides exhibit reasonable catalytic activity for DCL of Blind Canyon coal (DECS-17) at 350°C , increasing total conversion by about 10%, split approximately between increases in asphaltene and oil + gas yields. At 400°C , however, the catalytic conversion and yields are only slightly higher than those observed thermally for the DECS-17 coal. A novel aerosol reactor for generation of ultrafine iron sulfide catalysts has been designed and is now under construction.

In situ transmission electron microscopy (TEM) studies were carried out to elucidate the basic mechanisms of the catalytic reaction between hydrogen and graphite in the presence of either iron sulfide or molybdenum sulfide. Studies were carried out at temperatures up to 850°C in 0.2 Torr hydrogen. It was observed that hydrogasification could occur at a distance from the catalyst particles, suggesting gas transport of the active species in addition to surface migration. It is believed that the metal sulfides act as dissociation catalysts for the molecular hydrogen, causing this type of reaction. This action increased with temperature up to about 500°C , then

decreased. Above about 750°C, metallic iron and Fe₃C were formed from the iron sulfide (pyrrhotite) phase and a channeling type of reaction between the catalyst particles and graphite was observed.

A laser pyrolysis method has been used to generate ultrafine iron carbide catalysts for DCL. The procedure consists of irradiating a stream of ethylene saturated with iron pentacarbonyl with an intense infrared beam from a CW CO₂ laser. By tuning the laser to an absorption band of CH₄, the gases are rapidly heated in a small volume, causing formation of the ultrafine carbide particles. Characterization of the material by XRD and Mossbauer spectroscopy established that either Fe₃C or Fe₇C₃ could be formed by variation of flow rates. The latter phase, which is normally very difficult to form, proved to be the better DCL catalyst. However, the higher catalytic activity of Fe₇C₃ is believed to be due to its smaller particle size, rather than its structure, since both Fe₇C₃ and Fe₃C converted to pyrrhotite under liquefaction conditions. This behavior is different than observed for molybdenum and tungsten carbides and nitrides, which exhibit good liquefaction activity, but resist transformation to sulfides[4].

Slurry phase iron catalysts exhibit a small amount of activity for the hydrogenation of naphthalene. A somewhat higher temperature of 425°C and a 3:1 addition of sulfur to iron increased the activity of the slurry phase iron catalyst; however, the activity of the iron sulfide catalyst formed was substantially less than that observed from the slurry phase MoS₂ catalyst generated from molybdenum naphthenate and excess sulfur. The activity of the slurry phase iron catalysts for pyrene hydrogenation depended upon the ligand, reaction temperature, and the addition of sulfur. Iron naphthenate was the most active of the iron precursors. The higher reaction temperature of 425°C and longer reaction time of 60 min were also beneficial for pyrene hydrogenation. The method by which the catalyst was dispersed in the pyrene/hexadecane system made a substantial difference in the activity of the catalyst. Iron naphthenate showed the greatest activity using the *in situ* dispersion method and the least using the *ex situ* method. Molybdenum naphthenate also showed less activity with the *ex situ* method compared to the *in situ* method but

showed the most activity with the two-stage method. Analysis of the stability of iron naphthenate at liquefaction conditions revealed that the iron complex broke down quickly, making the Fe available for further reaction with sulfur. The other iron and molybdenum complexes are currently being tested to evaluate their stability.

Experiments have initiated using a trickle flow reactor system with a fixed bed of powdered catalyst and a tubing bomb microreactor. Model compound experiments are being performed using iron catalysts in order to develop insight into how these catalysts function in coal liquefaction.

Fundamental Research

The CFFLS ^{13}C NMR research program focussed on the development and testing of a number of techniques that can provide chemical shift information on polycyclic aromatic hydrocarbons, which serve as models of the structural features in the aromatic clusters found in coal. Obtaining the principal components of the chemical shift tensor from compounds with more than four distinct carbons using the standard static solid NMR techniques is often impossible due to overlap of the shielding patterns of each of the carbons. However, there have been many techniques developed to isolate the lineshape of a single carbon from the remaining carbons, either by separating the individual patterns in a two dimensional space or selectively looking at only one carbon.

In research conducted this year, we have developed the capability to obtain the chemical shift tensor components in solids by two different 2-D methods. In addition, our efforts to add dynamic angle spinning (DAS) as a third method are continuing. These 2-D methods greatly expand the molecules that are feasible to study, as we are no longer limited to looking at only smaller aromatic systems with high degrees of symmetry in order to have only three or four magnetically inequivalent carbons. In future research, we will explore the possibility to extend the application of these techniques to coals, and determine whether any useful information can be extracted

from the complex patterns expected in the 2-D space.

A high pressure thermogravimetric (TG) system has been successfully interfaced with a gas chromatography/mass spectrometry (GC/MS) system. To our knowledge, this is the only high pressure TG/GC/MS system of its kind. The system is capable of operating at pressures up to 1500 psi and temperatures up to 650°C. A preliminary TG/FTIR/MS study of the pyrolysis products derived from a rubber tire and a mixture of the tire with Blind Canyon was carried out. The organic matrix of the tire devolatilizes rapidly at relatively low temperatures, leaving a highly stable residue, presumably consisting of carbon black plus inorganic fillers. A 1:1 blend of tire rubber with coal reacts to a first approximation as a simple sum of both components, with the exception of an enhanced high temperature CO² yield.

Fabrication of a microwave cavity system for in-situ high pressure/high temperature ESR spectroscopy studies of free radicals in coals and coal conversion processes was completed. With this apparatus, ESR studies can be carried out from ambient to 500°C and for gaseous pressures up to 800 psi (1 MPa = 145 psi) at x-band frequencies (9 GHz) and ESR signals can be monitored as a function of time, temperature or pressure in the above stated ranges. A number of experiments on the hydrogenation of a Blind Canyon coal (DECS-17, obtained through the courtesy of the Penn State Coal Bank) have been carried out using this apparatus, with and without the Shell 324 catalysts (NiMo/Al₂O₃). These experiments show that presence of hydrogen reduces the free radical density above 400°C and in the presence of the catalyst, additional cracking mechanisms are operative resulting in an increase in the free radical density.

A methodology was developed for generating anionic and cationic radical species of 21 ring-substituted organic compounds considered to be model compounds for investigating coal liquefaction. ESR spectra were obtained for each compound. However, the ESR spectra for several compounds were too complex for direct analysis. The spin-lattice relaxation time (T₁) and spin-spin relaxation time (T₂) were measured for free radicals in several chars being investigated by ¹³C. ESR measurements detected covalently bonded iron and organic free radicals in Utah coal.

subjected to the Shabtai liquefaction treatment.

An investigation is underway to elucidate the nature of dehydrogenation reactions, the ease of removal of hydroaromatic hydrogen from different structural components, and the effects of solvents. The results demonstrate that the course of the dehydrogenation of a number of model compounds involves hydrogen transfer to identifiable intermediates, indicating that the determination of the relative rates of hydrogen donation of hydroaromatics in recycle solvents is of particular importance in achieving insights into the chemistry of coal liquefaction. There is evidence that the quality of hydroaromatic hydrogen in recycled solvents might be more important than the total hydroaromatic content itself. Catalytic dehydrogenation, in addition to gaining information on hydrogen transfer to coal from hydroaromatic compounds, promises to be a valuable analytical technique to determine the amount and nature of hydroaromatic hydrogen in coal and to be an assessment technique for evaluation of coal liquefaction catalysts.

X-ray photoelectron spectroscopy(XPS) measurements were carried out on an $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst after presulfiding in a liquefaction environment and on several residues from liquefaction runs that used the catalyst. The presulfided sample exhibited a S/Fe ratio of approximately 10/8, indicating pyrrhotite. No iron could be detected on the surfaces of the residue particles, indicating that the catalyst was imbedded.

A computational chemistry study of the basic mechanisms of bond cleavage focused this year on possible mechanisms of catalytic bond cleavage in model compounds. Specifically, the radical cation, radical hydrogen transfer, and protonation mechanisms were investigated as possibilities. The theoretical results were compared to the experimental results of Farcasiu et al. [5,6]. Calculations using procedures described elsewhere [7,8] indicate that the radical cation mechanism gives the best agreement with experiment for model compounds such as 4-(1-naphthylmethyl) bibenzyl. A certain degree of selective catalytic action is predicted for carbon black, which was present in the experimental study.

A large quantity of the coal liquefaction intermediate products, asphaltenes

and preasphaltenes, were prepared and separated from the total reaction product of a Western Kentucky #9 coal and a heavy petroleum resid. Liquefaction of these intermediates indicate that the thermally defined pathways are similar to those observed previously in the liquefaction of the bituminous coals. In the initial stage of the pathway, the primary reaction is the conversion of coal to the asphaltene plus preasphaltene (A+P) intermediates. In this stage of the pathway, the oil plus gas (O+G) yields remain fairly constant. The second stage of the liquefaction pathway begins upon reaching a maximum coal conversion (and A+P yield). The primary reaction taking place in the second stage of the pathway is the conversion of A+P to O+G. Coal conversion remains fairly constant in this stage of the pathway. All of the high volatile bituminous coals investigated exhibited this pathway during thermal liquefaction. In an attempt to circumvent the observed maximum in the intermediate A+P yields prior to the increase in the production of oils, a number of catalyst and solvents with different hydrogen donor abilities were investigated. The catalytic pathway was found to be similar to the thermal liquefaction pathway; the catalyst increased the rate of reaction but had no major effect on the selectivity.

An electrodynamic balance was modified to allow Raman spectra to be collected from suspended single coal particles, 10-20 microns in diameter. The modified system uses a focusing mirror and lens to direct all scattered light to the entrance of a spectrometer. Apparatus has also been designed to allow the collection of ultrafine (50-100Å) particles on a larger suspended droplet.

HPLC methods and techniques are being developed to separate coal liquids by hydrocarbon type. These separations will classify coal liquids by their content of saturate, aromatic and polar molecules. The aromatic fraction would be subdivided by aromatic ring size to distinguish one ring aromatics from others with two three four, five and more rings; the polar fraction would be separated by nitrogen and oxygen functional groups. The HPLC method developed to this point uses three solvents, two types of column and a column switching valve to separate a single injection of oil sample by molecular type, and further separates its aromatic molecules by ring size. These same separations using ASTM open column method

require several days of work. Current research is directed toward further compound identification and quantitation of the HPLC methods.

Novel Liquefaction Concepts

In-situ catalyst formation studies with *Sulfolobus brierleyi* showed the formation of FeOOH crystals. Deposition of molybdenum from solution onto coal particles also increased in biotreated samples. The chemical liquefaction yield of the biotreated coal was dramatically increased from 3 to 25% when sulfur was added to the liquefaction reactor. Coal treated with *Thiobacillus ferrooxidans* in the presence of air and CO₂ followed by hydrogen, improved liquefaction yield by 10%.

Hydrogen uptake hydrogenase-possessing thermoacidophilic archaebacterium *Sulfolobus brierleyi* and mesophilic sulfate-reducing bacteria *Desulfovibrio desulfuricans* were used to study the biological hydrogenation of different coals and various model compounds such as diphenyl methane (DPM), 1,2-diquinolyl ethane, α -naphthyl hexane. Hydrogen uptake by the model compounds and various coal types catalyzed by the microbial systems was also determined using G.C. The experiments with the model compounds indeed showed hydrogen uptake ranging from 0.28 μ moles H₂/ μ mole of DPM to 6.55 μ moles H₂/ μ moles of 1,2-diquinolyl ethane in the presence of *S. brierleyi* and *D. desulfuricans* respectively. Chloroform extract of aqueous phase analysis using GC-MS did show that DPM was fragmented into lower parent fragments of M/Z values 73, 95 and 147 depending upon the microorganism used. We also observed significant spectral variation of the liquid phase of medium with coal (KCER # 4677 & 91182) and asphaltenes, when treated with *S. brierleyi* and *D. desulfuricans* under a H₂ atmosphere. Our previous results showed hydrogen uptake by these coals and asphaltenes. Fumarate was reduced (36% conversion) to succinate in the presence of *D. desulfuricans* under hydrogen atmosphere. Stilbene (1,2-diphenylethylene) was also reduced (~5%) to bibenzyl (1,2-dephenylethane) when treated with *D. desulfuricans* under H₂ gas.

Hydrogen starvation in the initial stages of coal liquefaction appears to have a permanent, negative impact on product yields. A novel liquefaction reactor has been designed which incorporates versatility in reaction controllability and a gas-liquid contactor design that provides very high mass transfer rates. Several types of gas-liquid contactors were investigated, including slot-type injectors, motionless mixers, and high-shearing mechanical agitators. Of these types, the slot-type injector showed the greatest potential for increasing gas-liquid mass transfer in coal liquefaction. One type of slot injector, a jet nozzle, showed significantly better performance than the other types tested.

Catalytic hydropyrolysis of Blind Canyon was investigated using iron, nickel, and molybdenum as catalysts, either singly or in combination. The catalysts were incorporated into the coal from aqueous solutions containing metal salts, either by ultrasonic impregnation (for molybdenum) or by incipient wetness impregnation. The highest yields of THF solubles at 350°C were obtained by using combinations of 0.05% Mo with 0.01 - 1.0% of either Fe or Ni. There was no significant difference between yields observed using the incipient wetness or the ultrasonic impregnation methods. At 400°C, Mo was a very effective catalyst at concentrations of 0.01-0.1% while Ni was found to be a good promoter for the Mo catalyst. Combinations of Fe with Mo were less effective than Mo alone at 400°C.

Ultrasonic enhancement in low temperature solvent extraction of coal is effective for solvent mixtures of pyridine/methanol/TBAH (tetra-n-butylammonium hydroxide) and also THF/methanol/TBAH. Higher yields might be due to the high coal swelling ratio of TBAH, which could assist the ultrasonic energy to rupture the van der Waals and/or hydrogen bonds between bituminous coal lamellae. In order to understand the function of the ultrasonic energy in solvent extraction of coal products, analyses need to be completed. SFC and SFC/MS will be used to get more detailed information on the nature of the solvent extracts as a function of solvents used, energy level applied, and other variables in the system.

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Task I

Iron-based Catalysts for Coal Liquefaction

Program Coordinators: Irving Wender and Gerald P. Huffman

Project I.1

Catalysis by Anion-Modified Iron Oxides in Coal Liquefaction

Irving Wender, John W. Tierney, Gerald D. Holder
University of Pittsburgh

SUMMARY

The main goal of this work was to study highly dispersed (finely divided) catalysts based on iron, tin, and/or molybdenum for coal dissolution. Catalysts employed in this study were the novel anion-treated (mainly sulfated) oxides and oxyhydroxides of iron [$\text{Fe}_x\text{O}_y/\text{SO}_4$]. In addition, sulfated oxides of tin as well as molybdenum promoted iron oxides were used. Incorporation of small amounts of sulfate, molybdate, or tungstate anions by wet precipitation/impregnation methods was found to increase the surface acidic character of iron oxides; more importantly, it reduced the grain sizes significantly with corresponding increases in specific surface areas. These anion-treated iron and tin oxides were more active for direct coal liquefaction and coal-heavy oil coprocessing than their untreated counterparts. With these catalyst systems, higher conversion levels are obtained as compared to the soluble precursors of iron and molybdenum at the same catalyst metal loading (3500 ppm iron and 50 ppm molybdenum with respect to coal). Sulfated iron oxides and oxyhydroxides were equally active as coal liquefaction catalysts. The sulfate, molybdate, and tungstate anions were found to have similar promotional effects on the properties and activities of iron oxides.

One step in the synthesis of anion-treated iron and tin oxides is precipitation as hydroxides using either urea or ammonium hydroxide. The catalysts prepared using urea as a precipitation agent were more reproducible than those using ammonium hydroxide in terms of activities and properties. These catalysts/catalyst precursors were characterized by several techniques to determine their physical (size and structure related) and chemical (acidity) properties. Sulfated and molybdated iron oxides were found to have grain sizes as small as 10-20 nm. An attempt was made to correlate the physicochemical properties of these catalysts with their activity for coal liquefaction.

Direct coal liquefaction and coal-oil coprocessing reactions were carried out at

temperatures between 375-425°C and 1000 psig (cold) H₂ in a well stirred 300 cc stainless steel autoclave to assess the activity of sulfated catalysts. Coal conversions as high as 90% maf (for the Argonne Illinois No. 6 and Wyodak coals) with over 50% yield of light oils (n-pentane soluble products) were obtained. Substantial heteroatom (N, S, O) removal was also observed. Incorporation of small amounts of molybdenum (20-100 ppm relative to coal) in sulfated iron oxides/oxyhydroxides resulted in improved conversions. The system Mo/Fe₂O₃/SO₄ resulted, for example, in 80+% total conversion and 40+% yield of oil for direct liquefaction of the low pyrite high volatile bituminous Blind Canyon coal at 400°C when 2500 ppm iron and 50 ppm molybdenum were used relative to coal (Figure 1 and 2).

Sulfated iron oxide catalysts, with or without molybdenum, were also active for coal-oil coprocessing reactions. Pure compound reactions carried out so far indicate that the surface acidity of these catalysts has an influence on the product distribution, although the role of acidity in reactions involving coal has not yet been studied because of our inability to ascertain product distribution. The activity of sulfated and other anion treated iron oxides for coal liquefaction seems to bear a strong relationship to their small initial grain sizes (< 20 nm) and their somewhat surprising ability of preserving their grain size under reaction conditions without much agglomeration.

From kinetic modeling studies^[1], it is apparent that sulfated iron oxides are active for catalysis for conversion of the intermediate coal asphaltenes to lighter oils in direct liquefaction of a subbituminous Wyodak coal. Reaction rate constants for sulfated iron oxides as catalysts were almost an order of magnitude higher than those with unsulfated iron oxide. This correlated well with the ratio of their specific surface areas.

Studies of the catalysts after reaction were carried out to quantify the composition and the extent of dispersion (grain sizes) of the inorganic sulfided phases formed during coal liquefaction. Anionic modification of iron oxide precursors prevents their sintering at high temperature. It takes about five minutes at 400°C for the conversion of initially added Fe₂O₃/SO₄ to finely dispersed pyrrhotites. A very thin layer of carbonaceous material (wt% C by elemental analysis = 2-3 %) forms on the surface of iron-containing particles in the liquefaction reactor; it is likely that this keeps the particles of pyrrhotite from agglomerating during the course of the reaction. An investigation of catalytic reactions of model compounds would help improve our understanding of the mode of

action and reaction pathways with sulfated and other anion-treated iron oxides in coal liquefaction.

IMPORTANT FINDINGS

I. Catalyst Synthesis and Characterization: Catalysts prepared by precipitation using urea were more reproducible in terms of particle size and surface area. Anion-treated oxides, prepared by wet precipitation, showed better dispersion properties than untreated oxides. In all the catalysts, over 95% of the sulfur was on the surface in a S^{6+} oxidation state. These catalysts are crystallites as small as 100-200 Å (by TEM, XRD, and Mossbauer) which at room temperature form loose physical agglomerates (confirmed by SEM). These physical agglomerates were about 1-10 microns in size (laser scattering). Effects of the presence of sulfate anions both during precipitation and calcination on the properties of the resulting oxide particles were studied. It was found that the presence of sulfate anions during precipitation was necessary in order to form well-dispersed nano-sized oxide particles, resistant to sintering at high temperatures. Sulfate anions bring about surface charge modification of the precipitate particles which affects the chemistry and kinetics of precipitation/crystallization. Effect of precipitation time (rapid/slow) on the properties of the resulting particles was also investigated. Rapid precipitation resulted in crystallites as small as 50-100 Å; this catalyst was also as active for direct liquefaction as the catalysts obtained by slow precipitation. Tungstate (WO_4) and molybdate (MoO_4) anions were found to have similar improvement/modification effects on the properties of the iron oxide catalysts. The physical agglomerates mentioned above had void channels, which were on average 150 Å in diameter (N_2 adsorption-porosimetry). These sulfated and molybdated iron oxide catalysts were found to have both Lewis and Bronsted acid sites (FTIR) and chemisorbed large amounts of base (pyridine) at temperatures as high as 450°C.

II. Reaction Studies: Activity assessment for different sulfate-promoted iron and tin oxides was carried out by determining the conversion levels (total conversion and conversion to oil) for direct liquefaction of a bituminous (Argonne Illinois No.6) and a subbituminous coal (Argonne Wyodak coal). The use of sulfated iron (and tin) oxides gave total conversions as high as 90% (maf) for Illinois No.6 and 86% (maf) for Wyodak coal with high yields of light oil: 50+% for Illinois No.6 and 60+% for Wyodak coal. In these activity assessment reactions only 3500 ppm of iron (or 4000 ppm of tin) were used

relative to coal. It was then thought desirable to determine how sulfated iron oxide catalysts compare with other possible precursors of iron as far as catalyst activity is concerned under similar reaction conditions. At the same loading of iron relative to coal, sulfated iron oxides were more active for direct liquefaction and coal-oil coprocessing than other precursors such as $\text{Fe}(\text{CO})_5$, 30 Å size iron oxide ($+\text{H}_2\text{SO}_4$), and $\text{Fe}_2(\text{SO}_4)_3$. Also, the sulfated iron oxyhydroxides (FeOOH/SO_4 , without calcination), amorphous according to XRD results, were almost as active as the calcined sulfated iron oxides ($\text{Fe}_2\text{O}_3/\text{SO}_4$).

Effects of various reaction variables were studied on the catalytic performance of sulfated oxides. The optimum performance of sulfated iron oxides in direct coal liquefaction was obtained with tetralin as reaction solvent (recycle oil and 1-methylnaphthalene were the other solvents used), solvent-to-coal weight ratio of 3:1, sulfur:catalyst ratio of 2:1 (by weight), hydrogen pressure of 1000 psig (cold), at 1200 rpm impeller speed, and with undried coals.

Kinetic modelling studies indicated that, for direct liquefaction of Wyodak coal, as the temperature was raised from 375°C to 425°C, the yield of light oil increased from about 46% to 65% with a sulfated iron oxide catalyst (3.4 wt% sulfate). The model parameters indicated that, in going from unsulfated iron oxide (surface area = 28 m²/g) to the molybdenum-promoted sulfated iron oxide, the rate constant for the conversion of asphaltenes to oils increased by almost an order of magnitude. A mathematical model obtained by correlating liquefaction data was used successfully to extrapolate conversion at temperatures as low as 300°C and to predict conversions during autoclave heat-up periods. It was found that the onset of catalysis in subbituminous coal liquefaction occurs after the first five minutes of reaction at 400°C. This means that sufficient asphaltenes must be formed from coal before sulfated catalysts can hydrogenate/hydrocrack asphaltenes to light oil.

The effects of small amounts of iron (added to the reactor as FeOOH/SO_4) and iron-molybdenum (added as $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$) catalysts were determined using a low-pyritic Blind Canyon coal. High total coal conversions (75-85% maf) and high oil yields (40-45%) were obtained at 400°C and 1000 psig H_2 (thermal total conversion was 60% and oil yield was 21%). The activities of other anion-promoted (WO_4 and MoO_4) iron oxides were found to be similar to that of sulfated iron oxides (Figure 3), although tungstated and molybdated iron oxides resulted in slightly higher yields of oil than the sulfated ones.

This could be due to the presence of highly active sulfides of tungsten (WS_2) and molybdenum (MoS_2) formed during the reaction.

We also presulfided the sulfated iron oxide/oxyhydroxides by reacting them with tetralin alone (but no coal) under coal liquefaction conditions. This procedure yielded mainly Fe_7S_8 as determined by XRD with a crystallite size of about 20 nm (XRD, TEM). These preformed sulfides were as active for direct liquefaction of Blind Canyon coal as the sulfated catalysts from which they were prepared. Interestingly, these preformed sulfides were even more active (especially for oil formation) with added elemental sulfur. This suggests that pyrrhotites act as the reservoirs of sulfur/ H_2S during reaction. The finer the size of the pyrrhotites, the faster is the diffusion of sulfur from the bulk of pyrrhotite to its surface, where it reacts with chemisorbed hydrogen forming H_2S which probably plays an active part in catalyzing hydrogenation/hydrocracking reactions during coal liquefaction.

III. Characterization of Reaction Products: The liquid products (methylene chloride solubles and n-pentane solubles) obtained from direct liquefaction and coprocessing of Illinois No.6 coal catalyzed by sulfated oxides were found to have higher H/C atomic ratios than the starting coal. Coprocessing products were more aromatic than the starting heavy oil due to incorporation of coal liquids. The heteroatom content (N, S, O) of the reaction products was lower than the starting materials. In most of the catalytic runs, over 90 wt% of the added tetralin was recovered after reaction. The remainder reacted to form cracked, isomerized, and hydrogenated/dehydrogenated products.

The residues of coal liquefaction (containing IOM, ash, and transformed catalyst) were characterized by XRD, electron microscopy, and Mossbauer spectroscopy. The added iron was found to have been converted to pyrrhotites. The resulting pyrrhotites were in a highly dispersed state (average size = 20 nm). Our catalyst transformation and sintering studies (using either a low pyrite Blind Canyon coal or active carbon), were carried out to determine how fast the initially added sulfated iron oxide was converted to pyrrhotites and to quantify the dispersion and composition of the resulting sulfide particles. The results imply that, starting with 10-15 nm particles of sulfated iron oxide/oxyhydroxides, pyrrhotites, mainly Fe_7S_8 , as small as 20-30 nm size are formed after about five minutes of reaction at 400°C. These pyrrhotite crystallites are hexagonal

in shape and exhibit a very high crystallinity, as indicated by sharp single crystal boundaries and a distinct iron sulfide "spot" diffraction pattern. The change in size of iron-bearing particles was observed only during this chemical transformation; once the pyrrhotite particles were formed, their size did not grow further.

Future Work

It is difficult to obtain a clear picture of the mode of action of sulfated catalysts and the reaction pathways from product distributions of the complex coal liquefaction reactions. Reactions of suitable model compounds which contain structures believed to be present in coals will help us shed light on the nature of catalytic action by sulfated catalysts under "coal conversion conditions". We will endeavor to use model compounds with high molecular weights (about 300) which will contain C-C, C-N, C-O, and other types of bonds and heteroatom linkages that would yield significant information when used with these catalysts. Model compounds containing specific "single" covalent bonds and compounds containing two or more potentially reactive structural units in the same molecule will be explored.

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Figure 1. Conversion and oil yields from direct liquefaction of the low pyrite Blind Canyon DECS-17 coal as a function of loading of iron, added as an FeOOH/SO₄ catalyst, at 400°C, 1000 psig H₂ (cold), in a 27 cc tubing bomb microreactor, 150 cpm, 60 min, 3:1 tetralin-to-coal.

Figure 2. Conversion and oil yields from direct liquefaction of the low pyrite Blind Canyon DECS-1 coal as a function of loading of molybdenum, added as an $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4$ catalyst, at 2500 ppm relative to coal, 400°C , 1000 psig H_2 (cold), in a 27 cc tubing bomb microreactor, 150 cpm, 6 min, 3:1 tetralin-to-coal.

Figure 3. Effect of iron(III) oxides, promoted by different anions, on their activity for direct liquefaction of DECS-17 coal at 400°C.

Project I.2

Low-Temperature Depolymerization and Liquefaction of Premium U.S. Coal Samples

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- The main lines of research during the May 1991 - April 1992 period were as follows:
1. Continuation of hydrogenolysis studies with coal-simulating model compounds, using Fe-containing acid catalysts. Initiation of a comparative hydrogenolysis activity study of soluble vs. fine particle-size solid catalysts.
 2. Hydrolysis and aquathermolysis studies with coal-simulating diaryl ethers and thioethers as feeds.
 3. Continuation of HT-BCD-HPR process development studies using Lewiston-Stockton coal as feed, and structural analysis of products.
 4. Completion of the construction and initial testing of a flow reactor system for the feasibility study of the two-stage, viz., depolymerization (combined HT-BCD)-hydroprocessing (HPR), coal liquefaction process.
- Following is a short description of progress achieved on these subjects.

I.2.1. Hydrogenolysis Studies with Coal-Simulating Polycluster Aromatic Hydrocarbons.

The mild hydrotreatment (HT) step of the HT-BCD-HPR procedure involves primarily hydrogenolytic C-C cleavage reactions of various intercluster linkages. To be able to develop or identify optimal hydrogenolysis catalysts and, at the same time, determine the rate and relative ease of hydrogenolytic cleavage at various C-C bond sites in the polymeric coal network, it is necessary to perform comparative kinetic studies with appropriate polycluster aromatic hydrocarbons as feeds. Four relevant compounds 1 - 4 (diphenylmethane; 1,2-dinaphthylethane; 4-benzylbiphenyl; and 9-benzylfluorene, respectively) were selected for this purpose (see Figure I.2.1).

There are ten different types of bonds (a to j) susceptible to hydrogenolysis in these compounds, as follows (AR indicates single aromatic ring; BAR indicates condensed bicyclic aromatic system):

- a - α -bond relative to AR, and at the same time benzylic bond relative to another AR
- b - α -bond relative to BAR
- c - bibenzylic bond
- d - α -bond relative to AR, and at the same time benzylic bond relative to a biphenyl system
- e - α -bond relative to a biphenyl system, and at the same time benzylic bond relative to AR
- f - direct (Ar)C-C(Ar), viz., biaryl bond

- g - direct (Ar)C-C(Ar), viz., biaryl bond, which is part of a naphthenic ring condensed with two Ar
- h - α -bond relative to AR (benzylic relative to another AR), and simultaneously part of a naphthenic ring.
- i - benzylic bond relative to three AR's
- j - α -bond relative to AR

The above types of bonds differ in regard to (1) bond dissociation energies; and (2) relative protonation rate of the relevant aromatic rings.

An example of the work performed is provided by a kinetic study of the reactions of compound 3 (4-benzylbiphenyl). The study was performed in a 50 ml Microclave, using $\text{Fe}(\text{H}_2\text{O})_6\text{Cl}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst and cyclooctane as a non-reacting solvent. Three temperatures in the range of 275-350°C and a H_2 pressure of 1,000 psig were employed. The results showed that bond e, i.e., the α -bond position relative to the biphenyl ring system, undergoes faster hydrogenolysis. The alternative α -bond position d is cleaved at a lower rate, while cleavage at the (Ar)C-C(Ar) position f is the slowest, viz., the corresponding rate constants are in the order $k_e > k_d > k_f$. These results are consistent with the corresponding bond dissociation energies (BDE) which are in the order $\text{BDE}_f > \text{BDE}_e \approx \text{BDE}_d$, as well as with the anticipated relative rate of protonation of rings D, E and F (see Figure I.2.1) which is in the order $E \approx F > D$. Although the protonation rates of rings E and F may be similar, the protonation of F will not lead to any cleavage products (due to the high BDE of bond f), whereas protonation of E leads to fast cleavage of bond e.

In conjunction with the above work, a comparative hydrogenolysis activity study of soluble Fe salts (supported on non-catalytic SiO_2) vs. fine particle size solid catalysts, was initiated. $\text{Fe}(\text{H}_2\text{O})_6\text{Cl}_3/\text{SiO}_2$ and $\text{Fe}_2(\text{H}_2\text{O})_9(\text{SO}_4)_3/\text{SiO}_2$ were selected as representative catalysts of the former type, whereas finely dispersed sulfated iron oxide was selected as representative of solid superacid catalysts. It was found that the activity of both catalyst types depends strongly on their water content and an optimal water concentration is being sought. Further, preliminary results indicate that at low temperatures (275-325°C) the supported Fe salts are somewhat more active than the $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst. Studies at higher temperatures (350-400°C) are continuing.

I.2.2 Hydrolysis and Aquathermolysis Studies of Coal-Simulating Ethers and Thioethers

Work on the improvement of the hydrolytic (BCD, or as newly designated HD) step of the coal depolymerization stage of the process were continued using model diaryl ethers and thioethers as feeds. An example is provided by the reactions of diphenyl sulfide (DPS), using a dilute aqueous KOH solution (instead of methanolic KOH) as depolymerizing agent.

Table I.2.1 summarizes the effect of reaction temperature, in the range of 290-350°C upon the conversion of DPS into hydrolysis and aquathermolysis products (thiophenol, phenol and benzene), using 6% aqueous KOH as catalyst-solvent system. As seen, the conversion of DPS increases steeply with temperature, i.e., from 4.0% at 290°C to 54.1% at 350°C. Furthermore, there is a major change in the composition of the product, as follows. At the lowest temperature (290°C) the main components are the anticipated hydrolysis products from DPS, i.e.,

thiophenol and phenol, accompanied by a smaller amount of benzene. As the temperature is increased to 325°C the concentration of the hydrolysis products decreases whereas that of benzene correspondingly increases. At 350°C, benzene becomes the predominant product (92.2 wt%) indicating the occurrence of a fast aquathermolysis reaction resulting in the elimination of the S atom from DPS either by direct cleavage or via the thiophenol intermediate. Such a reaction takes place to some extent (14.8%) even in the absence of a catalyst (run HD-33).

Studies with DPS and diphenylether (DPE) as feeds are continuing. Studies with HT (partially depolymerized) coals are also in progress.

I.2.3. Continuation of HT-BCD-HPR Studies Using Lewiston-Stockton (WV) Coal as Feed

The systematic studies of a premium Lewiston-Stockton (W.V.) coal, with the purpose of determining suitable HT-BCD processing conditions for high-yield conversion of this feed into depolymerized products, were continued. Table I.2.2 summarizes some of the relevant results obtained. As seen, for a selected set of conditions in the initial HT step (reaction temperature, 275°C; H₂ pressure, 1500 psig; reaction time, 1 h), the total yield of depolymerized (THF-soluble) products in the subsequent BCD step increases markedly with increase in BCD temperature (from 27.1 wt% at 250°C to 85.9 wt% at 305°C). Furthermore, the proportion of the oil fraction in the solubilized product increases from 54.3 wt% at 250°C to 71.7 wt% at 305°C. It should be noted that the oil fraction consists mainly of cyclohexane-solubles together with a small amount of toluene-solubles. GC/MS analysis of the latter showed that those are predominantly monocluster compounds having molecular weights similar to those of the cyclohexane-solubles (M.W. in the approximate range of 100-280) and differing only in somewhat higher oxygen content (higher concentration of O-containing groups) which results in lower solubility in cyclohexane. For this reason, the cyclohexane-solubles and the small amount of toluene-solubles are reported in Table I.2.2 as a single oil fraction.

In another part of the study the hydrogenolytic activity of the Fe(H₂O)₆Cl₃ catalyst in the HT step was compared with that of anhydrous FeCl₃. Comparative runs were performed with Lewiston-Stockton coal as feed, using equivalent amounts (in terms of Fe content) of the impregnated salts. The HT temperature range was from 250-305°C. An identical H₂ pressure of 1,500 psig and a reaction time of 1 h were kept in all runs. The total yields of THF-soluble products were as follows:

Reaction temp, °C	Fe(H ₂ O) ₆ Cl ₃ catalyst	anh. FeCl ₃ catalyst
250	7.2	5.6
275	15.3	9.7
290	18.5	12.6
305	26.7	15.9

The results demonstrate the markedly higher hydrogenolytic activity of the pre-formed Fe(H₂O)₆³⁺ ion as compared with that of the anhydrous Fe³⁺ ion. It should be noted, however, that the anhydrous FeCl₃ is converted in part into the aqua complex by interaction with water

present in the coal. The higher activity of the aqua complex can be ascribed to its transformation into a strong protonic acid at temperatures above 250°C.

Recent Mossbauer studies by Prof. G. Huffman and co-workers indicate that in coal impregnated with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ions, the Fe-containing species is essentially at a molecular level of dispersion. In the aqua complex the Fe^{3+} ion is coordinated with six water ligands and the structure is quite stable up to ~250°C (or possibly higher temperature) and resistant to agglomeration. Under the influence of the polarizing coal medium, some of the water ligands may undergo dissociation (and partial dehydroxylation) to yield protons and a FeOOH structure which, however, remains partially hydrated by residual, non-dissociated water ligands. This structure remains resistant to agglomeration even after hydrotreatment of the coal at 275-290°C.

I.2.4. Completion of the Construction and Initial Testing of a Flow Reactor System for the Feasibility Study of the Depolymerization (Combined HT-BCD)-Hydroprocessing (HPR) Coal Liquefaction Process.

The construction of the above reactor system has been recently completed and its present configuration is shown in Figures I.2.2 and I.2.3. The unified flow reactor (*viz.* reactor in series) for the Stage I coal depolymerization consists of a HT stirred tank reactor, followed by a BCD tubular reactor. The reactor for the Stage II hydroprocessing (HPR) of depolymerized coal consists of a flow microclave reactor, equipped with a Robinson-Mahoney catalyst basket (Figure I.2.3).

Testing of the system components was recently initiated using a finely powdered Blin Canyon coal (DECS-17) as feed.

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Table I.2.1
Effect of Reaction Temperature upon the Hydrolysis and
Aquathermolysis of Diphenyl Sulfide (DPS)^{a,b}

Run No.	HD-28	HD-27	HD-32	HD-33 ^c
Reaction temp, °C	290	325	350	350
Conversion of DPS, wt%	4.0	39.2	54.1	14.8
Product distribution, wt%				
Benzene	12.4	25.3	92.2	74.6
Phenol	37.0	32.5	7.5	7.8
Thiophenol	50.6	42.2	0.3	17.6

^a All runs were performed using a 300 ml stirred autoclave, an initial N₂ pressure of 500 psig, and a reaction time of 6 hr.

^b In each run was used 0.043 mole (8.0 g) of DPS, 83 g of 6% aqueous KOH, and 8.0 g of n-dodecane as a non-reacting diluent for the organic phase (DPS plus products).

^c No catalyst (KOH) was used in this run.

Table I.2.2

Yields and Distribution of Depolymerized Products from HT-BCDTreatment of Lewiston-Stockton (WV) Coal,as a Function of BCD Temperature

Run No.	BCD ^a temp., °C	Total yield, wt% ^b	Product distribution	
			Oil fr. ^c	Incompletely depol. fr. ^d
CH-1	250	27.1	54.3	45.7
CH-2	275	53.7	63.5	36.5
CH-3	290	76.0	67.0	33.0
CH-4	305	85.9	71.7	28.3

^a The conditions used in the preceding HT step were as follows:
temperature, 275°C; initial H₂ pressure, 1500 psig; reaction time, 1 h.

^b Total yield of THF-soluble products, in addition to 10.2 wt% of THF-soluble pre-extract (MAF basis).

^c Cyclohexane-solubles, plus a small amount of toluene-solubles (see text).

^d THF-solubles (toluene-insolubles).

Figure I.2.1. Examples of Representative Polycluster Aromatic Compounds with Indicated Bond Positions Susceptible to Acid-Catalyzed Hydrogenolytic Cleavage.

Figure I.2.2. Configuration of the Unified Coal Depolymerization (HT-BCD) Reactor System.

Reactor: 50 mL Microclave with R/M Basket (Basket Volume 7.5 mL)

Reaction Condition: 300–375°C, 1500–2500 psig H₂

Figure I.2.3. Diagram of HPR Reactor System for Conversion of Depolymerized Coals into Distillable Fuels.

Project L3

Generic Structural Characterization and Liquefaction Research

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I. INTRODUCTION

During the contract period from May 1, 1991 to April 30, 1992, significant progress has been made on a number of topics. These topics include development of an improved model for Mossbauer characterization of superparamagnetic iron-based catalysts, completion of an XAFS investigation of the bulk and surface structure of ultrafine iron oxide catalysts, TEM studies of a number of iron catalysts, and investigation of the liquefaction behavior of lignite containing cation-exchanged iron.

All of these results were presented in several oral and poster presentations at the Sixth Annual CFFLS Technical Meeting. Two papers [1,2] have been submitted for publication summarizing some the results of this research, and an additional four papers [3-6] are in preparation. In this report, the principal results of this work are briefly summarized.

II. MÖSSBAUER SPECTROSCOPY RESEARCH

1. Derivation of Particle Size Distribution From Superparamagnetic Modelling

Highly dispersed iron oxides and oxyhydroxides are very effective catalysts in the conversion of coal to liquids. As demonstrated in previous reports, the structure and dispersion of such catalysts can be determined by Mössbauer spectroscopy as a consequence of their superparamagnetical behavior. In this section, a new model for the analysis of Mössbauer spectra of fine-particle iron-based catalysts for DCL is described. Spectra were obtained for all catalysts at temperatures of 10 - 295K. The spectra are least-squares analyzed using a model that includes one or several broadened magnetic hyperfine spectra and quadrupole doublets, and a superparamagnetic relaxation spectrum based on the theoretical model given by Wickman. This fitting model does not

assume any kind of standard distribution, but numerically fits the data itself as a combination of magnetics, superparamagnetics and quadrupole doublets. The fitting routine is written in FORTRAN and is carried out on a microVAX II computer.

The area under each component (e.g., magnetic, quadrupole doublet, and superparamagnetic component) is calculated numerically by the program, giving an estimate of the relative percentage of the different components. Appropriate correction in the area under the peak due to absorber thickness is taken into account by the program. In the case of pure oxides and oxyhydroxides, this new method of fitting the Mössbauer spectra as a function of temperature directly yields the size distribution profile. An approximate distribution can sometimes be obtained from a spectrum at only one temperature. However, to get a better estimate of the size distribution, the samples are normally run at several temperatures. The percentage of iron contributing to the magnetic hyperfine component is taken as the percentage of iron contained in particles of volume greater than the critical volume at that temperature, and size distributions are calculated by running the spectra at several temperatures. This new model of fitting the Mössbauer spectra gives better size distributions because the size range giving rise to the superparamagnetic part in the Mössbauer spectrum is treated separately from the magnetic part. A more detailed discussion is given elsewhere [1,3].

2. Effect of Particle Size on the Mössbauer Recoilless Fraction of an Ultrafine Fe-oxyhydroxide catalyst

Figure 1 shows the 45K and 10K spectra of a 30Å Fe-oxide catalyst provided by Mach I. It is evident that the recoilless fraction, f , as measured by the absorption area A , decreases drastically in going from 10K to 45K. Several Mössbauer spectra were taken from room temperature down to 10K on this sample and it was found that no significant Mössbauer effect is observed above approximately 45K, below which temperature a six-line pattern emerges and the area under the curve increases rapidly with the decreasing temperature. At 12K this sample showed a very clear six-line magnetic pattern with about 3% absorption. A similar set of experiments were performed on the same sample pressed under a hydraulic press at a pressure of 600kg/cm². The sample was then crushed into a powder form and run at 10K, 50K, 100K and room temperature. It was found that the Mössbauer effect is significantly enhanced by

pressing the powder, indicating that the degree of packing plays an important role in determining the Mössbauer effect. In the 'unpressed' sample, the particles are bound to each other by very weak forces and can be considered as sufficiently independent of each other to recoil individually upon absorption of a gamma ray. The 12K spectrum of the pressed and 'unpressed' sample give exactly same Mössbauer absorption spectrum other than a significant increase in absorption percentage for the pressed sample. Both this result and TEM data indicate that the particle size was not affected by pressing, but rather that the particles get locked to each other, giving rise to a significant increase in the recoil-free fraction. A detailed discussion of this interesting result will be given elsewhere [4].

3. Mössbauer Work on Fe Catalysts Developed by the CFFLS

As in past years, we have continued to carry out Mössbauer analyses of a variety of iron catalysts developed in the CFFLS program. Most of the results have been reported directly to the scientists developing the catalysts and are also presented in recent publications [1,6]. Mössbauer experiments were carried out on two samples of ultrafine Fe carbide particles made in the laser pyrolysis apparatus by X.X. Bi and P.C. Eklund, described elsewhere in this report, in order to characterize the carbide phase generated. These samples were made carefully in order to produce a single carbide phase, believed to be Fe_7C_3 . Mössbauer analysis were done on these two samples at room temperature and 12K. The Mössbauer parameters of these two samples were identical and indicated the presence of Fe_3C , Fe_5C_2 and another phase, believed to be Fe_7C_3 . The Mössbauer parameters for Fe_7C_3 have not been previously reported in the literature.

III. XAFS Spectroscopy Research

X-ray absorption fine structure (XAFS) has been carried out to determine the structure of a 30 Å iron oxide catalyst (NANOCAT™, supplied by Mach I Inc.) and several additional iron-based catalyst samples. Based on the XAFS results, a structural model for the iron oxide/oxyhydroxide catalysts has been developed.

The 30 Å catalyst was first annealed at various temperatures from 250°C to 500°C in air for 24 hrs. Larger particles are formed after annealing and the particle size increases with annealing temperature, as shown by STEM micrograph. The radial

structure functions (RSF) of the 30 Å sample and several annealed samples is shown in Figure 2. Using the single scattering theory of EXAFS, least squares fitting of the spectra reveals that the larger particles formed after annealing are α -Fe₂O₃. The first Fe shell distance of the 30 Å catalyst is found to be 3.01 Å compared with 3.00-3.05 Å for oxyhydroxides and 2.93-2.95 Å for iron oxides. A second Fe shell distance is found at 3.1 Å and is believed to be the Fe-Fe distance on the particle surface. The X-ray absorptio near edge structure (XANES) of the 30 Å catalyst also resembles those for iron oxyhydroxides. It is therefore concluded that the 30 Å catalyst sample is an iron oxyhydroxide phase, rather than α -Fe₂O₃, as was indicated by the manufacturer.

The XAFS pre-edge structure for the 30 Å catalyst shows some unexpected features. The intensity and the splitting of the pre-edge peak are very sensitive to the site symmetry. As the sample structure changes from octahedral to tetrahedral symmetry, the intensity of the pre-edge increases by a factor of 3. It is found that the intensity of the pre-edge peak of the 30 Å sample is 1.7 times that for the model compounds in which iron ions are coordinated by six oxygen or oxygen/hydroxyl neighbors. If one assumes the change is due to the tetrahedral sites, as much as 25% of the iron ions in the sample may reside at the tetrahedral sites. This result is attributed to the Lewis acid sites on the particle surface produced by dehydroxylation at which sites iron ions may have 3, 4, or 5 oxygen/hydroxyl nearest neighbors. After long time exposure to air, the pre-edge peak intensity decreases to 0.11, indicating that water molecules may be absorbed on the surface, resulting in an increase of the coordination numbers of the surface iron ions. The proposed structure for the 30 Å sample is shown in Figure 3. For the iron-based catalysts prepared by University of Pittsburgh and University of Utah, the intensity of the pre-edge peaks are also increased considerably relative to the bulk phase (Table 1), suggesting that Lewis acid sites may exist on the surfaces of these catalysts as well.

Based on the above observations, structural models for the active iron oxide/oxyhydroxide catalysts are proposed. The model consists of three parts, a bulk component, a surface layer with thickness $d = 2$ Å, and the Lewis acid sites on the surface (Figure 4). For the 30 Å catalyst and other oxyhydroxide catalysts, the interior of the particles is FeOOH with octahedral symmetry, whereas the surface layer is FeOOH with tetrahedral symmetry. For the sulfated Fe₂O₃/SO₄ catalyst, its bulk part

remains $\alpha\text{-Fe}_2\text{O}_3$, and the surface layer is $\text{Fe}_2\text{O}_3/\text{SO}_4$, which promotes the formation of Lewis acid sites. It is interesting to note that by adding moisture to the reaction process, the catalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ has been improved. This may be due to fact that with the presence of moisture, the surface layer of Fe_2O_3 is converted to an FeOOH layer, which favors the formation of Lewis acid sites.

IV. STEM STUDIES

The morphology and structural properties of an ultrafine iron oxide catalyst (mean diameter $\sim 30\text{\AA}$, NANOCATTM), an $\text{Fe}_2\text{O}_3/\text{SO}_4(6.1\%)$ catalyst and a Beulah lignite subjected to cation-exchange in an iron acetate solution were examined using scanning transmission electron microscopy (STEM). All samples were prepared by suspending the powder in ethyl alcohol and the suspension was constantly agitated in an ultrasonic bath for about an hour. A drop of the well-mixed suspension was carefully placed with a syringe on a thin carbon formvar film predeposited on 200-mesh copper grids. The specimen was placed in the sample holder of the microscope after the alcohol evaporated leaving the sample on the grid. The operating voltage (Hitachi H800 NA microscope) was set at 200kV, with the magnification ranging from 50k $\times$ to 200k $\times$, and the microdiffraction probe was set to 5nm in diameter.

I. An ultrafine iron oxide (NANOCATTM)

(a). Particle size

Figure 5a shows particle size distribution for the as-prepared sample. The average diameter (approximately spherical shape) is $32\text{\AA}$. Samples annealed in air at 250, 275, 300, 320, 350, 400 and 500°C for 24 hours exhibit increasing particle size with increasing annealing temperature. The average particle dimension of the sample annealed at 500°C is approximately $450\text{\AA}$. Not surprisingly, the number of significantly elongated particles also increases with annealing temperature.

(b). Microdiffraction

Only a ring diffraction pattern is observed for the as-prepared sample because the particle size is comparable to the electron beam size. From the ring spacing, the following ratios of interplanar spacing are observed: $d_1/d_2 = 1.25$ and $d_1/d_3 = 1.72$. Comparison of d_1/d_2 and d_1/d_3 from the TEM data to x-ray and neutron diffraction results indicates that the as-prepared sample is most similar to orthorhombic FeOOH prepared

under high pressure.

All spot diffraction patterns of larger particles of the annealed samples exhibit hexagonal structure symmetry with lattice constants $a=b=5.03$ and $c=13.75\text{\AA}$. The diffraction patterns of these larger particles are identical to $\alpha\text{-Fe}_2\text{O}_3$. A paper summarizing these results is now being prepared [5].

II. Beulah lignite subjected to iron cation-exchange

(a). Particle size

Small particles with a light grey color and dark, larger, particles were observed in the STEM. The light particle size distribution, shown in figure 5b, ranged from 2.5 to 30nm, and peaked at 10 nm. The average light particle dimension is 12nm. The dark particle size distribution peaked at 15nm.

(b). Microdiffraction

All spot diffraction patterns of different dark particles exhibited $\alpha\text{-FeOOH}$ (orthorhombic structure, $a=9.95\text{\AA}$, $b=3.01\text{\AA}$ and $c=4.61\text{\AA}$). The light particles did not exhibit a diffraction pattern.

III. $\text{Fe}_2\text{O}_3/\text{SO}_4(6.1\%)$

(a). Particle size

Figure 5c shows the particle size distribution. The dimensions ranged from 25 to 300 $\text{\AA}$ and peaked at 150 $\text{\AA}$. The average diameter is 143 $\text{\AA}$.

V. LIQUEFACTION OF LIGNITE CONTAINING CATION-EXCHANGED IRON

One of the most important features in achieving optimum conversions during direct coal liquefaction is the use of an efficient catalyst that can be highly dispersed in the coal structure. The catalyst dispersion and its intimate contact with the coal also determine the required concentration of the catalyst in coal liquefaction. Iron ion exchanged into the coal structure constitutes a catalyst that can be in a state of dispersion ranging from molecular to particles a few nanometers in diameter.

Two lignites were used in this study; Beulah (DECS-11) and Hagel (PSOC 1482) from the Fort Union region in North Dakota. The original iron content in these coals is less than 0.15 percent. The ion-exchange experiments were carried out in a 10 liter fermenter using a freshly made ferric acetate solution at a controlled pH of about 2.8 and constant

temperature of 60°C for 20 hrs. At the completion of the procedure, the ion-exchanged lignites were repeatedly washed with distilled water until the pH value of the filtrate for two consecutive washes was constant. A heavily loaded and a lightly loaded sample of both Beulah and Hagel lignite were prepared. The iron contents of the Beulah and Hagel lignites after the ion exchange process for the heavy loading of iron were 7.8% and 5.33%, respectively, and those for low load loading of iron were 0.93% and 0.88%, respectively.

Two sets of coal liquefaction experiments, were performed. The first set of experiments were designed to characterize the molecular structure and reactions of the added iron. The apparatus used to prepare samples for these experiments was a 2 liter autoclave with four nitrogen purged sampling lines and sample tubes connected directly to the outlet valve of the autoclave. The collected liquefaction samples are therefore not exposed to oxidation.

Iron K-edge x-ray absorption fine structure (XAFS) and ^{57}Fe Mössbauer spectroscopies were used to characterize the state of iron in coal and showed that the iron in the ion-exchanged coal is present initially in an $\alpha\text{-FeOOH}$ structure. A STEM study showed that the average diameter for the iron particles was 100Å while superparamagnetic relaxation Mössbauer spectra indicated an average particle size of 85Å. During liquefaction, with added DMDS, the $\alpha\text{-FeOOH}$ is converted to pyrrhotite.

The second set of experiments were performed using tubing bombs to investigate the effect of the iron ion-exchange catalyst on liquefaction product distributions. Control liquefaction experiments, using 30Å iron oxide incorporated by thorough mixing with both coal samples, were run to compare product yields with those obtained for the ion-exchanged coal samples. Liquefaction reactions were conducted at a temperature of 400°C and 800psi hydrogen. The products were separated into toluene soluble (asphaltenes), THF soluble (preasphaltenes), and pentane soluble (oil) fractions by successive extraction with toluene, THF, and pentane. Iron in the ion-exchanged coal with addition of appropriate sulfur significantly enhanced the total conversion and interconversion of heavy materials to oil in liquefaction reactions as shown in Figure 6. It is seen that the ion-exchanged iron yielded substantially better results than the 30Å iron oxide catalyst. A paper is being prepared summarizing these results[6] and further experiments are in progress.

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Table 1. XANES pre-edge intensities for iron catalyts and standards

SAMPLE	PHASE	1s-3d peak intensity
Fe_3O_4	Standard	0.141
$\gamma\text{-Fe}_2\text{O}_3$	standard	0.125
30 Å catal (Mach I)	$\text{FeOOH}\cdot x\text{H}_2\text{O}$	0.127
30 Å catal (air exposed)	$\text{FeOOH}\cdot x\text{H}_2\text{O}$	0.110
Utah #1 EST10/Fe(III) treated with desferoximine	FeOOH	0.110
Utah #2 EST10/Fe(III) ion exchanged	FeOOH	0.095
$\text{Fe}_2\text{O}_3/\text{SO}_4$ (Pitt)	$\alpha\text{-Fe}_2\text{O}_3$	0.105
FeOOH/SO_4 (Pitt)	FeOOH	0.09
$\text{FeOOH}/\text{SnO}(\text{OH})_2/\text{SO}_4$	FeOOH	0.105
$\alpha\text{-Fe}_2\text{O}_3$, $\alpha,\gamma,\delta\text{-FeOOH}$	Standard	0.068-0.083

Figure 1. Mossbauer spectra of 30Å catalyst at 45K and 10K.

Figure 2. EXAFS RSF's for the 30 Å catalyst, two annealed samples, and α -Fe₂O₃ standard compound.

a. Structure of the 30 Å catalyst.

b. Structural model for iron oxide and iron oxyhydroxide catalyst.

Figure 3. Proposed structural models.

Fig. 4. Structural model for the active iron oxide catalysts.

Figure 5. Particle size distribution for (a) the 30Å as-prepared sample, (b) Be (Fe-exchanged) sample and (c) Fe₂O₃/SO₄(6.1%) sample.

Project I.4

Catalyst Dispersion in Three Argonne Coals

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V.3.1 Tracking Metals in Coal Depolymerization Experiments

Coal research in the Eyring labs between May 1, 1991 and April 30, 1992 has concentrated on two projects: verification of catalyst dispersion in coals and catalysis of the decomposition of a coal model compound. The catalyst dispersion studies are a continuation of last year's work in which the dispersion of Fe/Mo and Ni/Mo depolymerization catalysts was studied in demineralized Blind Canyon (UT) coal. In the past twelve months three coals from the Argonne Premium Coal Sample Program (Blind Canyon, Wyodak, and Pittsburgh #8) were studied as received (i.e. undemineralized.) Our experiments answered the following questions: Does the catalyst impregnation technique significantly affect the yields of THF solubles? How much catalyst actually enters the interior of the coal particles?

Coal samples were impregnated sequentially with FeCl_3 and $(\text{NH}_4)_2\text{MoS}_4$ in aqueous solutions that were initially 1 wt% Fe and 1 wt% Mo. Catalyst impregnation was carried out using both the incipient wetness and the ultrasound techniques. Coal samples were then hydrotreated at 350°C and 1500 psig H_2 for 1 hour. After hydrotreatment the samples were extracted with THF to determine the yields and the insoluble products were prepared for electron probe microanalysis (EPMA) to examine the iron/molybdenum dispersion.

THF solubles were measured in Larry Anderson's laboratory (Table I.4.1) and indicate that for this catalyst system the impregnation technique only affects the yields from the low rank Wyodak coal. No significant difference in yields was apparent for the higher rank coal samples regardless of whether incipient wetness or ultrasound was used to introduce the catalyst into/onto the coal particles (see Table I.4.1). The best yields of THF solubles, 68% maf, were obtained from Wyodak coal. Blind Canyon coal produced the second best yields, and Pittsburgh #8 samples had the lowest yields (at 63% and 54% maf respectively.)

The EPMA micrographs showed the same pattern as seen in our previous studies with demineralized Blind Canyon coal: Before hydrotreatment the iron and molybdenum are found coating the coal particles. After hydrotreatment both the iron and molybdenum are dispersed throughout the interior of the coal particles. When quantitative EPMA techniques are applied to the samples after hydrotreatment we find a catalyst loading of 0.15 wt% throughout the coal particles. Thus the EPMA data indicate that catalyst dispersion occurs during the hydrotreatment process.

One possible explanation for the measured differences in yields involves coal rank and catalyst dispersion. As Derbyshire has shown¹ coal structure can change quite significantly at relatively low temperatures. During the early stages of hydrotreatment, the coal structure begins

to collapse. If the coal has a low wt% carbon and high wt% oxygen, as is true for Wyodak coal, then the coal structure undergoes crosslinking. The amount of crosslinking decreases with the increase in wt% carbon of the coal resulting in the graphitization of the coal structure. Therefore, the ease with which the catalyst can enter the coal particle depends on the coal rank. For low rank coals catalyst dispersion at the submicron level occurs more fully resulting in an increase in THF soluble yields. Higher rank coals, such as Blind Canyon and Pittsburgh #8, have lower THF soluble yields because of the graphitization of the coal structure during the early stages of hydrotreatment. Research is being continued in this area to determine when catalyst dispersion occurs during the hydrotreatment process.

V.3.2 Catalysis of Model Compound Decomposition

The second project completed in the Eyring labs involved the iron-catalyzed cleavage of carbon-carbon bonds in a coal model compound. Several different catalysts have been used including a new molecular sieve supported iron catalyst to achieve selective bond breaking in a coal model compound. The coal model compound is 4-(1-naphthylmethyl)biphenyl (I) [see formula below] (synthesized in our laboratory and characterized by proton NMR and mass spectrometry). The supported iron catalyst was prepared by loading Fe(III) into the pores of titanium silicate molecular sieves (ETAS-10 and ETS-10 from Engelhard Corp. and the zeolite LZY-52) using ion exchange from aqueous solution. Characterization of this supported metal catalyst was accomplished by electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD). The XRD results show that the catalyst support retains its structure upon ion-exchange at pH 2.5. EPR spectra indicate the presence of two Fe(III) coordination symmetries: orthorhombic ($g = 4.3$) and tetragonal ($g = 6.0$). XPS data indicate the presence of exterior surface iron. It appears that an iron oxide on the exterior surface of the Fe(III) impregnated ETS-10 and ETAS-10 molecular sieves catalyzes the decomposition of the model compound. One of the advantages of using a model compound in the study of coal liquefaction is that both the starting materials and products can be easily identified by gas chromatography and gas chromatography/mass spectrometry. Gas chromatographic analyses were carried out on a Shimadzu Model 14 Gas Chromatograph equipped with an SE-54, 30 m long capillary column. Experimental results are found in Table I.4.2.

Reaction of model compound I with 9,10-dihydrophenanthrene (acting as hydrogen donor and solvent) in the presence of a supported iron catalyst [ETAS-10(Fe)] was permitted to take place at 350°C for 1 hour in a sealed glass tube. It is important to note that we have used 50 wt% of catalyst which contains only about 1 wt% of iron. It was found that bond cleavage in compound I takes place with high overall conversion (> 95%) and high selectivity (entry 5, Table I.4.2). Two mechanisms have been proposed² to explain the two major products: naphthalene and biphenyl. The two possibilities are as follows: (1) naphthalene and biphenyl could result from the initial cleavage of bond a giving naphthalene and a methylbiphenyl intermediate which quickly transfers a methyl group to the solvent. (2) Alternatively, bond b could cleave initially resulting in biphenyl and a methylnaphthalene intermediate which then transmethylylates in the presence of the solvent (9,10-DHP). Reaction of methylnaphthalene, 9,10-DHP and ETAS-10 (Fe) (50 wt%) was carried out at 350°C for 1 hour in a sealed tube. No naphthalene was observed chromatographically as a reaction product. This result favors mechanism #1 which does not

involve the methylnaphthalene intermediate and the subsequent breaking of the bond between the naphthyl and methyl moieties. A greater than 95% overall conversion with similar reaction products was observed with LZY-52 (Fe) (entry 6). Compound I and 9,10-DHP undergo no reaction at 350°C in the presence alone of either the molecular sieves [ETAS-10] or the iron compounds [FeCl_2 (1 wt%), FeCl_3 (1 wt%), or ultrafine Fe_2O_3 from Mach I Inc. (10 wt%)] (entries 1-4). Thus the effect of these supported iron catalysts on selective bond cleavage appears to rely on the combination of the molecular sieves with the iron metal. Model compound I reactions in the presence of different molecular sieve supported catalysts containing Cu [ETAS-10 (Cu)], Mo[ETS-10(Mo)], Co[ETS-10(Co)]Cr[ETS-10(Cr)], Ru[ETS-10(Ru)], and Sn[ETS-10(Sn)] have also been carried out as noted in Table I.4.2.

In the cases of ETAS-10(Cu) and ETS-10(Mo), we observed that bond cleavage takes place with high overall conversion (>95%) and high selectivity (entries 7-8). The major products are naphthalene and bibenzyl. However, in the case of ETS-10(Co), no reaction takes place at all (entry 12). Thus, the activity of different molecular sieve supported metal catalysts depends on the specific metal present. In addition, preliminary experiments show that in the cases of ETS-10(Cr), ETS-10(Ru), and ETS-10(Sn) the overall conversion of I and the selectivity of bond cleavage are both lower (entries 9-11) than for the cases of ETAS-10(Fe), LZY-52(Fe), ETAS-10(Cu) and ETS-10(Mo).

The EPMA study described above was reported in a contributed paper³ at the San Francisco American Chemical Society Meeting in April, 1992. A manuscript describing an earlier EPMA study of catalyst dispersion in coal macerals was revised extensively during the year and has been accepted for publication.⁴ Papers describing the coal model compound study⁵ and the characterization of the ETAS-10 and ETS-10 molecular sieve catalysts⁶ (described above) are in preparation.

Compound I : 4-(1-naphthylmethyl)bibenzyl

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Table I.4.1. Comparison of Yields and Impregnation Technique

Coal	Impregnation	%THF soluble	%THF insoluble
Wyodak	ultrasound	55	36
Wyodak	incipient wetness	68	20
Pittsburgh #8	ultrasound	53	45
Pittsburgh #8	incipient wetness	56	42
Blind Canyon	ultrasound	62	36
Blind Canyon	incipient wetness	63	38

Table I.4.2 Influence of Catalysts on the Overall of Compound I.^a

entry	catalyst	wt % catalyst ^b	selectivity ^c (%)	overall conversion of I (%)
1	FeCl ₂	1	--	0
2	FeCl ₃	1	--	0
3	Fe ₂ O ₃	10	--	0
4	ETAS-10	50	--	0
5	ETAS-10(Fe)	50	72	>95
6	LZY-52(Fe)	50	64	>95
7	ETAS-10(Cu)	50	51	>95
8	ETS-10(Mo)	50	64	>95
9	ETS-10(Cr)	50	34	~80
10	ETS-10(Ru)	50	18	~80
11	ETS-10(Sn)	50	11	~30
12	ETS-10(Co)	50	--	0

a) Reaction conditions: sealed tube; 1 h; 350°C; weight ratio, 9,10-DHP:I 4:1; catalyst wt % based on I

b) We have used 50 wt % of catalyst which contains only about 1 wt % of metal.

c) Selectivity = [(major products)/(major products + by-products)] x 100.

In-Situ Electron Microscopy Studies of Metal Sulfide Catalysts

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INTRODUCTION

Over recent years a considerable wealth of knowledge has been amassed on the manner by which catalysts can modify both the rate and selectivity of various reactions involving the conversion of petroleum feedstocks into a variety of fuel fractions and chemicals. There are tremendous opportunities available if one can learn how to exploit the potential of these petroleum-related catalyst systems to manipulate the decomposition of coal to produce a similar spectrum of specialty chemicals. Of particular importance with regard to the conversion of carbonaceous solids such as coal to high molecular weight hydrocarbons are the catalytic reactions involving hydrogen. In this context, it is well worth considering the phenomenon of migration or "spillover" of absorbed species which is known to occur with certain supported metal catalyst systems. Perhaps the most widely known example of spillover behavior is that associated with dissociation of molecular hydrogen over certain metal catalysts.

The phenomenon of hydrogen spillover was first suggested from the observations that the rate of decomposition of GeH_4 to Ge was accelerated in the presence of platinum¹. The effect was also demonstrated by very elegant experiments in which the transformation of WO_3 to HxWO_3 during treatment in hydrogen in the presence of $\text{Pt/Al}_2\text{O}_3$ induced a color change from yellow to blue². Hydrogen spillover also appears to play an important role in the extent of reduction of a titanium oxide support when platinum was introduced onto this material and the system heated in hydrogen^{3,4}. Early work by Boudart and coworkers⁵ showed that hydrogen spillover from platinum to carbon occurred at 350°C and subsequently it has been demonstrated that this behavior can lead to methanation of the solid carbon⁶⁻⁸. Although the nature of the diffusing species is not yet established, it does appear that atomic hydrogen could be involved in the reaction mechanism.

The concept of using atomic hydrogen to convert carbonaceous solids to an assortment of hydrocarbon products has been reported by a number of workers⁹⁻¹⁸. In these studies hydrogen atoms were generated either in low pressure microwave discharge systems or by dissociation of molecular hydrogen over a hot tungsten filament. There is a general agreement that the interaction of atomic hydrogen with carbonaceous solids can take place at a relatively rapid rate even at room temperature. On the other hand, a wide variation in the hydrocarbon product distribution and composition has been reported from such reactions, which appears to be related to the type of discharge system used to produce atomic hydrogen, the hydrogen pressure and the time of exposure. Vastola and coworkers¹¹ and later Gesser and Czubryt¹⁸ found that acetylene and methane were the major products with minor amounts of ethane, methylacetylene and pentane arising from the reaction of atomic hydrogen with graphite. In another study, Gill and coworkers produced hydrogen atoms by dissociation of H₂ over a tungsten filament and allowed these atoms to react with a carbon solid at 77K. At low pressure conditions methane, ethane, propane and butane along with an identified higher molecular weight compound were produced from the reaction with graphite. In contrast only methane and ethane were formed at higher pressures when helium was added to the hydrogen.

From this brief overview of the interaction of atomic hydrogen species with coal and carbons, it is clear that this approach holds a great deal of potential for the conversion of such solids into a variety of extremely useful precursor hydrocarbon molecules. The notion of producing atomic hydrogen via various discharge techniques is extremely interesting and offers the opportunity of controlling the energy of the atomic species, however, this experimental approach is fraught with technical difficulties when one attempts to scale up such a reactor system. The question which arises is can we perform such reactions by generating atomic hydrogen species from a somewhat simpler route, i.e. by catalytic dissociation of molecular hydrogen.

The characteristics of a suitable candidate for this operation would be one which has the capacity to dissociate molecular hydrogen in a reversible manner at relatively low temperatures. Examination of the literature shows that while the majority of metals are capable of dissociating molecular hydrogen, they do not readily release the atomic species. In contrast, it appears that certain metal sulfides and in particular molybdenum disulfide may well possess the desired characteristics¹⁹.

In the current investigation we have attempted to gain a clearer understanding of the manner by which hydrogen interacts with various metal sulfides, including MoS_2 , FeS_2 and FeS as a function of temperature by using controlled atmosphere electron microscopy techniques to investigate a model system consisting of single crystal graphite, a well characterized material, whose reactivity with hydrogen in the presence of metal additives has been extensively studied²⁰.

RESULTS

In this investigation two types of specimen arrangements were utilized, which are shown schematically in Figure 1. In layout (a), the catalyst particles (metal or metal sulfide) were placed in direct contact with the graphite specimen, and the observations made were limited to areas in the vicinity of the catalyst particles. For the second design (b), a microscope grid was cut in half and one section contained a pristine transmission graphite specimen and on the other, the catalyst mounted in the same manner as shown in (a) or in the form of a crystal of molybdenum disulfide. In the arrangement the catalyst and graphite probe reactant were physically separated. It was essential that when this type of specimen was placed into the environmental cell the reactant gas stream came into contact with the catalyst prior to passing over the clean graphite, the component under observation.

When graphite specimens containing particulates of either molybdenum disulfide or the iron sulfides (FeS_2 or FeS) were exposed to 0.2 Torr hydrogen, a very unusual pattern of behavior was observed. Immediately following the introduction of the gas attack of the basal plane regions of the graphite support took place at room temperature. This action initially took the form of the creation of very tiny pits which became visible when their width had expended to approximately 1.2 nm and their depths reached a level sufficient to allow a contrast difference to be observed in the transmission image between the pit and the surrounding unattacked graphite. In some cases the presence of very shallow pits, which would not be observed by conventional transmission electron microscopy, was revealed due to the formation of relatively dense residues produced in the reaction which accumulated at the pit boundaries.

It was evident that in the early stages of the reaction the pits tended to be generated in clusters which were aligned in definite directions with respect to the

graphite substrate. Examination of numerous areas showed that the hexagonal arrangement was predominant. On continued reaction at the same temperature the pits increased in size and in a given group gradually merged with each other to form a single larger entity up to 10 nm in width. Examination of these more highly developed pits showed that they tended to acquire a hexagonal outline and at this stage generally contained an internal region of unattacked carbon.

A feature which must always be taken into consideration with experiments carried out within the electron microscope is whether the electron beam exerts any effect on either the gas or the solid under investigation. Concern that this problem was being encountered in the current work was dispelled by performing "blank experiments" in which specimens were reacted in hydrogen with the beam turned off for periods of up to two hours. When such specimens were eventually examined, it was clear that there had been extensive reaction prior to exposure to the beam. As mentioned above, during prolonged exposure to the electron beam a carbonaceous residue was observed to form on the surface and tended to accumulate at edge and steps sites including the walls of pits. Eventually this deposit became so heavy that many surface features were obscured and it was apparent that the gasification reaction was being inhibited. In contrast, this detrimental effect was not so pronounced in "blank experiments" carried out over the same time periods. Furthermore, when various metal/graphite specimens were reacted under the same conditions under continuous electron beam exposure, then no deposition of material was observed.

As the temperature was increased to 100°C, it was evident that attack became more random in nature so that the entire graphite surface gradually acquired a textured appearance. It was also apparent that pits which had been produced at lower temperatures increased in depth and tended to become progressively more circular in shape. At this stage of the reaction many pits had expanded reaching sizes of up to 4.0 μm in diameter, and frequently merged with adjacent ones with a consequence that there was wide spread removal of entire layers from the graphite surface.

The intensity of the reaction increased significantly as the temperature was gradually raised to 200°C. Unfortunately, the indiscriminate mode of attack made it impossible to identify any dynamic events that could be followed for the purposes of estimating rates of graphite hydrogenation. Moreover, the gradual deterioration in

quality in the transmission image due to collection of deposit on the specimen made it difficult to resolve many surface features. In studies where the temperature was held at 350°C for extended periods of time the attack became so extensive that specimens lost their integrity and experiments were normally terminated.

On the other hand, when specimens which has been allowed to react in hydrogen at room temperature for periods of up to 2 hours were subsequently heated in a continuous fashion to about 500°C an entirely different pattern of behavior was observed. Under these conditions, the expansion of pits was arrested and the surface underwent a cleansing operation as the carbonaceous residue was removed as a result of volatilization and/or gasification. If, at this stage, the temperature was lowered to room temperature, then restoration of pitting activity could be achieved. On continued heating to above 500°C, the sulfide particles were observed to exhibit a change in morphological characteristics from faceted structures to a more globular geometry. This transformation which occurred at about 725°C with the iron sulfides and at 775°C for molybdenum disulfide, was most clearly evident with particles located at edge regions which appeared to be quite fluid and tended to wet the graphite. This behavior was a prelude to the restoration of catalytic activity, seen as the propagation of channels by these particles when the temperature was increased by a further 100°C.

In an attempt to determine whether the catalytic action could be sustained at even greater distances from the sulfide particles, another set of experiments was carried out using a different specimen design. This involved complete physical separation of the supported metal sulfide and the graphite probe component. When this combination was treated in 0.2 Torr hydrogen, then attack of the unadulterated graphite surface was once again observed at room temperature. In these systems, however, there was a modulation in the severity of the reaction compared to that where the catalyst and graphite were in intimate contact. It was significant to find that the incidence of pit formation showed a steady decline as one scanned across the graphite surface in the opposite direction to that where the sulfide catalyst particles were located.

In-Situ Electron Diffraction Analysis

In a final series of experiments the electron microscope was operated in the *in-situ* diffraction mode and patterns taken of the FeS₂/graphite specimens at various stages of

the reaction during heating from room temperature up to 850°C in 0.2 Torr hydrogen. Table 1 shows the distribution of possible chemical species which are present during the reduction of iron disulfide over the temperature range 240 to 850°C. Examination of the data shows that reduction of FeS_2 to FeS and Fe_7S_8 (Pyrrhotite) starts to occur at 240°C and at 500°C these latter sulfides become the stable phases. On increasing the temperature to 750°C, metallic iron (both α and γ phases) begin to appear along with Fe_3C . This sequence of events is similar to that observed in a previous study where the same approach was used to follow the progressive reduction of MoS_2 ²¹.

DISCUSSION

The major feature which emerges from this study is that the interaction of hydrogen with certain metal sulfides produces a species, which even at room temperature is highly reactive towards the π -electrons present on the graphite basal plane and this action leads to the creation of pits. The observation that the carbonaceous solid does not necessarily have to be in direct contact with the metal sulfide particles in order for hydrogen gasification to occur, indicates that at the gas pressure used in these experiments, it is possible for the active species to be transported to the gas phase in addition to the surface migration route. The intensity of this action appears to increase with temperature up to a certain point and then come to a complete halt. Catalytic activity could, however, be regenerated by lowering of the temperature to a previously active regime.

This intriguing pattern of behavior can be rationalized according to the following arguments. At low temperature graphite can only undergo attack due to interaction with atomic species, generated from the dissociation of molecular hydrogen with metal sulfide via a reversible chemisorption process. This reaction will continue until conditions are reached which favor weakening of sulfur-metal bonds and the concomitant release of hydrogen sulfide. At higher temperatures, the sulfides are converted to the metallic state and the mode of gasification of graphite will revert to that normally associated with the metal, i.e. channeling. In this regard, the data obtained from the *in-situ* electron diffraction analysis is extremely relevant in establishing the limitation of the sulfides examined in the present study with respect to their chemical stability at a given temperature. In the case of FeS_2 , decomposition into pyrrhotite and/or FeS appears to

take place at around 300°C and as a consequence this reaction would interfere with the dissociative hydrogen chemisorption step. A somewhat more extended reactivity range was found with MoS₂, where decomposition into Mo₂S₃ starts at ~ 450°C²¹. On the other hand, decomposition of FeS does not occur until temperatures in excess of 750°C and as a result it is probable that this sulfide will exhibit the widest temperature range of the regeneration of atomic hydrogen species.

Hydrogen is known to undergo reversible dissociative adsorption on molybdenum disulfide¹⁹, and it might be expected that other metal sulfides, including iron sulfide, would exhibit similar chemisorption characteristics. As a consequence provided that the rate of the recombination step can be minimized, such systems may be regarded as atomic hydrogen generators. In order to minimize the utilization of such atomic species in a chemical reaction transportation processes become a major concern. In this regard, it is important to consider the phenomenon of migration or "spillover" of adsorbed species which is known to occur in a number of supported metal catalyst systems.

It is clear that this approach holds a great deal of potential for the conversion of carbonaceous solids into a variety of extremely useful precursor hydrocarbon molecules. The notion of producing atomic hydrogen via various discharge techniques is extremely interesting and offers the opportunity of controlling the energy of the atomic species, however, this experimental approach is fraught with technical difficulties when one attempts to scale up such a reactor system. The question which arises is can one perform such reactions by generating atomic hydrogen species from a somewhat simpler route, i.e. by catalytic dissociation of molecular hydrogen. The model studies carried out in the present investigation indicate that this is a viable proposition at the low pressures used in the in-situ electron microscopy experiments. The verification that similar conversions can be achieved on a larger scale must await the results of further studies.

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Table 1.

Electron Diffraction Pattern Analysis of FeS₂/Graphite as a function of Temperature in 0.2 Torr H₂

Temperature (°C)	Calculated d -spacings (nm)	d -spacings				
		FeS ₂	FeS	Fe ₇ S ₈	Fe ₃ C	α -Fe γ -Fe
240	0.2861	0.2873(011)		0.2873(222)		
	0.2651		0.2661(112)	0.2639(224)		
	0.1902	0.1911(121)				
300	0.3939		0.3882(102)			
	0.2908		0.2892(111)			
	0.2680	0.2693(101)	0.2661(112)			
	0.1953	0.1960(006)	0.1953(120)	0.1952(602)		
400	0.3945		0.3882(120)			
	0.2867	0.2873(011)	0.2892(111)	0.2873(222)		
	0.2715	0.2712(020)		0.2734(315)		
	0.1949	0.1941(204)	0.1953(120)	0.1952(602)		
500	0.2944		0.2940(004)			
	0.2727	0.2712(020)		0.2734(315)		
	0.2543		0.2556(104)	0.2545(026)		
	0.2127	0.2117(021)	0.2141(105)			
	0.1974		0.1960(006)	0.1974($\bar{3}$ 31)		
	0.1698	0.1693(002)	0.1705(031)	0.1695($\bar{3}$ 37)		
	0.1655		0.1653(032)			
	0.1491		0.1492(220)	0.1486(440)		

Table 1 (Continued)

Temperature (°C)	Calculated d -spacings (nm)	d -spacings					
		FeS ₂	FeS	Fe ₇ S ₈	Fe ₃ C	α -Fe	γ -Fe
600	0.3005		0.2984(110)				
	0.2590		0.2584(200)				
	0.2125		0.2141(015)				
	0.1754		0.1748(123)				
	0.1636		0.1638(116)				
	0.1500		0.1503(125)				
700	0.5099		0.5168(100)				
	0.3077		0.3123(103)				
	0.2623		0.2661(112)				
	0.2126		0.2141(105)				
	0.1765		0.1748(123)				
	0.1653		0.1653(302)				
	0.1513		0.1503(125)				
	0.1304		0.1294(306)				
	0.1060		0.1059(325)				
750	0.3044				0.3044(111)		
	0.2589		0.2584(200)				0.2579(110)
	0.2121						0.2105(111)
	0.2055				0.2056(130)	0.2041(110)	
	0.1743		0.1739(205)				
	0.1644		0.1638(116)		0.1646(310)		0.1631(210)
	0.1506		0.1503(125)		0.1509(003)		
	0.1331		0.1330(224)		0.1331(312)		
	0.1296		0.1294(036)		0.1298(203)		0.1289(220)
	0.1236		0.1227(403)				

Table 1 (Continued)

Temperature (°C)	Calculated <i>d</i> -spacings (nm)	<i>d</i> -spacings					
		FeS ₂	FeS	Fe ₇ S ₈	Fe ₃ C	α-Fe	γ-Fe
800	0.3034				0.3023(111)		
	0.2584		0.2584(020)				0.2579(110)
	0.2151		0.2158(023)				
	0.1864		0.1854(212)				
	0.1701		0.1705(301)				
	0.1541				0.1547(311)		
	0.1319		0.1330(224)		0.1329(123)		
	0.1119		0.1123(141)		0.1116(014)		
850	0.3059				0.3023(111)		
	0.2636		0.2661(112)				
	0.2157		0.2158(023)				
	0.1849		0.1847(115)				
	0.1831		0.1833(016)				0.1823(200)

Project L6

Novel Test Reactors for Coal Liquefaction

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Introduction

In this report, the development of two types of agitated liquefaction reactors will be discussed. Both systems utilize tubing-bomb-type reactors which are agitated with a specially designed crank-type mechanism. This mechanism allows shaking speeds in excess of 1000 strokes per minute while still maintaining structural integrity and operator safety. Both reactors are heated by immersion in a fluidized sand bath which can be quickly raised and lowered to facilitate rapid heating and quenching. One of the reactor systems is the standard batch-type tubing bomb microreactor while the second, which is similar in design, incorporates a hydrogen purge, associated gas preheat and downstream product collection. Both reactors will be described in detail below, but since the hydrogen-purged reactor is still under development, liquefaction results will be presented only for the batch-type reactor.

A. Batch Tubing Bomb Microreactor System

The batch tubing bomb microreactors are constructed out of 316 stainless steel and have a capacity of about 17 ml. Details of the reactor are shown in Figure 1. The reactor bodies are about 0.75-inch in diameter and are oriented on the horizontal axis. A 10-inch long, 0.125-inch diameter tube is attached to the midsection of the reactor and provides access for hydrogen pressurization. Two Swagelok plugs are located on either end of the reactor to allow for loading or cleaning the reaction products. A high-temperature needle valve with grafoil packing is attached to the top of the tube to make sure that the gaseous products remain in the reactor for the duration of the test. This valve may also be attached to a gas delivery system that allows for the addition of hydrogen to the reactor.

A Techne Sand Bath, model SBL-2, is used as the constant temperature bath for the coal liquefaction reactions.

Both the batch reactor and the hydrogen-purged reactors are agitated by a similar crank-type agitation mechanism shown schematically in Figure 2. The agitation motion is in the vertical plane and has a 1-inch reciprocating stroke. The mechanism is controlled by a variable speed motor and is capable of agitation rates exceeding 1000 strokes per minute. The shaft and reactor holder arm attach to the bottom of the shaker mechanism. Two tubing bomb reactors must be placed in the holder clamp at all times in order to maintain the weight balance of the shaker mechanism. The reactors are secured in the holder by a sliding sleeve which is tightened with a large nut and lock washer. The agitation speed is monitored by means of a tachometer attached directly to the motor shaft. Heating is accomplished by raising and lowering the sand bath on a platform which is controlled by a winch.

After the reactor/agitator system was constructed and tested, the batch reactor was subjected to a parametric study in order to determine its behavior and any limitations under actual liquefaction conditions. The parameters studied in this regard were the reaction temperature, the reaction time, and the agitation speed. For all the liquefaction runs presented below, the premium Blind Canyon Coal (DECS-17) was used. Approximately 3 grams of coal, preground to -60 mesh, were added to the reactor along with 5 ml of the hydrogen donor solvent tetralin. The reactors were then sealed and pressurized with hydrogen up to 1000 psi cold.

Following liquefaction, product fractionation involved exhaustive Soxhlet extraction with THF followed by hexane extraction of the THF-soluble material. For this work, the overall liquefaction yield is determined from the THF extraction step while the oil fraction is considered as the hexane-soluble species. An attempt was made to remove selectively the tetralin from the oil fraction, however, this procedure was fraught with experimental problems. While it was possible to separate the oil fraction from the tetralin, considerable scatter in the oil fraction yield was realized due to the distillation of some oil products along with the tetralin. Henceforth in the work below, oils and gases are calculated by difference and lumped together. For reference, the fractionation scheme is outlined in flow chart form in Figure 3.

1. Effect of Agitation Speed

In order to assess the effect of agitation speed on the liquefaction reaction of the DECS-17

coal, the batch reactor was loaded as above and operated at two different temperatures, 350 and 400°C. At each temperature, several different agitation speeds were tested in the range from 0 - 600 strokes per minute. All reactions were performed without the addition of external catalyst. Shown in Figure 4 are the liquefaction results for the 350°C runs. The results indicate that liquefaction conversion, at least for the DECS-17 coal under these reaction conditions, is quite insensitive to agitation speed. A slight peak in conversion at 300 strokes per minute is not significantly different from the conversion at 0 - 200 and 400 - 600 strokes per minute, since the standard deviation of the work-up procedure is about ± 2.5 wt % for most of the reactions. It should be noted that the reaction time for all these reactions was set at 60 minutes. This time may have been too long to discern any appreciable effect of agitation speed.

Figure 5 shows a similar set of reactions conducted at 400°C. Again, it appears that the agitation speed has little effect on the liquefaction yield for the DECS-17 coal. The indication here is that as long as the reactor is agitated at least 300 strokes per minute, there is sufficient means of agitation available to facilitate effective hydrogen transfer to the coal.

2. The Effect of Temperature on Liquefaction Conversion

The effect of temperature on coal liquefaction yield is well known. It is perhaps the single most important process variable affecting coal liquefaction conversion. Two liquefaction temperatures were extensively studied in this work, viz. 350°C and 400°C. Reactions were also carried out at 250°C but the process was found to be basically unreactive at this temperature. The effect of temperature on reaction yield is shown in Figure 6 for the DECS-17 coal. The agitation speed for these experiments was set at 500 strokes per minutes and the reaction time was 60 minutes. The data show that the total conversion increases almost linearly with the reaction temperature while the asphaltene fraction appears to peak at about 58 wt %. The oil and gas fraction increases dramatically over the temperature range, most likely due to an increase in gas production. Note that at 250°C very little coal is converted into THF soluble material.

It is evident from Figure 6 that the asphaltene fraction levels at around 350°C. Additional increases in temperature increase the conversion to oils and gases and thus increase hydrogen utilization.

3. The Effect of Time on Liquefaction Conversion

Most of the liquefaction reactions reported herein were operated for a reaction time of one hour. It became clear towards the end of the work that this reaction time may have been too long. Hence a time study was conducted to elucidate the effect of varying time intervals on the conversion of DECS-17 coal. Two temperatures, 350 and 400°C were selected and an agitation speed of 500 strokes per minute was set. The data for these runs are shown in Figure 7 for 350°C and Figure 8 for 400°C. For both temperatures, the total coal conversion increases with increasing time. However most of the conversion occurs within the first 15 minutes. The asphaltene fraction for 350°C follows the same trend as the total conversion. At 400°C, the asphaltene fraction is essentially constant. At both temperatures, the oil and gas fraction increases monotonically with increasing time.

B. Hydrogen-Purged Microreactor

The design and construction of the hydrogen-purged, semi-batch reactor has been completed. The general shape of the reactor is similar to the batch reactor which was used in the above studies. The incoming gas, hydrogen for example, passes through an on-off valve and an in-line filter, and then through a mass flowmeter, a pressure transducer, a check valve and a pressure gauge. Before entering the reactor, the gas is preheated by electrical heating tapes and a heating coil which is immersed in the sand-bath during the reaction.

The reactor itself is similar in construction to the batch reactor described above but the hydrogen purge required some additional hardware. In order to accommodate the flowing hydrogen gas stream, the agitating reactor must be connected to the gas delivery and collection systems. To this end, high-pressure flexible hoses are used to make this transition (see Figure 9 for details). The incoming hydrogen passes through a preheater consisting of an 18-foot long coil of 1/8-inch stainless steel tubing and immersed in the fluidized sand bath heater. The gas flow passes through the reactor in an annular-flow configuration and sweeps out the product gases from the reaction zone. Figure 10 shows the details of the reactor.

The reactor effluent passes through a heated line and a high-temperature valve before entering the condensers. Depending on the requirements of the study, up to three condensers can be used in series. The trap coolant could be air, ice, dry ice or liquid nitrogen. The noncondensable gases leaving the last condenser pass through an in-line filter, a mass flowmeter,

a relief valve, a pressure gauge, a backpressure regulator and an in-line sampling loop for GC analysis. An overall process flow diagram of the entire system is shown in Figure 11.

The volume of the reactor and each condenser is 57 and 15 ml, respectively. For a reaction temperature of 325°C and a hydrogen flow of 10 sccm, the residence times for the reactor and one condenser (at 25°C) are 2.9 and 1.4 min, respectively. The gas flow can be varied from 0 to 100 sccm.

A 1/16" thermocouple is placed in the reactor through the feed line with its tip in the reaction zone to allow accurate monitoring of the reaction temperature.

All the process parameters (temperature, pressure and flow rate) are shown on a control panel and automatically logged on an IBM-compatible computer using a high-speed, high-resolution interface (WV-FAI-B16, OMEGA) and a data acquisition and control software program (LABTECH NOTEBOOK, LABTECH).

At the present time, we are in the stage of testing all hardware and installing and debugging the software. We expect the system to be operational by the end of August, 1992.

Figure Captions

- Figure 1: Batch tubing bomb microreactor used in the coal liquefaction experiments
- Figure 2: Cross-sectional view of the crank-type agitation mechanism used to mix the tubing bomb microreactors.
- Figure 3: Flow chart of the solvent fractionation scheme used to determine total liquefaction conversion and oil yield.
- Figure 4: The effect of agitation speed on the conversion to liquefaction products at 350°C.
- Figure 5: The effect of agitation speed on the conversion to liquefaction products at 400°C.
- Figure 6: The effect of temperature on liquefaction conversion of DECS-17 coal in the batch microreactor.
- Figure 7: The effect of time on liquefaction conversion in the batch microreactor at 350°C.
- Figure 8: The effect of time on liquefaction conversion in the batch microreactor at 400°C.
- Figure 9: An overall view of the flow-through reactor showing the flexible tubing, gas pre-heat coil and the reactor/holder assembly.
- Figure 10: A detailed view of the flow-through liquefaction reactor.
- Figure 11: An overall schematic diagram of the gas-phase flow path in the hydrogen-purged tubing bomb microreactor system.

Figure 1: Batch tubing bomb microreactor used in the coal liquefaction experiments.

Figure 2: Cross-sectional view of the crank-type agitation mechanism used to mix the tubing bomb microreactors.

Figure 3: Flow chart of the solvent fractionation scheme used to determine total liquefaction conversion and oil yield.

Figure 4:

The effect of agitation speed on the conversion to liquefaction products at 350°C.

Figure 5:

The effect of agitation speed on the conversion to liquefaction products at 400°C.

DECS-17 Coal
Reaction Time: 60 min
Pressure: 1000 psig H₂ (cold)
Speed: 500 RPM

Figure 6:

The effect of temperature on liquefaction conversion of DECS-coal in the batch microreactor.

Figure 7:

The effect of time on liquefaction conversion in the batch microreactor at 350°C.

Figure 8: The effect of time on liquefaction conversion in the batch microreactor at 400°C.

Figure 9: An overall view of the flow-through reactor showing the flexible tubing, gas pre-heat coil and the reactor/holder assembly.

Figure 10: A detailed view of the flow-through liquefaction reactor.

Figure 11: An overall schematic diagram of the gas-phase flow path in the hydrogen-purged tubing bomb microreactor system.

Project L7

Ferric Sulfide as a Precursor for Coal Liquefaction and Surface Studies of Activity and Selectivity

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Introduction

Iron sulfides, particularly nonstoichiometric pyrrhotites (FeS_x , x about equal 1), have catalytic activity in coal liquefaction reactions. These iron-based materials are good candidates for a disposable or once-through direct-coal-liquefaction catalyst because of their low cost and reasonable availability. Most of the studies which are used to test catalytic activity involve bulk mixing of powdered iron sulfides with coal in the reaction medium. The literature indicates that nonstoichiometric pyrrhotites are formed from pyrite (FeS_2) under typical liquefaction conditions, and that the combination of pyrrhotite and pyrite in intimate contact form an active catalyst. However, the exact nature and role of iron catalysts in coal liquefaction remains uncertain.

We have developed an alternative route to iron sulfide synthesis. By reacting ferric chloride with a stoichiometric quantity of aqueous sodium sulfide at 5°C , we obtain a black colloid whose composition is Fe_2S_3 . Mossbauer studies show that the precipitate is ferric in nature. As the ferric sulfide is heated, it disproportionates to pyrite, pyrrhotite, and elemental sulfur. The degree of disproportionation is dependent upon the time and temperature history of the material, among other variables. The dependence of catalytic activity on these two variables is reported below.

The size of the clusters is as important as the chemical nature of the iron sulfide system. The size of the natural iron sulfides in the coal matrix ranges from 0.5 microns to 200 micron euhedral crystals. The disproportionation route, described above, yields sizes around 200 angstroms. However, particles of even smaller sizes are preferred for more effective catalysis of the gas-liquid-solid liquefaction reaction. Particles of 50 angstroms should be capable of

being suspended in a carrier solvent, so that catalyst dispersion during the liquefaction would be maximized. An aerosol reactor capable of generating the catalyst in these small sizes is being constructed and tested. This phase of the work is also reported below.

In addition to catalyst synthesis and evaluation, surface studies have been performed to establish a microscopic basis for relating the performance of the iron sulfide catalysts to their stoichiometry and structure. The specific goal of this research is to establish the factors which control iron sulfide catalyst surface composition and structure. Insight gained from these studies will define the synthesis conditions for effective catalyst preparation. Most importantly, the studies will provide an understanding of the mechanisms of catalyst function.

RESULTS

1. Preparation Effects

The ferric sulfide was produced by a procedure which involves the addition of 1.0 M ferric chloride to a 1.5 M solution of sodium sulfide in a nitrogen-purged glove box at 5 °C. The precipitate in the reaction, Fe_2S_3 , tends to disproportionate above 10 °C; therefore the reaction was carried out below 5 °C for the duration of the synthesis process. The precipitate was filtered and thoroughly washed with distilled water to remove NaCl from the ferric sulfide before the disproportionation reaction was performed.

Ferric sulfide was disproportionated by sealing the material in a hydrothermal reactor and annealing at specified temperatures for 1-hour reaction times. The ratio of pyrite to pyrrhotite changed depending upon the annealing time and heating rate. The ratios of pyrrhotite to pyrite (PH:P) for the different annealing temperatures of 25 °C, 100 °C, and 200 °C were approximately 6:1, 2:1, and 1:1 respectively.

The activity of the iron sulfide catalysts was determined with the liquefaction study of high-volatile bituminous coal (Blind Canyon, Utah, DECS-17) obtained from the Pennsylvania State University coal bank. The coal was chosen (by the Consortium) because of the relatively low total iron content indigenous to the coal. The low iron content is beneficial to elucidate the activity of the iron catalysts used in the liquefaction experiments.

The liquefaction reactions were conducted in batch tubing-bomb reactors (27 ml nominal volume) using about 3 g of coal and 5 ml of tetralin. The catalyst was physically mixed with the coal before addition to the reactor. In some cases, carbon disulfide was added to the reactor

to maintain the catalyst in a sulfided form. All liquefactions used 1000 psig hydrogen (initial cold pressure) and were conducted at either 350 or 400 °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 was carried out until the THF became clear. The THF-soluble material was then partitioned into various products defined here as asphaltenes (THF soluble but hexane insoluble) and oils (hexane soluble). Total conversion was determined as the difference in weight between the starting coal and recovered residue; asphaltene was measured; and oil plus gas was obtained by difference. All products are expressed on a daf basis.

As shown in Table 1, the 350 °C liquefaction results show that all of the catalysts improve the total conversion of the coal, both with and without the addition of carbon disulfide. Without carbon disulfide, all of the catalysts improve the baseline total conversion by about 10 wt%. The increase in the conversion is split almost equally between the asphaltene yield and the oil plus gas yield, as both of these fractions increased by about 5 wt%. However, the addition of 0.1 ml of carbon disulfide to the uncatalyzed reaction mixture results in an increase in oil conversion.

Marked increases in total, asphaltene, and oil conversions occur with the 200 °C disproportionated catalyst containing carbon disulfide. As mentioned earlier, the pyrrhotite to pyrite ratio for this catalyst is 1:1. Similar results occurred in an earlier study with a Humphrey Mine #7 bituminous coal (Stansberry et al., 1991).

Similar liquefaction reactions were conducted with the same set of Fe_2S_3 catalysts at a higher reaction temperature of 400 °C. The higher reaction temperature was expected to increase the total conversion and the oil plus gas yield. Table 2 shows the data that were obtained. All of the catalysts increase the overall conversion in THF by about 5 wt% over the baseline data. The asphaltene yields do not change appreciably in the catalytic reactions and decrease in the room temperature (RT) catalytic reaction. The oil yield is increased by the addition of catalysts over the baseline conditions with all of the catalysts. The RT catalyst showed the most selectivity to oils as the conversion increased by about 9 wt%.

The addition of carbon disulfide to the reactions did little to improve the yields or selectivity to the desired products. The entire set of 400 °C reactions produced very high liquefaction yields for the DECS-17 coal. The effect of temperature far and away dictated the

results of the liquefaction reactions.

The expected uncertainty for most of the data obtained are ± 2.5 wt% and, therefore, the catalytic effects of the 400 °C results are not discernable. The difference between 90 and 95 wt% should not be considered significant, although no statistical testing was conducted in this regard. The unusually high conversion of DECS-17 coal at 400 °C with no catalyst added may be a result of the very high maceral content of exinite. It is known that the thermal changes and accompanying weight loss of coal at increasing temperatures are related to the maceral content within the coal (Speight, 1983). At temperatures in excess of 400 °C, exinite can lose nearly 50 wt% to gases and, hence, coal conversions are very high.

For the reasons mentioned above, the results of the liquefaction reactions at 350 °C will allow a better comparison of the catalysts for evaluation and ranking according to the overall activity and selectivity. The data from the 350 °C reactions clearly show that the highest conversion to THF-solubles and the most selectivity to oils are obtained using the 200 °C disproportionated catalyst with the addition of carbon disulfide. This catalyst was further tested to show the effect of catalyst loading on conversion.

The 200 °C disproportionated catalyst was loaded into reactors with and without the addition of carbon disulfide to determine the effect of catalyst concentration on the liquefaction results. Figure 1 shows the results from varying the catalyst concentrations from 0.4 to 8 wt% while holding all other parameters constant. The results show that, with or without the addition of carbon disulfide, coal conversion increases monotonically with yield. The addition of carbon disulfide increases the conversions of all of the reactions, including the baseline case with no catalyst, by approximately the same extent. The oil plus gas yield for the unsulfided catalyst appears to pass through a minimum around 4 percent loading; sulfided catalysts also pass through a minimum, but at a much lower loading of catalyst.

2. Comparison with Other Catalyst

Several catalysts from Consortium members were compared with the disproportionated catalyst under similar reaction conditions and product analysis procedures. Mr. Vivek Pradhan (University of Pittsburgh) sent two samples of iron oxide sulfate samples; one a mixed metal iron sulfate (Mo/FeOOH/SO_4), and the other a sulfated iron oxide (FeOOH/SO_4). An iron oxide catalyst (FeOOH) developed by Mobay Corporation was provided by Dr. Malvina Farcasiu from the Pittsburgh Energy Technology Center (PETC).

The sulfated iron oxide catalysts were mixed with DECS-17 coal. Concentrations were taken as 0.5 wt% based on the iron content within the catalyst, corresponding to 1.47 wt% of FeOOH/SO_4 and 2.21 wt% of $\text{Mo}/\text{FeOOH}/\text{SO}_4$ based on the total weight of catalyst to coal. The results of the reactions at 400 °C, shown in Table 3, are compared with baseline conditions with no catalysts.

The results of the catalyst testing of the sulfated iron oxides on DECS-17 show that the total conversion is slightly increased by 2-3 wt%, while the asphaltene fraction increases by 8 wt% for the FeOOH/SO_4 catalyst and 10 wt% for the $\text{Mo}/\text{FeOOH}/\text{SO}_4$ catalyst. The increase in the asphaltene fraction is accompanied by a decrease in the oil fraction. The oils decrease by 5.6 and 7.7 wt% for the FeOOH/SO_4 and the $\text{Mo}/\text{FeOOH}/\text{SO}_4$ respectively. Hence the catalysts were not useful in the selectivity to the oil fractions.

The catalysts were used as received and may have required presulfiding before use. The University of Pittsburgh found little-to-no catalytic activity at lower reaction temperatures. Therefore, the only conditions tested were at 400 °C. For these experiments, additives such as carbon disulfide were not placed in the reactors.

The Mobay (FeOOH) catalyst supplied by PETC was tested in liquefaction reactions at lower temperature. The catalyst was added at concentrations of 0.44 wt% based on catalyst to coal weight. The reactions were conducted at 350 °C and were tested with and without carbon disulfide. The results of the reactions are compared with those from the 200 °C disproportionated catalyst; see Table 4.

The results show that the FeOOH catalyst is simply not active without being sulfided with carbon disulfide. However, the 200 °C disproportionated catalyst, also unsulfided, results in significantly higher total coal conversion than the FeOOH . When sulfided, the 200 °C disproportionated catalyst and the FeOOH catalyst perform equally well.

The addition of sulfur has been shown in the literature to be a key in increasing the yields of coal to liquids. It may be that the catalytic activity of the iron oxide is derived from the fact that the addition of carbon disulfide reaction converts the iron into pyrrhotite before any influence on conversion is noted.

The catalytic results show that the 200 °C disproportionated catalyst is an effective liquefaction catalyst in the presence of carbon disulfide at 350 °C. The total conversion increased by almost 20 wt% above baseline conditions with no catalysts while selectivity to oils

increased by about 4 wt% over the baseline. The catalyst is equivalent to the iron oxide catalyst and, at least at lower temperatures, is superior to the sulfated iron oxide catalysts.

3. Generation of Small Particles of Disproportionated Catalyst

Work this year was also concerned with the construction and evaluation of an aerosol reactor. The goal is to prepare very small clusters of iron sulfide catalysts for coal liquefaction. The process involves reaction of aerosol droplets with a hydrogen sulfide atmosphere.

The focus in the first part of the process is the generation of aerosol droplets which are composed of ferric ion solutions. These droplets are to be generated by the action of a standard diesel fuel injector. The spray of the injector is to be directed into a large stainless steel vessel which will be heated and then pressurized with hydrogen sulfide. It is anticipated that the ferric sulfide will be produced and simultaneously disproportionated to pyrrhotite and pyrite mixture. Figure 2 is a schematic of the reactor.

The size of the clusters will depend upon the size of the aerosol droplets and the concentration of the ferric ion solution. The droplet size depends upon the orifice size of the nozzle, the release pressure of the injector, and the pressure inside the vessel. Typically the release pressure will be 13,000 psig and the hydrogen sulfide partial pressure around 200 psig. At this pressure drop, the droplet size will be on the order of 0.5 micron. The concentration of the ferric ion solution can be adjusted down to 10^{-4} M so the amount of iron sulfide in each droplet should be very small. During the reaction, iron ions in the core of the droplet will migrate to the surface, where iron sulfide will be produced as the droplet volatilizes. The final product is a cenosphere of iron sulfide. As the sphere falls, it will contact tetralin at the bottom of the reactor. The tetralin is sonicated such that the sonic energy shatters the catalyst and disperses the products as an emulsion in tetralin.

At the present time, the major parts for the reactor have been purchased. Assembly is currently being carried out by a local contractor. Preliminary tests have been done on the injector system and release pressures have been adjusted. A low-pressure glass reactor is available to examine visually the spray patterns.

4. Surface Studies

During the year, work has focused on setting up the required laboratory facilities, establishing a database for iron oxide and iron sulfide materials, and performing analyses of the ferric sulfide catalysts. An effort has also been made to develop an understanding of the

electronic structure of the iron sulfides. This latter effort has been described in previous reports and will not be reported here.

Three ultrahigh vacuum surface analysis systems (non- CFFLS funded) were received and set-up during the year. Analysis capabilities provided by these systems include Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), and low energy electron diffraction (LEED). Both AES and EELS provide information on atomic and molecular composition of the surface and near surface layers, while LEED provides structural information. A schematic diagram of the system used in the CFFLS studies is shown in Figure 3. Future plans call for the addition of X-ray photoelectron spectroscopy (XPS), scanning tunneling microscope, and interfaced reaction chambers which will allow the study of even more sophisticated chemical reaction processes.

A number of system modifications and small construction projects were performed specifically for the CFFLS program. An automated data acquisition system has been installed. This will significantly improve the quality and reliability of the data while increasing the number of experiments which can be performed. Two molecular beam gas sources have been constructed to allow controlled exposure of the catalysts to reactive gas species such as hydrogen, hydrogen sulfide, and water as well as to model hydrocarbon species. Finally a heated/cooled sample manipulator has been installed. This will allow the sample temperature to be maintained in the range of 123 K to 1300 K during reaction and analysis.

AES analyses of iron sulfide and iron oxide compounds have been performed to provide quantitative information (sensitivity factors) on stoichiometry as well as information on chemical state. Figure 4 is representative of this AES data. Figure 4a is an AES survey spectrum for pyrrhotite showing the characteristic peaks for Fe, S, O, and C. Based on the peak intensities for this and other compounds, quantitative standards have been developed. Figure 4b shows the Fe MVV peaks (30 - 60 eV spectral region) for troilite, pyrrhotite, and pyrite. It is evident from these spectra that the Fe MVV peak is a doublet and is quite distinct for each compound. (This is true for the iron oxides as well.) These differences are extremely reproducible and are being used in this program to distinguish different Fe-S compounds and to understand their thermal stability and surface chemistry.

Catalyst samples analyzed to date have S/Fe ratios on the order of 2 and are heavily oxidized. Work now in progress is aimed at a more detailed analyses of the catalysts and

characterization of the surface structure of various iron sulfides using LEED. The combined capabilities of AES and LEED will be used to establish sulfide surface composition and structure as a function of temperature and exposure to reactive gases including H_2 and H_2O .

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Table 1 Liquefaction results of DECS-17 coal with various iron sulfide catalysts (-8.0 wt% catalyst loading, 350 °C, 1 hr, 1000 psig H₂, 500 RPM).

Catalyst	CS ₂	Cat Add	Yields (DAF basis)		
			Conv(%)	Asph(%)	Oil+gas(%)
None	N		58.7	51.2	7.5
None	Y		61.6	47.3	14.3
RT	N	Mixed	69.5	54.8	14.8
RT	Y	Mixed	70.6	57.3	13.3
100 °C	N	Mixed	69.1	56.1	12.9
100 °C	Y	Mixed	69.4	57.8	11.6
200 °C	N	Mixed	68.8	56.8	12.0
200 °C	Y	Mixed	79.5	61.6	18.0

Table 2 Liquefaction results of DECS-17 coal with various iron sulfide catalysts (-8.0 wt% loading, 400 °C, 1 hr, 1000 psig H₂, 500 RPM).

Catalyst	CS ₂	Cat Add	Yields (DAF basis)		
			Conv(%)	Asph(%)	Oil+gas(%)
None	N		83.7	55.4	34.4
None	Y		91.8	55.3	36.4
RT	N	Mixed	95.1	52.0	43.1
RT	Y	Mixed	94.2	51.2	43.1
100 °C	N	Mixed	95.1	58.6	36.5
100 °C	Y	Mixed	96.2	56.0	40.2
200 °C	N	Mixed	94.8	57.4	37.5
200 °C	Y	Mixed	94.7	55.0	39.7

Table 3 Liquefaction results from DECS-17 coal with sulfated iron catalysts (400 °C, 1 hr, 1000 psig H₂, 500 RPM).

Catalyst	Yields (DAF basis)		
	Conv(%)	Asph(%)	Oil+gas(%)
None	89.7	55.4	34.4
FeOOH/SO ₄	91.7	61.1	30.7
	91.7	64.9	26.9
Mo/FeOOH/SO ₄	91.2	62.3	28.9
	92.5	68.0	24.5

Table 4 Liquefaction results from DECS-17 coal with FeOOH catalyst (350 °C, 1 hr, 1000 psig H₂, 500 RPM, 0.44 wt% cat).

Catalyst	CS.	Yields (DAF basis)		
		Conv(%)	Asph(%)	Oil+gas(%)
None	N	58.7	51.2	7.5
None	Y	61.6	47.3	14.3
FeOOH	N	58.3	52.7	10.1
FeOOH	Y	66.3	54.9	11.4
200 °C	N	62.8	52.7	10.1
200 °C	Y	65.9	56.9	9.0

Figure 1. Effect of catalyst loading on DECS-17 coal conversion

Figure 2 Aerosol Reactor

Figure 3. Schematic diagram of the surface analysis systems.

Figure 4. Representative AES derivative spectra ($dN(E)/dE$). a) Survey spectra for pyrrhotite showing characteristic peaks for Fe, S, O, and C and b) Fe MVV spectra for troilite, pyrrhotite, and pyrite.

Laser Pyrolysis of Ultrafine Particle Catalysts

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INTRODUCTION

Considerable work has been done on the use of iron-based coal liquefaction catalysts. While much of the work has focused on the addition of iron in various form to increase the reaction rate and to selectively produce hydrocarbon with a particular range of molecular weight, some research has attempted to identify the active form of the iron-based catalysts [1,2,3,4]. The evidence to date points toward the supposition that pyrrhotite is the active catalytic phase, regardless of the form of the precursor [1]. That is, sufficient sulfur is inherently present in most coals studies, and the reaction condition are such that a conversion to pyrrhotite is achieved. The addition of sulfur to the reactor aids in the formation of the pyrrhotite phase and a subsequent increase in conversion is usually observed [4]. Interestingly, in the presence of sulfur, most molybdenum compounds also tend to sulfide to MoS_2 . However, recent work has shown that the carbides and nitrides of molybdenum and tungsten showed high catalytic activity while resisting the transformation to the sulfide phase [5,6,7]. The purpose of this research was to determine if the iron carbides would also yield a high activity while remaining in the carbide phase.

RESULTS: Experimental Methods

a. Laser pyrolysis synthesis of UFP catalysts

During the past year, we have studied the catalytic benefit of ultra-fine Fe_3C and Fe_7C_3 particles. The synthesis of these carbide catalysts was carried out at CAER using CO_2 laser pyrolysis, which is a gas-phase synthesis method first proposed by Haggerty [8] and later applied by Exxon [9] to the generation of Fe_3C particles for the Fischer-Tropsch catalysis. We have found that this technique is successful in synthesizing ultrafine $\alpha\text{-Fe}$, Fe_3C and Fe_7C_3 nano-particles (UFPs) in nearly single phase form with

average size controllable in the range of 5 - 30nm. Fe_3C , known as "cementite", appears to be the most stable phase among the known iron carbides, and in bulk form has been studied extensively for many years [10]. Much less attention has been given to Fe_7C_3 primarily due to the difficulty in producing this carbide as a single phase. This phase is usually stabilized by the addition of a second transition metal (e.g. Mn). However, the laser pyrolysis technique seeds and grows single crystal carbides on a time scale of milliseconds, rapidly quenching in otherwise thermodynamically unstable phases. In this investigation, we have characterized our nano-particles by using XRD and ^{57}Fe Mossbauer. The application of these techniques has allowed us to systematically study the chemical composition and structure of the particles produced by the CO_2 laser pyrolysis.

The laser pyrolysis system [8], used for producing iron carbide nanoparticles is shown in Figure 1. The cell was constructed using a six-way stainless steel cross with a tubular inner diameter of ~ 4cm. For carbide formation, ethylene (C_2H_4) saturated with iron pentacarbonyl ($\text{Fe}(\text{CO})_5$), flows vertically out of the tip of a narrow stainless steel tube and intersects the horizontal intense infrared beam from a CW CO_2 laser. The energy coupling from the laser to the reactant gas is realized by tuning the laser frequency to a strong rotational-vibrational absorption band of C_2H_4 at 940 cm^{-1} , thereby heating the reactant gases. The energy absorbed by the ethylene is transferred to the iron pentacarbonyl which, in turn, undergoes thermal decomposition to Fe and (CO). The nanoscale iron carbide particles form as a result of a recombination of Fe and C. It is not clear, however, whether C_2H_4 or CO contributes the carbon to the particle growth. The total pressure in the cell was controlled by adjusting a needle valve located between the rotary vacuum pump and the cross. Particles are collected in a pyrex trap as indicated in Figure 1. Since most of the particles produced by this method are ferromagnetic in their bulk form, a magnetic field, supplied by a large permanent ferrite magnet, was employed to remove the particles from the gas stream and retain them in the trap. A teflon membrane filter with a pore size of 0.2 μm was used to prevent the particles from leaving the magnetic trap, and reaching the vacuum pump where they might do damage.

Subsequent to the synthesis, the UFP's were extracted from the trap after a surface passivation with 4% - 10% O_2 in He gas flowing over the particles for a period of several hours. This passivation is necessary to handle the particles in air without

inducing a pyroforic reaction. The phase identification of the UFP's in this study was performed mainly by XRD and Mossbauer spectroscopy. Other techniques including TEM, SEM, Raman spectroscopy and EDX analysis have also been employed, to a lesser extent, to study the surface morphology, particle size distribution, existence of oxygen and amorphous carbon on the UFP's. Two carbide phases, Fe_3C and Fe_7C_3 , and $\alpha\text{-Fe}$ have been produced by this technique by adjusting the reaction conditions. The reaction parameters which generate these particles, i.e., chamber pressure, nozzle diameter, laser intensity and C_2H_4 flow rate, are given in Table 1.

b. Coal liquefaction

The liquefaction studies were carried out in ~25 ml vertical tubing bomb reactors. The coal was a low sulfur, low iron, subbituminous Wyodak coal. The reactor was loaded with 3 g. of coal in 5 g. of tetralin, used as a hydrogen donor solvent. A steel ball was added to the mixture to aid in mixing and to reduce any mass transfer constraints. When used, the catalyst was loaded at 1 wt.% Fe with respect to coal. Dimethyldisulfide was added as a source of sulfur to ensure complete sulfidation of the catalyst during the reaction. The tubing bomb was sealed and purged with hydrogen before being pressurized to 800 psig(cold). The pressurized bomb was attached to a shaker mechanism which agitated the tubing bomb in a vertical plane at a rate of 400 cycles/min. Heat was provided via a fluidized sand bath in which the tubing bombs were immersed during reaction. A reaction time of 15 minutes was used in these reactions. After reaction the tubing bomb reactor was removed from the shaker apparatus and quenched in a cool sand bath. The pressure of the bomb was recorded and a sample of the gas phase was retained for analysis by gas chromatography. The remainder of the gas was vented, allowing the disassembly of the reactor. The contents of the reactor were analyzed for conversion using a soxhlet extraction technique. The yields were determined using the solvents shown in Table 2.

Since it has previously been reported that some transition metal carbides and nitrides were resistant to sulfidation under liquefaction conditions [5,6,7] a series of experiments were carried out to determine the effect of sulfur on the iron carbide UFPs under these conditions. In these experiments 200 mg of the iron carbide Fe_7C_3 was loaded into a 20 ml tubing bomb reactor with 5 g tetralin. When used, excess sulfur was

added as DMDS at twice the amount needed for formation of pyrite. The bombs were pressurized to 800 psig (cold) with hydrogen and agitated in a fluidized sand bath for 30 minutes.

RESULTS: Characterization

a. XRD and Mossbauer studies of the passivated UFP particles

Shown in Fig. 2 are the XRD results for passivated UFP Fe_3C and Fe_7C_3 produced by using the reaction parameter values given in Table 1. In this figure, the dots represent experimental data and the lines are calculated using a sum of Lorentzian functions whose peak positions and relative strengths are obtained from published powder diffraction data [11]. The same width parameter is used for all diffraction lines and an exponential function is introduced to simulate the background. The Debye-Scherrer equation has been used to convert the X-ray line width into an average particle diameter. We find that these X-ray derived values for the particle diameter are in good agreement with Transmission Electron Microscopy (TEM) results, indicating that the UFPs are, for the most part, single crystal particles. The calculated diffraction pattern is seen to agree reasonably well with the data [11], leading to our identification of the phases as Fe_3C and Fe_7C_3 .

We have found that higher chamber pressures (> 300 torr) and higher reactant gas flow rates (> 30 sccm) favor the formation of high carbon content crystalline phases such as Fe_7C_3 . On the other hand, lower chamber pressures and reactant gas flow rates favor the formation of $\alpha\text{-Fe}$. A detailed study of the correlation between reaction parameter values and the associated solid UFP phases produced will appear elsewhere [12].

In Fig. 3, we show ^{57}Fe Mossbauer spectra collected in collaboration with G. Huffman's group. The data were taken at 12K for two batches of particles which have majority phase of Fe_3C and Fe_7C_3 , as determined by X-ray diffraction pattern shown in Fig. 2. The solid line in Fig. 3 represents the calculated Mossbauer spectrum by fitting the data in the usual way. The results from the fit to room temperature data (not shown here) including internal magnetic field, isomer shift and quadruple splitting parameters are listed in Table 3. The parameter values for the Fe_3C particles at room temperature are found in good agreement with the results of Le Caer et al. [13]. To our knowledge, Mossbauer results for Fe_7C_3 have not been reported. We find in this study that a model

with four inequivalent magnetic sites is necessary to fit the data of Fe_7C_3 sample. Fe_7C_3 has only three chemically inequivalent sites [10]. One of the sets of Mossbauer parameters matches closely with that of Fe_3C , indicating the forth site results from contamination from Fe_3C .

b. Catalytic reactivity of the UFP particles

The results of the XRD taken on the product from the reactor where Fe_xC and DMDS were subjected to $T=385^\circ\text{C}$ and $P_{\text{H}_2}=800$ psig (cold) for 30 minutes indicate, that the Fe_xC is transformed into pyrrhotite. This would seem to agree well with the majority of the literature which indicates that, regardless of the form of the precursor, iron based catalysts in the presence of added sulfur transform into pyrrhotite. The lack of sulfidation of the other transition metal carbides and nitrides (Mo & W) indicates a higher stability under these conditions. In the absence of added sulfur, we have observed that Fe_xC transforms under liquefaction conditions to a mixture of an unidentified carbide phase and an oxide phase. The presence of an oxide phase may be due to the O_2 physisorbed/chemisorbed on the surface of the catalyst particles physisorbed/chemisorbed as they are loaded into the reactor or oxygenated surface from the passivation process. However, the formation of an unstable intermediate (i.e. $\alpha\text{-Fe}$) at $\sim 350^\circ\text{C}$ in hydrogen is expected. These particles then are expected to oxidize upon contact with air after removal from the sample bomb. The $\text{Fe}_3\text{C} \rightarrow \alpha\text{-Fe}$ and $\text{Fe}_7\text{C}_3 \rightarrow \alpha\text{-Fe}$ conversion in hydrogen at 350°C is known from in situ X-ray diffraction studies we have carried out at ORNL [14] where both Fe_3C and Fe_7C_3 UFPs (~ 10 nm dia.) powders transformed under 1 atm of both He and H_2 to $\alpha\text{-Fe}$ in the temperature range $350 - 400^\circ\text{C}$.

The results from the liquefaction studies of the Wyodak coal indicate that the iron carbides exhibit a moderate catalytic effect over the temperature range studied. Preliminary studies indicated that the Fe_7C_3 phase exhibited a higher catalytic activity than the Fe_3C phase. However, this trend was not repeatable in subsequent experiments. It was concluded that the difference in catalytic activity may not be related to the phase of the carbide precursors, but rather to the difference in size of the particles tested. The initial tests were made on Fe_7C_3 particles which exhibited a smaller average particles size than the later studied Fe_3C particles. Further testing of the iron carbides was primarily limited to the study of the Fe_7C_3 phase. The effect of the catalyst on the

total conversion during the 15 minute runs are shown in Fig. 4. Blank runs using added DMDS in the absence of a catalyst confirmed that the DMDS had little or no catalytic effect on the reaction. A consistent increase in the total conversion over the thermal baseline is observed throughout the temperature range studied with the most prominent effect present near 370°C. At higher temperatures thermal hydrogenation tends to overshadow any catalytic effects resulting in a convergence of the thermal and catalytic conversions. Similarly, at lower temperatures the lack of thermal bond cleavage becomes the limiting factor in the conversion process again leading to convergence of the thermal and catalytic conversions. Although the maximum increase in the total conversion occurs near 370°C, Fig. 5 indicates that the relative increase in conversion increases steadily at lower temperatures with no maximum occurring in the range of temperatures studied. This relative increase, defined as the absolute increase divided by the thermal conversion, decreases steadily as the absolute thermal conversion increases. The conversion to preasphaltenes (pyridine soluble and toluene insoluble) and asphaltenes (toluene soluble and pentane insoluble) (Figures 6 and 7 respectively) follow similar trends with the maxima in absolute increase occurring at slightly different temperatures 360°C and 390°C respectively. The conversion to oils (Figure 8), however, shows a steady increase over the temperature range in question with a gradual leveling off effect seen near 430°C. This indicates the favorability of oils formation at the higher temperatures. Indeed, at the higher temperatures the conversion to oils is increasing apparently at the expense of preasphaltenes, asphaltenes and IOM. Therefore, it can be said that the addition of the iron carbide catalysts, at the higher temperatures, appears to improve the selectivity as well as the overall conversion. This trend is summarized in Figure 9.

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Table 1 Typical reaction parameters to generate three phases particles.

	Fe_3C	Fe_7C_3
Laser Intensity (W)	50	54
Beam Width (mm)	1	0.2
Nozzle Diameter (mm)	0.8	0.8
Chamber Pressure (Torr)	300	500
C_2H_4 Flow Rate (sccm)	9	25

Table 2 Solvents Used in Analysis of Coal Liquids

Fraction	Soluble in:	Insoluble in:
IOM*	N/A	Pyridine
Preasphaltenes	Pyridine	Toluene
Asphaltenes	Toluene	Pentane
Oils	Pentane	N/A

* Insoluble Organic Material

Table 3 Room-temperature ^{57}Fe Mossbauer parameters including hyperfine magnetic splitting (H_o), isomer shift (I.S.) and quadruple splitting (Q.S.) for UFP Fe_3C and Fe_7C_3

	H_o (KG)	I.S. (mm/s)	Q.S. (mm/s)
Fe_7C_3^*	228	0.32	-0.17
	210	0.23	0.03
	185	0.20	-0.04
	163	0.21	0.07
Fe_3C^*	210	0.19	0.02
	198	0.19	0.01
$\text{Fe}_3\text{C}[13]$	208	0.18	0.02
	206	0.18	0.02

* present work

UFP Production by Laser Pyrolysis

Fig. 1 Laser pyrolysis system for the synthesis of ultrafine iron carbide and sulfide particles.

Fig. 2 XRD data(dots) for Fe₃C and Fe₇C₃ UFPs and calculated results(solid curves) using standard diffraction data with an exponential background.

Fig. 3 ^{57}Fe Mossbauer spectra(dots) at $T=12$ K for Fe_3C and Fe_7C_3 . Solid lines are calculated using a set of parameters that fit the data.

Figure 4. Total Conversion

Figure 5. Relative and Absolute Increase in Total Conversion

Figure 6. Preasphaltenes Conversion

Figure 7. Asphaltene Conversion

Figure 8. Oils Conversion

Figure 9. Absolute effect of Fe7C3 on Conversions

Task II

Exploratory Research on Coal Conversion

Program Coordinators: Henk Meuzelaar and Mohindar Seehra

Project II.1

Coal Structure/Liquefaction Yield Correlation by Means of Advanced NMR Techniques

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During the period of May 1, 1991 to April 30, 1992 our efforts focussed on the development and testing of a number of techniques that can provide chemical shift information on polycyclic aromatic hydrocarbons, which serve as models of the structural features in the aromatic clusters found in coal. Obtaining the principal components of the chemical shift tensor from compounds with more than four distinct carbons using the standard static solid NMR techniques is often impossible due to overlap of the shielding patterns of each of the carbons. However, there have been many techniques developed to isolate the lineshape of a single carbon from the remaining carbons, either by separating the individual patterns in a two dimensional space or selectively looking at only one carbon.

Previously the application of variable angle sample spinning (VASS) technique to a series of substituted naphthalenes, each with three different aromatic shift tensors, were studied. A paper, entitled " ^{13}C Chemical Shift Tensors in Aromatic Compounds. 4. Substituted Naphthalenes", submitted to *J. Am. Chem. Soc.* at the end of the previous funding year, was accepted for publication and recently appeared (volume 114, page 2832).¹ This work was also the focus of a talk presented at the International Conference on Coal Science in England during August 1991.

A second paper, "Selective Saturation and Inversion of Multiple Resonances in High Resolution Solid State ^{13}C Experiments using Slow Spinning CP/MAS and Tailored DANTE Pulse Sequences" has been accepted for publication in *Solid State NMR*.² These results were also presented as a poster at the 33rd Experimental NMR Conference at Asilomar, California in March 1992³ and as a talk at the Annual National ACS Meeting held in San Francisco in April 1992.⁴ As this work was reported in the last two quarterly reports in detail only a brief review of this method is presented below.

By rapidly spinning a solid sample at the magic angle, the chemical shift anisotropy (CSA) of each distinct carbon in a sample collapses into a relatively narrow line at the isotropic or average chemical shift. If the spinning speed is less than the width of the shift pattern (the slow MAS condition) one does not obtain a single line but rather, one obtains a group of lines spaced about the central isotropic line at the interval of the spinning speed. By simulating the intensity pattern of this spinning sideband family, the tensor components of the tensor can be retrieved.

One of the methods that can be used to isolate a shift pattern from only one carbon is to selectively saturate the signals due to the remaining carbons in the sample. This has been done in the past; however, literature examples are limited to cases where only one or two resonances

are either saturated or inverted.⁵ By taking advantage of the long ^{13}C T_1 values commonly encountered in solids, one can selectively saturate a number of resonances by sequentially applying several DANTE pulse sequences centered at different frequency offsets. In addition, it has been demonstrated that if one sideband of a spinning sideband family is selectively saturated the entire family is saturated.⁶ Therefore, a spectrum of only one or two families of spinning sidebands can be isolated from a sample that contains a number of resonances.

The results obtained with this method are shown in Figure II.1.1 of 1,2,3-trimethoxybenzene. This compound has four magnetically inequivalent aromatic carbons and two inequivalent methoxy carbons. Figure II.1.1a shows the normal slow spinning MAS spectrum. By sequentially applying three DANTE sequences centered at 126, 146, and 154 ppm, a spectrum containing only the methoxy carbons and the aromatic C_2 (isotropic shift of 138 ppm) is obtained (Figure II.1.1b). The sideband patterns of the methoxy carbons can be isolated using four DANTE sequences to saturate all four aromatic patterns. The principal values of the chemical shift tensor obtained by simulation of the sideband intensity patterns is in very good agreement with the results of a single crystal study on this molecule⁷. The application of the saturation sequences does not affect the intensity pattern and therefore does not affect the resulting tensor components. The reproducibility of the technique has been shown to be good using duplicate experiments; the individual tensor components obtained from several runs (three to five, depending on the carbon) have a standard deviation of less than ± 2.5 ppm for the aromatic carbons and less than ± 3.5 ppm for the aliphatic carbons. In addition, the DANTE sequence is shown to have a high degree of selectivity, with the intensity of resonances as close as 300 Hz from the saturated resonance remaining unperturbed².

These techniques have been applied to the Lewiston-Stockton Coal from the Argonne Premium Coal Sample Bank in order to measure the aromaticity. One of the problems with going to higher field strengths for the measurement of coal aromaticities is that the spinning speed necessary to remove overlap between the aliphatic band and the aromatic spinning sidebands scales with the field strength. Furthermore, the mechanisms of magnetization transfer (i.e., the cross polarization processes) are attenuated for carbons with weak dipolar interactions as the spinning rate is increased.⁸ Using slow spinning conditions leads to overlap between the sidebands of the aromatic signal with the signal from the aliphatic carbons. Using the technique outlined above the entire aromatic signal in a slow MAS spectrum can be removed by the application of four DANTE sequences. Figure II.1.1d shows the normal slow spinning CP/MAS spectra of this coal. Figure II.1.1e is the aliphatic signal obtained using four DANTE sequences while Figure II.2.1f is the difference of 1d and 1e containing only the aromatic signal. The calculated aromaticity from these spectra is 0.77, in good agreement with results of 0.75 taken at a lower field strength (100 MHz vs 200 MHz used in this work).

More recent work has involved the continuation of efforts to determine the long term reliability of the DAS or dynamic angle spinning⁹ NMR probe purchased from Doty Scientific. We are still in the process of working with the company in order to obtain a working probe.

A probe to perform the magic angle hopping experiment, developed by Bax and Maciejowski in 1983,¹⁰ was built in our laboratory. The magic angle hopping experiment provides the same information as DAS, namely the individual chemical shift patterns are separated in a second

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

The original magic angle hopping experiment has several shortcomings, preventing its widespread use. A major problem was obtaining a motor to hop the sample very quickly, in a time short in comparison the spin lattice relaxation time of the sample. In addition the original pulse sequence was phase modulated requiring the spectrum to be obtained in an absolute mode intensity, leading to poor resolution in the second dimension.

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

This variation of the magic angle hopping experiment has been applied to eight model aromatic hydrocarbons (structures shown in Figure II.1.2) to date: 1,2,3-trimethoxybenzene (1), 1,4-dimethoxybenzene (2), 4-methoxyphenol (3), 3,4-dimethoxybenzaldehyde (4), 3-methoxy-4-hydroxybenzaldehyde (5), 2,6-dimethoxynaphthalene (6), 4,4'-dimethoxybiphenyl (7), and dl-tyrosine(8). As can be seen from the molecular structures, the complexity of the compounds and the number of magnetically inequivalent carbons can be greatly increased by going to a two dimensional technique.

A representative two dimensional spectrum obtained by this technique is shown in Figure II.1.3a. This figure is the 2-D space of the spectrum of compound 4. The computer software required to retrieve the individual powder patterns from this 2-D space is currently being developed. While the methods necessary to complete this process are known, they still need to be implemented in our laboratory. Once this step is complete, the tensor components can be obtained for each resolved pattern. The components are known for compounds 1 and 2; these cases will be used to compare the results of this technique with other methods.

In addition, a new experiment that was developed by Z. Gan has been implemented in our laboratory which we have named magic angle turning experiment¹¹. In this experiment the hopping between the three positions is replaced by continuous spinning at the magic angle at a relatively low rate (in the range of 100 Hz). The evolution time of this 2-D technique is then divided into three segments, each consisting of one third of a rotor cycle. Between these segments the prepared magnetization is stored along the magnetic field after evolving for one third of the evolution time. As the evolution time is about an order of magnitude less than the time it takes the rotor to rotate 120° , the sample is essentially static during this evolution time.

The chemical shift, which is the sum of the isotropic and the CSA contribution, is different during each of these segments. However, the average of the chemical shift over the entire sequence is again only the isotropic chemical shift due to the fact that the chemical shift is a second rank tensor. The resulting 2-D spectrum is identical to that obtained in the magic angle hopping experiment. The advantage of this new method, however, is that the need to mechanically hop the sample is removed. The magic angle turning experiment can be done on any magic angle spinning probe as long as a constant slow speed can be maintained. However, since most spinning systems are built for high speeds and are not stable enough for this experiment at lower speeds, the magic turning experiment can be difficult to perform on standard MAS probes since a very slight variation in the air pressure corresponds to a large change in the rotor spinning speed.

In our laboratory a very large volume (about 6 cm³) rotor system and a probe has been constructed. The maximum spinning speed of this system is several hundred Hz, and its speed is very constant (± 1 Hz) over 24 hours, the length of time needed for a typical experiment. In addition, the large sample volume allows for good signal to noise to be obtained in a relatively short time for a 2-D experiment. The experimental results reported by Gan¹¹ on 1,4-dimethoxybenzene (2) have been reproduced. This method has also been used to record the 2-D spectrum of compounds 3, 4, and 7 along with 2-methoxydibenzofuran (9) and *p*-tolyl ether (10). The structure of these compounds are shown in Figure II.1.2. Figure II.1.3b shows the spectrum obtained for compound 4. As can be seen, the 2-D space is identical to that in Figure II.1.3a, obtained by the magic angle hopping experiment. In Figure II.1.4 the slices of this 2-D space, showing the individual chemical shift patterns are shown. Table II.1.1 shows the preliminary tensor components extracted from these patterns for the compounds listed above. These values were obtained by inspection of the breakpoint positions; efforts are underway to be able to run SIMPLEX optimizations of the lineshape in order to obtain more accurate values for the components. Until this has been completed no effort to make assignments of tensors to individual carbons will be made.

To summarize, we now possess the capability in our laboratory to obtain the chemical shift tensor components in solids by two different 2-D methods. In addition our efforts to add DAS as a third method are continuing. These 2-D methods greatly expand the molecules that are feasible to study, as we are no longer limited to looking at only smaller aromatic systems with high degrees of symmetry in order to have only three or four magnetically inequivalent carbons. We will also explore the possibility to extend the application of these techniques to coals, and determine whether any useful information can be extracted from the complex patterns expected in the 2-D space.

Finally, during this year a comprehensive NMR study of anthracite coals was undertaken using both MAS and static measurements on a number of anthracite coals with different %C. The MAS measurement has been completed and information on the aromaticity and parameters describing properties of the average aromatic cluster have been extracted from the NMR data. These results were presented in detail in the second quarterly report of this funding period. However, our efforts to obtain tensor components from the static powder patterns of any of these anthracite coals have failed to date. The powder patterns obtained have unexpected lineshapes possibly due to relaxation and/or cross polarization processes which are dependent on orientation.

We will shortly examine these samples using the 2-D techniques described in this report in order to alleviate the "magic angle holes" observed in the powder patterns.

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Table II.1.1: Principal Components of the ^{13}C Chemical Shift Tensor as Measured by the Magic Angle Turning Experiment^a

δ_{11}	δ_{22}	δ_{33}	δ_{avg}
2-Methoxydibenzofuran (9)			
74	67	12	51
164	126	3	98
184	136	11	110
191	128	19	113
210	137	6	118
191	147	23	120
196	148	25	123
218	148	78	148
230	157	71	152
231	156	78	155
4,4'-Dimethoxybiphenyl (7)			
79	70	15	55
188	134	13	112
195	131	27	118
214	148	16	126
220	148	21	130
238	165	77	160
4-Methoxyphenol (6)			
79	73	16	56
186	139	11	112
194	136	25	118
233	147	69	150
230	160	74	155
3,4-Dimethoxybenzaldehyde (4)			
82	71	18	57
179	136	5	107
206	164	23	131
211	166	72	150
220	172	72	155
263	213	106	194
<i>p</i> -Toyl Ether (10)			
33	24	-1	19
38	24	3	22
192	139	32	121
227	153	20	133
238	149	79	155
239	161	80	160

^aComponents in ppm relative to TMS.

Figure II.1.1.1. Results of selective saturation experiments on 1,2,4-trimethoxybenzene (a-c) and Lewiston-Stockton Coal (d-f). See text for experimental details.

Figure II.1.2. Compounds for which chemical shift tensor principal components have been measured.

Figure II.1.1.3. 2D space of a) magic angle hopping experiment and b) magic angle turning on 3,4-dimethoxybenzaldehyde.

Figure II.1.4. Individual shift patterns for 3,4-dimethoxybenzaldehyde obtained by magic angle turning experiment.

Project IL2

Mass Spectrometric Studies of Liquefaction Mechanisms

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During the past year research activities in our group were focussed on three closely related areas, namely: (1) microscale simulation by high pressure TG/MS; (2) on-line monitoring of high pressure conversion reactions; and (3) co-processing of coal and used tire rubber.

1. Microscale Simulation by High Pressure TG/MS

A Cahn Instruments Model 151 high pressure TG system was installed in January and the design of a special interface for on-line, gas chromatography/mass spectrometry (GC/MS) was undertaken. To the best of our knowledge, a successful direct coupling of GC/MS to high pressure TG has not been reported before. Using our prior experience with the development of an on-line GC/MS system for monitoring conversion reactions in a flow-through micro-autoclave system [1,2] we designed an interface for high pressure TG/MS that combines an all-quartz, heated pressure reduction line with a so-called "transfer line" GC column and a small quadrupole MS system, the Hewlett Packard model 5971A MSD (Mass Selective Detector), as shown in Figure II.2.1. Note the ambient pressure dilution chamber with the special ambient vapor sampling (AVS) inlet to the transfer line GC column, based on a patented method developed in our laboratory [3]. Due to the microscale sample sizes used in the Cahn 151 high pressure TG (typically ≤ 1 gram) and the relatively high gas flows (equivalent to several hundreds of ml per minute at ambient pressure) GC/MS signals are expected to be relatively low. Consequently, the "dilution" chamber will probably have to be operated at minimal dilution settings.

The overall design of a high pressure TG system only permits operation in gaseous (or supercritical) reaction environments. This limits the relevant catalytic coal conversion processes that can be simulated to simple pyrolysis, hydropyrolysis and, possibly, hydrous pyrolysis. Currently, we are preparing to perform a series of catalytic hydropyrolysis experiments. However, in view of the relatively large flows (100-300 scc/min) hydrogen used, a special catalytic combustor has been constructed to enable safe disposal of hydrogen rich effluent streams. The first series of catalytic hydropyrolysis experiments using DECS-17 Blind Canyon coal samples are planned for mid July 1992.

2. On-line Monitoring of High Pressure Conversion Reactions

Development and testing of novel process monitoring and control techniques for high pressure reaction environments continued throughout the past year. Initially, transfer line GC/MS was successfully coupled to a flow-through micro-autoclave operating at pressures between 1,000 and 2,000 psi and temperatures up to 350 C. The results have been presented at the Spring 1992

ACS meeting in San Francisco [2].

Subsequently, a slightly modified version of this system was coupled to stainless steel as well as quartz tube reactors operating at pressures up to 1500 psi and temperatures up to 1250 F in order to study the thermal degradation behavior of hydrocarbon components of JP7 jet fuel under supercritical conditions. Some results are shown in Figure II.2.2. Finally, the TLGC/MS system was coupled to the Cahn Model 151 high pressure TG system, as explained in the previous paragraphs.

A new on-line spectroscopic technique for high pressure reaction environments now being tested consists of a high pressure (max. 2,000 psi) high temperature (max. 350-450 C) infrared cell designed for flow-through operation with liquid film thicknesses as low as 50 μm . The cell has been constructed by AABSPEC Corporation with special modifications for higher temperature operation. Dr. Christine Curtis (Auburn University) will be using the same IR cell design. Initial tests confirm that good quality IR spectra can be obtained.

3. Co-processing of Coal and Waste Rubber

This topic has recently become a focus of strong interest because of the opportunity to achieve several important goals in a single process: (a) production of syncrude; (b) recycling of valuable chemicals; and (c) reduction of environmental problems associated with current disposal practices for used rubber tires. Rather than attempting to simulate the exact conditions of any one of a range of potential co-liquefaction processes, we decided to investigate the interaction between a high volatile bituminous coal (Blind Canyon DECS 17) and a piece of scrap tire rubber during simple thermal decomposition (devolatilization; pyrolysis). Unfortunately, there is currently no recognized source of standardized tire rubber samples. In view of the marked variations in composition between rubber tires from different manufacturers or even from the same manufacturer, it would seem to be important that a source of standardized (e.g., carefully homogenized) tire rubber becomes available within the near future. Preferably, this standard sample should represent an average of many different tire brands. A complicating factor in establishing such a reference source is the great difficulty of preparing carefully homogenized tire material. Even at cryogenic temperatures highly vulcanized (crosslinked) rubber is difficult to grind. Use of powerful blenders may offer the only feasible approach. Unless such a standard sample is prepared and distributed to the various research groups investigating co-liquefaction, the threat exists that the results obtained by each group will be strongly influenced by the more or less randomly selected piece of tire rubber used in each case.

Well aware of this potential bias, but unable to prepare or obtain a standard sample, we decided to proceed with a pilot study aimed at investigating the interaction between a standard coal and a used car tire rubber sample using TG/FTIR/MS. Although it is unlikely that simple pyrolysis will be the eventual co-liquefaction procedure of choice, most liquefaction processes may be assumed to go through an initial thermal degradation or preconditioning step and/or to involve thermally controlled reactions. Moreover, the use of TG/FTIR/MS permits precise measurement of the mechanisms and kinetics involved and, if nothing else, probably represents one of the most advanced characterization methods for complex polymeric materials currently available.

Figure II.2.3 shows the TG (weight loss) and DTG (rate of weight loss) profiles of: (a) rubber from a used car tire; (b) a 1:1 mixture of hvb (Blind Canyon; DECS-17) coal and the tire rubber and (c) the DECS-17 coal. Note that in spite of the well known large percentages of carbon black in rubber tires this particular tire only produces 32% remaining char. The flat weight loss curve above 500 C, typical of relatively inert materials, suggests that only carbon black and inorganic fillers are left at higher temperatures and that the organic matrix has been completely volatilized. Moreover, the IR spectrum of rubber tire in Figure II.2.4a does not reveal the evolution of marked quantities of CO₂, CO, H₂O or small, hydrocarbon products in the C₂-C₃ range. Apparently, volatiles in the C₄ and higher range dominate among the devolatilization products. This is further confirmed by examination of the summed MS spectrum in Figure II.2.4d. By contrast, the TG and DTG profiles of coal show a much larger residue (~55% char) and a continuing slow weight loss above 500 C as the char gradually matures further. The coal profiles in Figures II.2.5 and II.2.6 also present a clear contrast with the rubber data. Not only are marked quantities of light gases (viz. H₂O, CO₂, CO, CH₄) produced, also the rate of tar production maximizes at higher temperatures (T_{max}~420 C rather than the C observed for the rubber sample). Together with the much higher yield of (alkyl) phenols and other hydroxy aromatics the more pronounced char forming tendencies of coal compared to rubber are readily explainable as the result of more severe recombination and condensation reactions. A third difference between rubber and coal can be observed at relatively low temperatures. Whereas the hvb Blind Canyon coal releases significant quantities of thermally extractable bitumen, primarily in the form of a higher aromatic oil (e.g., exemplified by the alkylnaphthalene fragment ion signal at m/z 141), rubber only produces relatively small quantities of additives, e.g., represented by a mass peak profile at m/z 158 (not shown).

Analysis of the chemical information contained in the 1:1 coal/rubber mixture data suggests that, at first approximation, the mixture profiles and spectra represent simple sums of the individual component profiles and spectra. Closer examination, however, reveals a strong increase in high temperature CO₂ yields. Since high temperature CO₂, CO, H₂O and H₂ yields are generally assumed to depend on several char/gas and gas/gas equilibria, such as the "water-gas shift" reaction ($\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$) and the "steam gasification" reaction ($\text{H}_2\text{O} + \text{C} \rightleftharpoons \text{H}_2 + \text{CO}$) respectively, the mixed char/carbon black residue most likely is the source of the enhanced CO₂ peak, e.g., due to possible catalytic effects of the carbon black. However, in view of the fact that a platinum crucible was used, as is standard practice in TG analysis, the possibility of catalytic reactions involving Pt (especially in the presence of trace amounts of oxygen) needs to be ruled out by further experiments using a quartz crucible.

From these preliminary coal/rubber co-processing experiments the following tentative conclusions may be drawn:

- The organic matrix in our tire rubber sample devolatilizes rapidly and completely at relatively low pyrolysis temperatures leaving a highly stable residue, presumably consisting of carbon black plus inorganic fillers.
- A 1:1 blend of tire rubber with coal reacts at first approximation as a simple linear sum of both components with the exception of an enhanced high temperature CO₂ yield.

- Meaningful interlaboratory comparisons of co-liquefaction experiments involving rubber tire samples require the availability of standardized, homogenized samples representative of a broad range of different rubber blends.
- TG/FTIR/MS provides detailed, reproducible thermal reactivity data on coal, rubber and coal/rubber mixtures.

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Figure II.2.2. On-line GC/MS monitoring of the thermal decomposition of JP-7 jet fuel under supercritical conditions (1500 psi) in a 1/16" s.s. flow-through reactor (residence time 0.8 sec).

Figure II.2.3. Thermogravimetry (TG) and differential thermogravimetry (DTG) profiles of: (a) tire rubber; (b) 1:1 rubber/coal mix; and (c) hvb coal (Blind Canyon, DECS 17), sample obtained at a heating rate of 20 C min^{-1} in a helium atmosphere. Sample size: 5-10 mg range. For explanation see text.

Figure II.2.4. Summed IR spectra (a, b, c) and mass spectra (d, e, f) of the TG runs shown in Figure II.2.3. Note higher gas (CO₂, H₂O, CO in Figure c) and lower tar (Figure f). Yields of coal sample and intermediate behavior of 1:1 rubber/coal mixture.

Figure II.2.6. Total mass spectrometry intensity profiles (TIPs, Figures a-c) and selected intensity profiles (Figures d-o) of the three sample runs shown in Figures 3 and 4. Note early (240 C) evolution of naphthalenes in coal sample (Figure l). Further note excellent correspondence between CO₂ profiles in Figures II.2.5 m-o and II.2.6 m-o.

Project II.3

Catalytic Cracking, Hydrogenation and Liquefaction of Coals Under Mild Conditions

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OBJECTIVES

For this period, the objectives of our project were as follows: (i) Determination of the particle size distribution of Fe-based catalysts used by the Consortium researchers employing SQUID magnetometry and x-ray diffraction; (ii) Fabrication of the high temperature/high pressure apparatus for in-situ studies of the free radicals by ESR (Electron Spin Resonance) spectroscopy and hydrogenation studies of the Blind Canyon coal using in-situ ESR spectroscopy of the free radicals with and without a catalyst; (iii) Characterization of the iron-sulfide catalysts provided by the Chemical Eng. team using x-ray diffraction. The research tasks were divided along the lines of the objectives noted above.

SUMMARY OF RESULTS

(i) Objective/Task 1:

Research on the "determination of the particle size distribution in a Fe_2O_3 -based catalyst using magnetometry and x-ray diffraction" was completed and results submitted for publication in September 1991 to the Journal of Materials Research. The paper was accepted for publication in March 1992 after the normal review process and is now scheduled for publication in the July 1992 issue of the JMR. In this work, magnetization versus temperature (5°K - 400°K) and magnetization versus field (up to 55 kOe) data are reported for an $\alpha\text{-Fe}_2\text{O}_3$ based catalyst prepared by the team of Dr. Wender at the University of Pittsburgh and obtained through Dr. Huffman of the University of Kentucky. After determining the region of superparamagnetism, the distribution function $f(r)$ is determined assuming a log normal distribution and Langevin paramagnetism of superparamagnetic particles. The distribution is found to be fairly symmetric with mean radius of the particles

near 65 Å and range of 35 to 115 Å. From line broadening of the Bragg peaks in x-ray diffraction, particle radii varying between 75 Å and 110 Å are obtained. The Mössbauer measurements of Huffman et al on the same sample yielded the following results: 12% of the particles have <29 Å diameter, 45% of the particles have diameter from 29 Å - 85 Å, and the remaining 43% have diameters larger than 85 Å. Overall, the average particle size determined from the Mössbauer analysis is somewhat smaller and that determined from x-ray diffraction is somewhat larger than the average determined from the magnetic studies. Of the three techniques, only the magnetic studies provide a particle size distribution, although the assumption of spherical particles is made in the analysis. In any case, the fact that the three techniques have provided reasonably similar results for the particle size of this catalyst is considered to be an important contribution of this work. Details are available in the paper by M. M. Ibrahim, J. Zhao and M. S. Seehra, *J. Mater. Res.* Vol 7, No. 7 (July 1992).

A second sample of α -Fe₂O₃ provided by Dr. Huffman was analyzed by x-ray diffraction and SQUID magnetometry. In Fig. 1, we show the x-ray diffractogram of this '30 Å' sample. Since only two of the lines of α -Fe₂O₃ are observed, it is quite likely that the material is not quite crystalline. From the widths of the (110)/(104) and (214)/300 lines, we find particle diameter $L \approx 14$ Å and 10 Å respectively for the undried sample and $L \approx 14$ Å and 22 Å respectively for the dried sample. It is evident that drying has resulted in some agglomeration. The magnetic studies revealed that the particle is not superparamagnetic and hence these studies could not be used for particle size determination.

(ii) Objective/Task 2:

Fabrication of a microwave cavity system for in-situ high pressure/high temperature ESR spectroscopy studies of free radicals in coals and coal conversion processes was completed. With this apparatus, ESR studies can be carried out from ambient to 500°C and for gaseous pressures up to 800 psi (1 MPa $\approx$ 145 psi) at x-band frequencies ($\approx$ 9 GHz) and ESR signals can be monitored as a function of time, temperature or pressure in the above stated ranges. As shown in Figs. 2, 3, 4, this system consists of three primary units: A heating unit and a quartz dewar (which is inserted into the TE₁₀₂ cavity for thermally isolating the cavity body from the sample heated to high temperatures), a high pressure unit to which a pyrex ESR tube is attached which in turn can be inserted into the quartz dewar inside the cavity, and a flow chamber unit which replaces the high pressure unit if

experiments in flowing gases (N_2 , H_2 , Ar) instead of high pressures are to be carried out. In this apparatus, the cavity remains at ambient temperature and pressure whereas the inside of the ESR tube can be exposed to pressures up to 800 psi and temperatures up to 500°C. To attain pressures higher than 800 psi, a stronger material than quartz or pyrex for the ESR tube is needed. The gage connected to the ESR tube enables us to read the pressure in-situ and pressure can be changed during an experiment. These versatile features are important new contributions of this design.

A number of experiments on the hydrogenation of a Blind Canyon coal (DECS-17 and obtained through the courtesy of the Penn State Coal Bank) have been carried out using the above apparatus, with and without the Shell 324 catalysts ($NiMo/Al_2O_3$). The catalyst was obtained through the courtesy of Dr. Brandes at Consolidated Coal Co and in our experiments, the catalyst was dry mixed with the coal in a mortar and pestle in the ratio of 2.1% by weight of the coal. X-ray diffraction studies of the catalyst showed that Al_2O_3 particle diameter is about 40 Å. The free radical density N is calculated by double integration of the derivative ESR spectra using an online computer and comparing it with a standard. Also $N = N_T(T/RT)$ [where N_T is the measured value at temperature T (°K) and RT = room temperature (°K)] is used to correct for the Curie-law variation of N_T . A plot of N versus T will be a horizontal line if there is no change in the free radical density.

In Fig. 5, we have plotted N vs T for the Blind Canyon coal under the conditions of vacuum-sealed, N_2 flow and H_2 flow and the data have been corrected for any mass changes from separate thermogravimetric experiments. In Fig. 6, we show the data under H_2 flow, with and without the shell 324 catalyst. These experiments show that presence of hydrogen reduces N above 400°C and in the presence of the catalyst, additional cracking mechanisms are operative resulting in an increase in N .

Since most of the experiments in direct coal liquefaction are carried out above 400°C and in H_2 pressures we studied the variation of N versus pressure at a fixed temperature of 440°C. As noted earlier, an important feature of our apparatus is that the pressure can be varied in-situ. The results of N vs pressure (H_2 , Ar), with and without the 324 catalyst, are shown in Fig. 7. We used Ar gas suspecting that N_2 gas may not be quite inert. However later experiments showed no variation of N with N_2 gas either. It is observed that in H_2 pressure, there are significant changes in N . For coal alone, N decreases nearly linearly

with initial H_2 pressures, approaching saturation above 400 psi. For the catalyst loaded coal sample, the results are different in that N is higher, initial H_2 pressures slightly increase N, followed by a near linear decrease above 150 psi and no saturation. From these experiments it is quite evident that molecular H_2 caps at least some of the free radicals, whereas in the presence of the 324 catalyst, an additional mechanism for the generation of free radicals is operative. The results of Fig. 7 are the first such results in literature where a systematic variation of N with H_2 pressures has been documented. These results will be presented at two forthcoming ACS meetings and a manuscript has been submitted for publication in the ACS Division of Fuel Chemistry Preprints. Further discussion of the results is presented in this paper.

Objective/Task 3:

Under this task, we analyzed about a dozen samples of iron-based catalyst by x-ray diffraction for their chemical components. An example of this work is shown in Fig. 8 where an iron-sulfide sample prepared at three different temperatures shows different amounts of sulfur, pyrite and pyrrhotite. These catalysts have been used by Dr. Zondlo and his collaborators for coal liquefaction studies.

PUBLICATIONS/PRESENTATIONS

1. M. M. Ibrahim, J. Zhao and M. S. Seehra; Determination of particle size distribution in an Fe_2O_3 -based catalyst using magnetometry and x-ray diffraction, J. Mater. Res. Vol. 7 (July 1992).
2. M. M. Ibrahim and M. S. Seehra: An apparatus for in-situ high temperature/high pressure ESR spectroscopy and its application in coal conversion studies, ACS Division of Fuel Chem. (submitted for publication). A talk on this work will be presented at the September 1992 meeting of ACS in Washington, D.C.
3. M. M. Ibrahim and M. S. Seehra, Catalytic hydrogenation of Blind Canyon coal studied by high temperature/high pressure ESR spectroscopy, to be presented at the ACS meeting (Colloid and Surface Chemistry) in June 1992 to be held in Morgantown, WV.

Figure 1: X-ray diffractograms of bulk Fe_2O_3 , and the '30Å sample' before and after drying.

Figure 2: Block diagram of the high temperature dewar for ESR cavity

Figure 3 : Block Diagram of the high pressure set up fabricated for in-situ experiments up to 800 psi of any gas and up to 500 °C

Figure 4 : Diagram of the flow chamber used for experiments under flowing gas.

Figure 5: Variation of N with T for blind canyon coal. Plot after applying mass correction is shown in the insert.

Figure 6: Variation of N with temperature for blind canyon with and without shell catalyst 324, in hydrogen flow. The values of N are corrected for the change in mass from TG data.

Figure 7: Variation of N with argon/hydrogen pressure for blind canyon coal with and without the shell catalyst 324.

Figure 8: X-ray diffractograms of FeS sample. (1-pyrite, 2-pyrrhotite, s-sulfur)

ESR and ENDOR Investigation of the Role of Free Radicals in Coal Liquefaction Under Mild Conditions

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West Virginia University

I. INTRODUCTION

This annual report summarizes our research activities during May 1, 1991 through April 30, 1992. The work carried out during this period was an extension of earlier investigations aimed at understanding the role of free radicals in the chemical pathways of coal liquefaction under mild, catalytic as well as noncatalytic, conditions. As in our earlier studies⁽¹⁾, we utilized ESR and ENDOR techniques because these are the most direct and unambiguous methodologies for characterizing free radicals⁽²⁾. As proposed, the focus of our subtask was to investigate free radical generation from a wide variety of ring-substituted organic compounds.

Our specific goal was to identify the charge on the radical species, i.e., whether the free radical was a neutral, anionic, or cationic species. As discussed in detail in our earlier reports, it is important to develop an experimental methodology for identifying charge on radicals involved in liquefaction reactions because various experimental studies by Farcasiu and Smith^(3,4) have indicated that the radicals involved are probably cations. This conclusion has been supported by molecular orbital calculations by Subbaswamy at the University of Kentucky⁽⁵⁾ as discussed at the 1991 CFFLS Technical Meeting held at Lexington⁽⁶⁾. We therefore initiated a program of assembling an atlas of EPR spectra of different free radical species generated from aromatic compounds that are considered model compounds for many coal liquefaction reactions.

Another significant study undertaken was the measurement of free radical generation by thermal heating of selected chars, and corresponding measurement of their spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2). These measurements were undertaken

in collaboration with the Utah NMR group headed by Pugmire. These authors reported very short NMR T_1 data on these same chars⁽⁷⁾. The ESR measurements clarify the role of polarization transfer via the electronic spin-dipolar interaction.

Additionally, free radical and iron coordination measurements were conducted on a Buelah Zap coal sample that had been subjected to the Shabtai liquefaction process. The goal here was to detect the presence of covalent bonding with the Fe^{3+} ion generated by the addition step of FeCl_3 utilized in the Shabtai treatment.

II. EXPERIMENTAL TECHNIQUES AND DATA ANALYSIS METHODOLOGIES

All ESR measurements were made at the X-band (9.5 G Hz) microwave frequency utilizing a Bruker ESR / ENDOR spectrometer system. The system has an accessory for carrying out in-situ ESR measurements at temperatures up to 800°C. For accurate measurements, the magnetic field is calibrated with a self-tracking NMR gaussmeter while the microwave frequency is measured with a digital frequency counter, Hewlett-Packard, model 5430A. For liquid samples, the radicals were produced via reaction with triflic acid or a sodium / potassium reaction. The radicals were identified by measurements of their hyperfine couplings, and comparison of the measured spectra with those simulated on a Bruker microcomputer using laboratory-developed ESR / ENDOR data collection and simulation programs.

For the relaxation time measurements, a lineshape saturation technique was utilized for determination of the relaxation times of electron spin state in Utah coal chars provided by Dr. Ron Pugmire of the University of Utah. In this technique, the compound is subjected to different microwave power levels while the area of the ESR transition peak is monitored. Under saturation conditions, an increase in power causes either no increase or a decrease in signal intensity. This behavior is described by the modified Bloch equations which provide that:

$$\gamma^2 H^2 T_1 T_2 \approx 0.5 \approx \text{s}^{-1}$$

$$T_2 = \frac{2}{\sqrt{3}\gamma\Delta H_{pp}^0} = \frac{1.3131 \times 10^{-7}}{g\Delta H_{pp}^0}$$

$$T_1 = \frac{\sqrt{3}\Delta H_{pp}^0}{2\gamma} \left(\frac{s^{-1} - 1}{0.25H_1^2} \right)$$

III. RESULTS

We generated both cationic and anionic radicals from 21 model compounds, as reported earlier⁽¹⁾. Figure 1 shows some representative ESR spectra. These spectra are too complex for direct ESR analysis. Therefore, ENDOR measurements are currently being carried out to assign the splittings.

In order to verify the accuracy of free radical generation and the analysis procedure, we generated cationic as well as anionic species of the polyacenes: anthracene, tetracene, and pentacene. The cations were generated via reactions in triflic acid whereas the anions were produced through alkali-metal reductions. The spectra yielded the following set of coupling constants (in Gauss):

Molecule	Position	Cation	Anion
Anthracene	9	6.6	5.3
	1	3.0	2.7
	2	1.4	1.5
Tetracene	5	5.0	4.0
	1	1.8	1.5
	2	1.0	1.1

The ESR spectra of the pentacene cation and anion radicals were too complicated to analyze. We are currently attempting to measure the ENDOR spectra of these radicals. In the ENDOR measurements, we expect to observe eight transitions, as compared to the 375 poorly resolved transitions found in the EPR spectra. The same procedures will be utilized to analyze the EPR spectra of anion and cation species from 21 other compounds. The compiled results will be used to identify complexes expected from radical species found in

coal.

III.2 RELAXATION BEHAVIOR OF CHARS

Figure 2 shows the ESR saturation behavior of two Utah chars, one heated at 200°C and one heated at 500°C. As is seen in Figure 1, the lower temperature char shows the saturation effect while the high temperature char does not. This implies that the 200°C char is a more suitable candidate for the ENDOR technique. It implies that this ESR transition, which will be probed via the ENDOR technique, can establish a suitable spin population difference for the detection of strong ENDOR response. It does not imply, however, that the 500°C char is incapable of saturation - only that at room temperature, the 200°C char is a more suitable ENDOR candidate than the 500°C char. Solution of the modified Bloch equations provides T_1 values of $\approx 10\text{ms}$ for the 200°C char and $\leq \mu\text{s}$ for the 500°C char, in reasonable agreement with the data from the Utah NMR group.

Figure 3 shows the variation in linear scale peak area versus the $\log_{10}$ scale microwave power. As is clearly seen, the integrated area for the 500°C and 600°C chars increase with respect to the $\log_{10}$ scale microwave power. However, the 200°C char appears to possess a flat plot of integrated area with respect to the $\log_{10}$ scale microwave power: this implies that the 200°C char is easily saturated and therefore, ENDOR can be easily performed. Chars examined were: ambient, 200°C, 300°C, 400°C, 500°C and 900°C, with saturation behaviors linearly consistent with heating (*i.e.*, 200°C char most saturable and 900°C char least saturable).

III.3 ESR CHARACTERIZATION OF BUELAH ZAP COAL

Figure 4 shows a typical spectrum of Buelah Zap coal. The broad line around 3000 G corresponds to an iron peak whereas the sharp peak in the center of the spectrum is clearly due to organic free radicals usually present in coal. An expanded version is shown in Figure 5.

IV. SUMMARY

A methodology was developed for generating anionic and cationic radical species of 21 ring-substituted organic compounds considered to be model compounds for investigating coal

liquefaction. ESR spectra were obtained for each compound. However, the ESR spectra for several compounds were too complex for direct analysis. Subsequently, ENDOR measurements are being undertaken for help in their analysis.

The spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) were measured for free radicals in several chars being investigated by the Utah (Pugmire) group via solid state NMR. These results are expected to be used to help better understand some of the Utah group's NMR relaxation data on coals and chars.

ESR measurements detected covalently bonded iron and organic free radicals in Utah coals subjected to the Shabtai liquefaction treatment. These results are considered to be relevant to the underlying chemistry of the Shabtai process.

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Figure Captions:

- Fig. 1 ESR Spectra of Anthracene, 9-Carboxylic Acid and 1,3-Dihydroxynaphthalene Radicals.
- Fig. 2 Saturation Effect in Chars.
- Fig. 3 Peak Area Versus Microwave Power (Log Scale) for Selected Chars (others omitted for clarity).
- Fig. 4 ESR Spectrum of Buelah Zap Coal Particles.
- Fig. 5 ESR Spectrum of the Free Radical in Buelah Zap Coal.

Fig. 1 ESR Spectra of Anthracene, 9-Carboxylic Acid and 1,3-Dihydroxynaphthalene Radicals.

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Fig. 4 ESR Spectrum of Buelazap Coal Particles.

Fig. 5 ESR Spectrum of the Free Radical in Buelazap Coal.

Project II.5

Surface Characterization of Catalysts and Catalyst Impregnated Liquefied Coal Residues

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University of Pittsburgh

Introduction

Highly dispersed forms of certain catalysts have been found 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] Since the surfaces of catalysts are the primary site of catalytic activity, efforts have been directed to characterizing catalyst surfaces in recent studies that have been carried out in the CFFLS program. In the last period, the studies have been focused on several new catalysts that have been developed at the University of Pittsburgh and a project has also been initiated to determine the surface and interface characteristics of catalyst impregnated Blind Canyon coal residues.

X-ray photoelectron spectroscopy (XPS) has been used to study the surface characteristics of three catalysts and catalyst ($\text{Fe}_2\text{O}_3/\text{SO}^{2-}_4$) impregnated liquefied Blind Canyon coal residues. This technique provides the surface elemental distribution and chemical information on the outermost 3-4 nm of the exposed solid surface. Preliminary characterization has shown that the concentration of elements at the outermost layer measured by XS is representative of that determined in the bulk by chemical analysis. Bulk analysis data will be available at a later date and a direct comparison will be made at that time.

XS was also employed to determine the oxidation states of major elements in each sample. Most elements showed the expected values for the most stable oxidation states.

1. Experimental

Three catalysts and catalyst ($\text{Fe}_{0.3}/\text{SO}^{2-}_4$) impregnated liquefied Blind Canyon co residues were used in the surface characterization studies. These samples were obtained from the University of Pittsburgh and the University of Kentucky, respectively. The powdered catalysts were examined in their as-received form. Their particle sizes were less than -100 mesh. The catalyst impregnated liquefied coal residues were obtained in liquid-like form and were kept in a vacuum oven at 65°C for 2 days to remove volatile materials in the residue without exposing to an air atmosphere. Experimental details have been described previously [5,6] and sample information is given in the next section.

2. Results and Discussion

2.1 Surface Characterization of Catalysts

2.1.1 Fe_7S_8

This is a presulfided sulfated iron oxide catalyst. It is essentially a pyrrhotite with Fe_7S_8 as the predominant phase. A representative XS wide-scan spectrum is shown in Figure 1. The spectrum shows distinct peaks for the major elements, iron, sulfur and oxygen. The C 1s peak was also observed in all catalysts and this can be ascribed to carbon contamination.

The binding energies of the carbon 1s and oxygen 1s peaks show the expected values with one photoline per element, while the sulfur 2p peak is split into two small background photolines at 170.8 eV and 164 eV, respectively. The higher binding energy photoline can be ascribed to the oxidized form of sulfur (sulfate) and the peak at 164 eV corresponds to inorganic sulfide. From the sample information, it appears that the low binding energy photoline represents inorganic pyrrhotite existing on the surface. The sulfur 2p spectrum is shown in more detail in Figure 2. Multiple splitting was also observed in the Fe 2p region. This is the result of spin interaction between an unpaired electron from the photoionization process and other unpaired electrons present in the system. In Fig. 3, the Fe 2p peak shows the characteristic 13.6 ± 0.05 eV splitting between the $2p(1/2)$ and $2p(3/2)$ peaks. The observed splitting corresponds well with the Fe 2p peak of Fe_2O_3 in model compound studies [7]. From the above results, it can be concluded that this catalyst surface shows the most stable oxidation states of these elements. To determine the relative concentrations of the various constituents observed in the surface of samples, peak area sensitivity factors have been employed as described before [6]. The

results are given in Table 1. The S:Fe ratio is somewhat higher than 8:7, presumably due to surface oxidation.

2.1.2 Pt/ZrO₂/SO₂-4 (SZD-17) and (SZD-7)

SZD-17: Zirconium hydroxide, presulfided with sulfate iron followed by impregnation with platinum salt. The sample was calcined at 600°C.

SZD-7: This sample was prepared in the same way as sample SZD-17, but exhibited low activity in coal liquefaction studies.

XS was also used to determine any differences in the surface chemistry of these two samples. No differences were observed in the wide scan spectra. The spectra showed the major elements, zirconium, sulfur, and oxygen as well as minor elements carbon and platinum. As mentioned earlier, SZD-7 exhibited low catalytic activity, but no major differences were observed in the quantitative analysis data as shown in Table 1. SZD-7 has about two thirds of the platinum concentration determined for SZD-17. This may be a reason for the lower catalytic activity obtained with SZD-7. Narrow scans of Pt, Zr and S were also carried out to determine the oxidation states. Each element showed the expected binding energy value for the most stable oxidation state. The observed spectra corresponded well with the standard Zr 3d peaks of ZrO₂ and the Pt 4f peak of PtO₂, for example. These results are shown in Figures 4 and 5, respectively. S 2p showed two photolines with binding energies of 170.5 eV and 164.4 eV. These peaks can again be ascribed to the oxidized forms of sulfur (sulfate) and inorganic sulfide, respectively.

2.2 Liquefied Blind Canyon coal residues with adding catalyst

During the liquefaction process, the highly dispersed forms of certain catalysts are believed to be very active in the conversion of coal to liquids. The studies have not as yet advanced sufficiently to allow a complete understanding of the effects of catalyst dispersion on the catalyst performance. However, in the preliminary studies it is important to determine the surface and interface chemistry changes of the catalyst impregnated coal residues during the liquefaction processing. Some preliminary results have been obtained on this topic during the recent period.**

Liquefaction conversions were carried out at 400°C with tetralin as solvent (1:1.5 coal/solvent ratio) after adding Fe₂O₃/SO₂-4 to Blind Canyon coal. Three samples were obtained from the liquefaction residues under different reaction conditions after 17, 30, and 60 min. at 400°C. No chemical element changes were observed in the qualitative

analysis. Small changes were observed in the concentration of certain mineral elements in the quantitative analysis, however. As the reaction time increased for example, the concentrations of Al and Si generally decreased. This indicates that the mineral elements are being reduced in concentration at the residue particle surface as the liquefaction process proceeds. The quantitative results showed similar surface concentrations of elements to those that were obtained previously from the Blind Canyon coal [8]. Fe and S from the catalyst were not observed on the surface of the residues indicating that these elements are in the bulk of the particles. The results are shown in Table 2.

XS depth profiling analysis will be employed in future studies to determine if there are any differences produced in the distribution of the catalyst components as the liquefaction reactions proceed. These studies are currently in progress.

** These studies have been conducted in collaboration with Dr. M. Taghiei, University of Kentucky.

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Table 1. XPS Analysis (at %) of Catalysts (U. of Pittsburgh)

Catalyst	C	O	S	Fe	Zr	Pt
Fe ₇ S ₈	44.6	37.2	10.4	7.8		
SZD-17	19.4	36.1	11.3		32.9	0.3
SZD-7	13.6	39.2	11.6		35.4	0.2

Table 2. XPS Analysis (at %) of Liquefaction Residues with Catalyst

Sample	C	O	N	S	Al	Si
17 min.	83.2	10.8	1.0	0.7	2.5	1.8
30 min.	84.2	10.0	0.7	0.7	2.6	1.8
60 min.	87.1	10.0	0.9	0.6	0.9	0.5

Figure 1. Representative XPS wide scan spectrum for Catalyst Fe₇S₈

Figure 2. XPS S 2p spectrum for Catalyst Fe_7S_8

Figure 3. XPS Fe 2p spectrum for Catalyst Fe₇S₈

Figure 4. XPS Zr 3d spectra for Catalysts SZD-17 (High Activity) and SZD-7 (Low Activity)

Figure 5. XPS Pt 4f spectra for Catalysts SZD-17 (High Activity) and SZD-7 (Low Activity)

Project II.6

Computational Chemistry of Model Compounds and Reaction Pathways of Relevance to Coal Liquefaction

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During the 1991-92 contract year the main focus of our work was the study of possible mechanisms for the catalytic cleavage of bonds in the model compounds studied by Farcasiu and coworkers and other members of this Consortium. Specifically, we studied the radical cation, radical hydrogen transfer, and protonation mechanisms as possibilities. We also spent a fraction of the time on initiating the study of Fe-S catalytic systems.

A. Radical Cation Mechanism

Farcasiu and coworkers have reported ([1]-[3]) on a series of model compounds (listed in Table 1) which have structural similarities to molecular fragments found in coal. Their experiments suggest that the presence of polycyclic condensed aromatic rings in a molecule makes its reactivity toward one-electron transfer reactions dramatically different from the reactivity of similar structures containing only monocyclic aromatic (benzenic) rings. In particular, Farcasiu, et al. find that the reactivities of compounds I-IV and VIII (see Table 1 for labels) are substantially increased in the presence of carbon black over the temperature range 350-410C and that the selectivity of the catalytic reaction is overwhelmingly in favor of the cleavage of the bond between the naphthyl (or polyaromatic) ring and the adjacent aliphatic carbon. Based on more detailed experiments on compound I, and the fact that the carbon black catalyst becomes positively charged at temperatures over 320C, they suggest that the catalytic process might proceed via the removal of an electron from the naphthyl portion of the compound.

The formation of radical cation intermediates is an important pathway in many organic reactions in the gas and liquid phase. However, bond fragmentation is not the only possible reaction pathway. Other common reaction pathways are [4] back electron transfer, deprotonation from the position alpha to the site of the radical cation, and nucleophilic addition. Most reactions involving radical cation intermediates studied have been compounds related to a bibenzyl backbone.[5] There are no universal rules to determine the preferred reaction pathway. Further, knowledge of cleavage products in the gas phase does not necessarily help predict the outcome of reactions in solution, let alone a heterogeneous catalytic process involving a solid surface.

For the first of these model compounds, 4-(1-naphthylmethyl) bibenzyl, we earlier carried out semiempirical quantum chemical calculations to elucidate the reaction mechanism.([6]-[8]) One of the methods studied (ASED-MO), a version of the extended Hückel method originally due to Anderson,[9] gave results in qualitative agreement with the experimental results. We have now extended these calculations to the remaining model compounds to see if any general trends can be detected. We also performed calculations by the AM1 method[10] using the MOPAC program developed by Stewart.[11]

The details of our calculational procedures are given in [6]-[8]. In Tables 2 and 3 we show the bond dissociation energies calculated by the ASED-MO and AM1 method respectively, for the neutral model compounds. Since the effect of the carbon black is thought to be the removal of an electron from the reactant, we have done bond dissociation energy calculations also for the positive radical ion formed from the compounds. The results are shown in Table 4 for the molecules without inversion symmetry.

The ASED-MO results indicate that a certain degree of selective catalytic action is present in all cases, in general agreement with the experimental trends. Further, the ASED-MO results suggest certain other trends. For the neutral molecules, bonds whose scission results in two methylaryl radicals are easier to break than those that yield one methylaryl and one aryl or one ethylaryl and one aryl radical. Upon formation of the radical cation, the aryl-aliphatic carbon bond is weakened more than other bonds.

For the molecules with inversion symmetry, certain additional assumptions are needed within our method since the electron removed is not localized to one moiety. We were also interested in seeing if the conclusions drawn from the study of model compounds could be extended to the fragment of the Shinn model [12] we had studied previously. We performed calculations using the procedures previously described. The results are summarized in Table 5, with bond labels shown in Figure 1. We find that the bond adjacent to the polycyclic aromatic ring is easiest to break both in the neutral molecule and in the positive radical ion. The unexpected cleavage of the bond adjacent to the polyaromatic group for the neutral species can be attributed to an unfavorable interaction of neighboring hydrogen groups.

Thus, we find that a semiempirical method, ASED-MO, gives results in qualitative agreement with experiments on the selective heterolytic catalytic action of carbon black for the cleavage of bonds in the model compounds discussed. We find that bonds whose scission leads to the formation of two arylmethyl radicals are the weakest in such model compounds in the neutral state. Formation of a radical cation (as is expected to happen in the presence of the carbon black) leads to a relatively strong reduction of the dissociation energy for the bond that results in the formation of a polycyclic condensed aromatic cation as one of the fragments. Clearly, more experimental and theoretical investigations are needed before the mechanism can be determined definitively.

B. Radical Hydrogen Transfer

Radical hydrogen transfer (RHT) ([13]-[15]) has recently been shown to be a viable explanation for the cleavage of strong bonds in coal related compounds, and thus needs to be considered as a possible mechanism for the cleavage of the bond adjacent to the naphthyl ring in the compounds studied by Farcasiu, et al. In this context we performed AM1 quantum chemical calculations to test whether the RHT mechanism can account for the experimental results observed.

We tested this mechanism with Model I. Since we are interested in relative energies of hydrogen transfer from the solvent radical to different positions in the same substrate, we believe that the activation energy for the transfer can be approximated by allowing a hydrogen atom to approach the molecule, rather than as a transfer from the solvent derived radical. The steps involved this process as modeled in our calculation are

illustrated in Fig. 2. A hydrogen atom (labeled H) is allowed to approach Model I towards each of four different positions (labeled 1 through 4); the barrier (E1) for hydrogen addition is computed. The resulting complex is optimized, and the energy (E2) released in the formation (compared to isolated H atom and Model I) is calculated. The activation energy (E3) for the cleavage of the relevant C-C bond, and the dissociation energy (E4) of the C-C bond are also calculated.

Our results for the four energies for hydrogen transfer to the various positions are shown in Table 6. The second step in RHT, namely the cleavage of the ipso bond of the radical complex, is generally the fast step.[15] Then, the barrier height for the first step i.e., E1, should control the final product distributions. The relative product distributions calculated on this basis are also shown in Table 6. As modeled here, RHT does not explain the experimentally observed product distribution.

C. Protonation

Another possibility for the catalytic cleavage of the bond adjacent to the naphthyl group is the protonation of the naphthyl ring followed by subsequent breaking of the relevant bond.

In order to model this protonation process, the Model I-H⁺ system was studied with the AM1 method. The proton is so reactive that we were unable to determine barrier heights as in the RHT studies. However, we were able to calculate the heat of formation and the C-C bond cleavage energies of the protonated bonds of the Model I-H⁺ complex which are listed in Table 7. The relevant bond labels are given in Figure 2. As expected, position 1 displayed the greatest thermodynamic stability upon protonation. However, bond b (protonation at position 2) displayed the lowest energy for C-C cleavage. The bond selectivity found in the experimental Model I studies is not reproduced by our calculation based on protonation.

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No.	Structure
I	
II	
III	
IV'	
VII	
VIII	

Table 1: Model compounds studied in this work. Designations are the same as Farcasiu, *et al.*,³ except for IV' and VIII.

Bond	Bond Dissociation Energy (eV)			
	ASED-MO		AM-1	
	neutral	radical cation	neutral	radical cation
a	4.28	3.82	3.85	-
b	3.79	3.21	2.66	-
c	3.52	2.47	3.35	-
d	3.81	2.67	3.46	-

Table 5: Bond dissociation energies of the fragment of the Shinn model studied. The +1 charge is placed on the fragment containing the phenanthrene moiety.

Position	E_1	E_2	E_3	E_4	%Distribution
1	0.53(0.57)	1.62(1.55)	1.28(1.30)	0.65(0.59)	9
2	0.44(0.51)	1.33(1.41)	1.22(1.21)	0.39(0.48)	42.3
3	0.44	1.42	1.36	0.52	42.3
4	0.55	1.35	1.29	0.51	6.4
bibenzyl	0.41	1.33	1.34	0.50	

Table 6: Activation barriers (E_1), bond formation energies (E_2), dissociation energy barriers (E_3), and bond cleavage energies (E_4) for radical hydrogen transfer. Energies are reported in eV's. See Figure 2 for bond labels. The numbers in parentheses refer to energies for the approach path from the other side of the molecule, when different. The percent distributions are given for the lowest energy approach path only.

Bond	Formation Energy(eV)	Bond Cleavage Energy(eV)
1(a)	2.92	0.91
2(b)	2.68	0.55
3(c)	2.72	1.91
4(d)	2.40	1.09

Table 7: Bond formation and dissociation energies for protonation of Model I calculated by the AM1 method.

Bond	ASED Dissociation Energy (eV)					
	I	II	III	IV'	VII	VIII
a	4.09	4.22	4.12	4.24	4.16	4.16
b	3.89	3.68	3.73	3.96	3.90	3.95
c	4.23	4.13	4.12	4.08	4.16	4.07
d	3.77	4.10				
e	4.18	4.01				

Table 2: Bond dissociation energies of the model compounds shown in Table 1 calculated by the ASED-MO method.

Bond	AM1 Dissociation Energy (eV)					
	I	II	III	IV'	VII	VIII
a	3.80	3.88	3.87	3.85	3.92	3.82
b	3.82	2.97	2.92	2.93	3.00	2.98
c	3.93	3.93	3.80	3.27	3.92	3.27
d	3.01	3.88				
e	3.93	3.88				

Table 3: Bond dissociation energies of the model compounds shown in Table 1 calculated by the AM1 method.

Bond	Bond Dissociation Energy (eV)							
	ASED-MO				AM-1			
	I	II	IV'	VIII	I	II	IV'	VIII
a	2.80	2.93	2.94	2.81	4.18	4.20	4.28	5.57
b	3.08	2.86	3.12	3.15	2.63	1.74	1.81	1.85
c	3.01	3.34	3.27	3.29	4.39	3.27	3.38	2.77
d	3.00	2.87			1.90	4.37		
e	3.40	3.24			3.43	2.78		

Table 4: Bond dissociation energies of the positively charged radical ions formed from the asymmetric model compounds shown in Table 1, calculated by the ASED-MO and AM1 methods. The +1 charge is always placed on the naphthyl fragment

• Figure 1. The portion of the Shinn model studied. The bonds whose cleavage energies were determined are indicated.

• Figure 2. The addition of a hydrogen atom (A), the Model I-H radical conformation (B), and the cleavage products (C) for the radical hydrogen transfer in (1-naphthylmethyl)bibenzyl. The aromaticities of the ring systems are shown.

Project II.7

Chemical Characterization and Hydrogenation Reactions of Single Coal Particles

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During this reporting period, we have devoted our efforts to chemical characterization of single coal particles, and the development of a technique for deposition of catalyst particles on single coal particles. For chemical characterization we have used Raman spectroscopy. The intensity of inelastically (i.e., Raman) scattered light from a microdroplet is very low. Therefore, detection 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 require 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 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 focal length beneath the particle but above the large focusing lens. 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. Using the experimental setup we have obtained Raman spectra in the range 400 cm^{-1} to 4000

cm^{-1} from coal particles in the size range 10 to 20 μm . The background counts without particles in the presence of the laser beam varied from 10 to 20 cps. In the Raman active region the counts as high as 1800 photons/s were 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 from Raman spectra.

For deposition of catalyst particles on single coal particles, we have devised an experimental system for suspending a single particle in a stream of small particles. The schematic of the experimental system is shown in Figure 1. An electrodynamic balance is mounted between two tubes whose ends are tapered to facilitate flow development and particle stream exit. The particle stream is generated from a volatile liquid containing a suspension of desired particles. Air enters a constant output atomizer generating a fine particle stream. The stream passes through an evaporation conditioner where the volatile liquid is evaporated. From the conditioner, the particle stream enters a packed stripping column where the volatile component is removed by water flowing down the column. The stripped particle stream is then fed into an electrostatic classifier where particles of a desired size are extracted based on their electrical mobilities. The extracted particle stream is then split into two parts: one part flows into a condensation nucleus counter (CNC) and the other part enters through the bottom of the balance and flows past the collector droplet. The stream leaving the balance is fed into an electrometer. The CNC and electrometer provide the number density of particles in the gas stream. We have tested the system with 50 to 100 $\text{\AA}$ DOP droplets depositing on single DOP droplets suspended in the electrodynamic balance. In a typical experiment a DOP droplet was captured in a stagnant environment inside the balance by adjusting the a.c. voltage and its frequency. The a.c. voltage ranged from 1000 V to 1500 V with a frequency range of 50 Hz to 200 Hz. The droplet was then positioned at the center of the balance by adjusting the d.c. voltage across the endcap electrodes. The laser was then scanned over about 15 nm wavelength (585 nm to 600 nm) in steps of 1000 MHz ($\approx 10^{-2}$ $\text{\AA}$) intervals and the intensity of scattered light as a function of wavelength was recorded in the computer. Wavelengths of the sharp peaks (resonances) observed in the intensity spectrum were determined using a software program. The wavelengths of the resonance were further determined with higher accuracies, using shorter, high resolution scans with 250 MHz ($\approx 3 \times 10^{-3}$ $\text{\AA}$) interval between data points. After the short scans, the aerosol

stream of desired flowrate was passed through the balance. The d.c. voltage needed to maintain the collector droplet in the presence of the aerosol stream was recorded for the velocity determination. After a predetermined period (about 20 minutes) the flow was halted, and the balancing d.c. voltage was recorded. A series of high resolution short scans were taken to determine the shifts in the wavelengths of the intensity peaks due to the deposition of aerosols on the collector droplet. The results show that the amount of particles depositing can be controlled by controlling the number density of particles in the gas stream, exposure time and velocity of the stream.

Project II.8

Liquefaction Pathways

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INTRODUCTION

There are a number of papers in the liquefaction literature describing the mechanism(s) of the conversion of coal to products. Most of the work utilizes solubility classes to define the thermal and catalytic reaction pathways as a set of series and/or parallel reactions. An approach taken by CAER has been to lump the product solubility classes into the following groups: (a) asphaltenes plus preasphaltenes (A+P), (b) oils plus gases (O+G), and (c) insoluble organic matter (IOM). These lumped parameters were plotted on a Wei-Prater diagram to define the liquefaction pathway of the coals studied.

In the initial work, only single residence time data (15 min.) for three reaction temperatures (385°C, 427°C and 445°C) were plotted on the Wei-Prater diagram (Figure 1). The results from this body of work suggest that the coals have a common liquefaction pathway. This observation was verified using a number of residence times and reaction temperatures for the liquefaction of a single coal. The reaction conditions were chosen in order that the entire range of conversions possible for the coals were obtained. The data from these experiments verified the liquefaction pathway that was suggested by the single residence time data (Figure 2).

In the initial stage of the pathway, the primary reaction is the conversion of coal (IOM) to the A+P intermediates. In this stage of the pathway, the O+G yields remain fairly constant. The second stage of the liquefaction pathway begins upon reaching a maximum coal conversion (and A+P yield). The primary reaction taking place in the second stage of the pathway is the conversion of A+P to O+G. Coal conversion remains fairly constant in this stage of the pathway. All of the high volatile bituminous coals exhibited this pathway during thermal liquefaction.

In an attempt to circumvent the observed maximum in the intermediate A+P yields prior to the increase in the production of oils, a number of catalyst and solvents

with different hydrogen donor abilities were investigated. The results of these experiments indicated that the catalytic pathway was similar to the thermal liquefaction pathway (Figure 3). The addition of the catalysts only increased the rate of reaction and had no major effect on the selectivity.

It would be of economic importance to find a way to circumvent the observed A+ yield in such a manner as to increase the yield of oils parallel to the increase in coal conversion. The objective of this project was to investigate additional methods to change the observed thermal and catalytic liquefaction reaction pathway through study of the conversion data for the asphaltene and preasphaltene intermediates.

EXPERIMENTAL

To accomplish the objectives of this project, a large amount of coal-derived asphaltenes and preasphaltenes was required. The products available from the Wilsonville plant are generated through catalytic conversions and may therefore not be representative of the thermally produced asphaltenes and preasphaltenes. These intermediates were produced by the liquefaction of a Western Kentucky #9 coal and heavy petroleum resid. The petroleum resid was analyzed and found to be 100% (wt.%) oils as defined by Soxhlet solubility extraction. It was assumed that processing the petroleum resid produced no asphaltenes and preasphaltenes. Therefore, the asphaltene and preasphaltenes obtained in the liquefaction experiments were coal derived. The analysis of the Western Kentucky #9 coal is given in Table 1.

The generation of the intermediates, asphaltenes and preasphaltenes, was accomplished using the CAER 1/8 tpd pilot plant. The plant was modified to include a 1 liter CSTR reactor instead of the ebullated bed reactor. The slurry feed system, gas delivery system and the high and low pressure separators were used in their current configuration. A simplified process diagram is shown in Figure 4. A 30 wt.% coal slurry was processed using a number of conditions (Table 2) on an around-the-clock basis. The solubility class distributions of the products are also given in Table 2.

The asphaltenes and preasphaltenes were separated from the total reactor product by Soxhlet extraction. Asphaltenes were defined by their solubility in benzene and their insolubility in n-pentane. Preasphaltenes were defined by their solubility in pyridine and their insolubility in benzene. The intermediates required several extractions to obtain

the desired purity (> 90 wt.%) for further study. For example, the initial separation of the asphaltenes yielded a product which contained 70 wt.% asphaltenes and 30 wt.% oils. Two additional separations resulted in an asphaltene fraction which was 99.3 wt.% asphaltenes (0.7 wt.% oils). Three different asphaltene and one preasphaltene fractions derived thermally were used as feedstocks for further liquefaction studies. The solubility class distributions of these fractions are given in Table 3.

The asphaltene and preasphaltene intermediates were reacted in 25 mL batch microautoclaves using a number of residence times (15-60 min.) and reaction temperatures (385°C, 427°C, 445°C), tetralin as the solvent, and a hydrogen atmosphere (800 psig, ambient temperature). The products of these runs were separated into their solubility classes by Soxhlet extraction.

RESULTS AND DISCUSSION

The liquefaction results using the three asphaltene feedstocks are shown in Figure 5. The lumping of the solubility classes for these runs are different from those used in the coal runs so that the reaction pathway of the intermediates can be followed. The oils plus gases were used as one of the lumped parameters, similar to the coal liquefaction runs. However, the asphaltenes were used as a separate parameter and the preasphaltenes and IOM were lumped together for these runs.

The thermal liquefaction pathway obtained for the asphaltenes derived from the 385°C total product, shown in Figure 5, was what was expected based on the data obtained from the coal liquefaction runs. The path defined from the products is a line nearly parallel to the axis indicating that the primary reaction is the conversion of the asphaltenes to oils plus gases. The oil fraction represents over 96% of the total lumped parameter (O+G) for all conditions studied. Therefore the major reaction of this asphaltene fraction is the production of oils, as expected. The fact that the line is not parallel to the axis is due to a small amount of preasphaltenes produced in the reactions, presumably due to retrogressive reactions.

The pathway defined for the asphaltene feedstock obtained from the 450°C total product is slightly different from the asphaltene feedstock obtained from the 385°C total product. In this case, the asphaltene initially produces a higher preasphaltene yield than the asphaltene feedstock from the 385°C product indicating a substantial amount of

retrogressive reactions are occurring. However, at higher thermal severities, the pathway parallels the one defined by the 385°C asphaltene feedstock. A similar pathway is obtained using the 70%/30 wt.% asphaltene/oil feedstock derived from the 450°C product. However, the amount of retrogressive reaction products (preasphaltenes) is significantly smaller than the pure asphaltene from the 450°C product.

The results were interpreted as follows. The asphaltenes thermally break down into reactive species. The reactive species can either be hydrogenated to form oils or they can repolymerize (retrogressive) to form, in this case, preasphaltenes and a minor amount of IOM. In the case for the asphaltenes separated from the 450°C derived product, the rate of retrogressive reactions is equal to or greater than the stabilization (hydrogenation) reactions. The presence of the oil fraction in the asphaltene/oil (70/30 wt.%) feedstock, appears to aid in the reduction of retrogressive reactions when compared to the pure 450°C asphaltene feedstock. Otherwise, we must conclude that the removal of the final 30% of the oil also caused transformations in the preasphaltene fraction. The asphaltene separated from the 385°C total product also shows a similar amount of retrogressive reactions occurring. At this point, there is insufficient data to suggest the causes in the reactivities of the three asphaltene feedstocks.

The thermal pathway defined for the preasphaltenes separated from the 385°C total product is shown in Figure 6. As can be seen, the preasphaltene path is significantly different from the corresponding asphaltene. As the conversion of the preasphaltene increases, both the asphaltene and the O+G yields increase until a maximum in the asphaltene yield is obtained. At this point in the pathway, the direction changes, similar to that observed for thermal liquefaction of the coal (Figure 2). The path indicates that the asphaltene yields decrease with an increase in the O+G yield. In this region, the conversion of the preasphaltenes increases slightly, also similar to the coal conversion pathway. If the coal conversion data is plotted in the same way as the intermediates presented in Figures 5 and 6 (soluble products only), a similar path to the preasphaltenes is obtained.

In the next set of experiments, a 50/50 (wt.%) mixture of asphaltenes (385°C) and preasphaltenes (385°C) was used as a feedstock. The pathway defined by this feedstock is shown in Figure 7. The resulting pathway is as expected based on the data obtained from the individual conversion data of the intermediates. The calculated solubility class

distribution of the mixture were very similar to the experimental distribution obtained for the asphaltene/preasphaltene feedstock.

SUMMARY

A large quantity of the coal liquefaction intermediate products, asphaltenes and preasphaltenes, were prepared and separated from the total reaction product of a Western Kentucky #9 coal and a heavy petroleum resid. Liquefaction of these intermediates indicate that the thermally defined pathways are similar to those observed in liquefaction of the bituminous coals previously studied.

Table 1

Coal Analysis

	AS DETERMINED	MOISTURE FREE	DRY AND ASH FREE	UNIT COAL (PARR)	
				DRY	WET
PROXIMATE ANALYSIS:					
MOISTURE	2.44				2.44
VOLATILE MATTER	38.30	39.26	43.37	42.32	41.15
FIXED CARBON	50.01	51.26	56.63	57.68	56.41
H-T ASH	9.25	9.48			
SULFATE SULFUR	0.01	0.01	0.01		
PYRITIC SULFUR	0.98	1.00	1.11		
ORGANIC SULFUR	2.01	2.06	2.28		
TOTAL SULFUR	3.00	3.08	3.40		
ULTIMATE ANALYSIS:					
CARBON	72.96	74.78	82.62		
HYDROGEN	5.49	5.35	5.91		
NITROGEN	1.62	1.66	1.83		
OXYGEN	7.68	5.65	6.24		
TOTAL CHLORINE	0.30	0.31	0.34		
BTU / LB	13210	13540	14958	15199	14780

FSI
7.0

PETROGRAPHIC ANALYSIS

MACERAL ANALYSIS:

	PSEUDO		SEMI			
VITRINITE	VITRINITE	FUSINITE	FUSINITE	MICRINITE	MACRINITE	EXINITE
81.2	3.2	6.1	3.4	1.0	0.7	4.0
RESINITE						
0.4						

VITRINITE REFLECTANCES:

MAXIMUM	MAX SD	MEAN	MEAN SD
0.774	0.039	0.706	0.057

VTYPE PERCENTAGES:

#6	#7	#8
4	60	36

Table 2

PIPU Process Conditions and Analysis of Products

Temperature (C)	450.00	385.00	385.00	385.00	385.00
Pressure (psig)	2000.00	2000.00	2000.00	2000.00	2000.00
Residence Times (min.)	26.00	40.00	41.00	44.00	40.00
Catalyst (Wt.%)				0.03 Mo	0.03 Mo
Gas (Wt.%)	0.77	0.09	0.12	0.05	0.06
Oil (Wt.%)	48.83	51.21	51.28	59.41	60.85
Asphaltenes (Wt.%)	19.80	18.10	17.74	15.21	17.66
Preasphaltenes (Wt.%)	3.60	6.60	6.86	7.33	7.43
Conversion (Wt.%)	73.00	76.00	76.00	82.00	86.00
H ₂ Consumption (Wt.%)	1.70	2.48	1.67	2.94	1.63
Mass Balance (%)	99.90	93.00	92.00	104.00	95.00

Coal = Kentucky #9

Solvent = Petroleum resid

Table 3

Solubility Class Analysis of the Thermally
Derived Asphaltenes and Preasphaltenes

	<u>Asphaltene (A-1)</u>	<u>Asphaltene (A-2)</u>	<u>Asphaltene (A-3)</u>	<u>Preasphaltene (P-1)</u>
Temperature (°C)	450	450	385	385
% Oils	31.5	99.3	94.3	0.0
% Asphaltenes	69.5	0.7	5.7	0.5
% Preasphaltenes	0.0	0.0	0.0	99.5
% IOM	0.0	0.0	0.0	0.0

Figure 1. Solubility class distributions for the liquefaction of bituminous coals using a single residence time (15 min.) and three temperatures (385°C, 425°C, 445°C).

Asphaltenes + Preasphaltenes
(wt.%, daf)

Residence
Time (min.)

Reaction
Temperature (°K)

598 658 700 718

2.5
5
10
15
20
30
40
60
90

a			
b	l	n	r
c			
d	j	o	s
e			
f	k	p	T
g			
h	l	q	
	m

Catalyst	Residence Time (min.)	Reaction . Temperature (°K)		
		658	700	718
Shell 324	5	I	N	R
Shell 324	15	J	O	S
Shell 324	30	K	P	T
Shell 324	60	L		U
Molybdenum Naphthenate	5	i		
Molybdenum Naphthenate	15	j	o	
Molybdenum Naphthenate	30	k		
Molybdenum Naphthenate	40	l		

Figure 3. Comparison of the catalytic pathway to the thermal (arrow) pathway of a Western Kentucky #6 coal.

Figure 4. PIPU reconfiguration for the production of the asphaltene

Figure 5. Thermal liquefaction pathway of the asphaltene intermediates.

Figure 6. Comparison of the thermal pathway of the asphaltene(385 C) and preasphaltene(385 C)

Figure 7. Thermal pathway of a 50 / 50 wt. % asphaltene/preasphaltene feedstock.

Project II.9

Development of Advanced Methods for Coal Liquefaction Product Analysis

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This research program has the goal of developing HPLC methods and techniques to separate coal liquids by hydrocarbon type. These separations would initially classify coal liquids by their content of saturate, aromatic and polar molecules. The aromatic fraction would be subdivided by aromatic ring size to distinguish one ring aromatics from others with two, three, four, five and more rings; the polar fraction would be separated by nitrogen and oxygen functional groups. This classification would provide information necessary to evaluate and understand coal liquefaction process chemistry.

Accomplishments

Since the onset of this project in May 1991, we have worked on separating the oil fraction of solvent separated coal liquids into saturate, aromatic and polar molecules. This is a difficult separation, in that HPLC columns that separate saturates and aromatics often irreversibly adsorb polar molecules so that they do not come off the column. On the other hand, HPLC columns that elute polar molecules do not resolve saturates and aromatics into their components so that all the non-polar molecules come off the column in a single peak. These problems have been solved by using three columns and a column switching valve so that both polar and aromatic molecules can be separated under optimum conditions.

The separation of an oil fraction on a DIOL column used for polar molecules is shown in Figure 1. Hexane and methylene chloride solvents were used for the separation. The uv detector trace shows that all of the aromatic molecules eluted in a single peak during the first 9 minutes when 100% hexane was used as the mobile phase. At 9 minutes, methylene chloride was added in a gradient at a rate of 5% per minute. Polar molecules came off the column with the addition of methylene chloride.

The separation of polynuclear aromatic standards on a DNAP column is shown in Figure 2. Again hexane and methylene chloride are used as the solvents as in the prior example. One and two ring aromatics eluted during the first 9 minutes when only hexane is used as the mobile phase. Introduction of methylene chloride caused the 3-ring (peaks 4,5), 4-ring (peaks 6,7,8,9) and 5-ring aromatics (peaks 10,11) to elute in order of ring size. The structures of these molecules are shown in Figure 3.

A complex coal liquid is separated by using both the DIOL and DNAP columns and a column switching valve. In our experimental setup, a sample is injected into an HPLC system pumping hexane and is initially separated on a DIOL pre-column that retains polar molecules. The saturates and aromatics pass through the DIOL pre-column and switching valve, proceeding onto the DNAP column (Figure 4a). At this point the switching valve is actuated, isolating the saturate and aromatic molecules on the DNAP column (Figure 4b). Solvent flow continues through the DIOL column. The polar molecules that were initially retained on the DIOL pre-column are now separated by introducing a methylene chloride gradient to the solvent stream. The solvent change from 100% hexane to 100% methylene chloride elutes most of the polar molecules. The remaining polars are desorbed from the column by adding 10% isopropyl alcohol to the methylene chloride.

After all the polar molecules have eluted from the DIOL column, the solvent is changed back to 100% hexane and the column-switching valve is actuated to bring the DNAP column back into the flow stream (Figure 4c). The saturates come off the column first, followed by aromatics separated by ring size as methylene chloride is blended into the hexane solvent.

This separation is demonstrated in Figure 5 with an oil fraction from the iron catalyzed liquefaction of Pittsburgh No. 8 coal. Using this separation method, the polar molecules elute first. At 40 minutes run time, analysis of the aromatic molecules begins. An overlay of aromatic standards with the coal liquid (Figure 6) shows that aromatic molecules in the oil phase begin with 3 aromatic rings and continue with molecules containing 5 rings or more. We had no standards with more than 5 rings.

This HPLC method, using three solvents, two types of column and a column switching valve separates a single injection of oil sample by molecular type, and further separates its aromatic molecules by ring size. These same separations using ASTM open

column methods require several days work. With the HPLC approach, similar separations are achieved in just over one hour.

Plans

Our current research is directed toward further compound identification and quantitation of the HPLC methods. The uv detector used for these studies is not satisfactory for quantitative analysis. Its response is vastly different for different molecular types, from not responding at all to saturate molecules to having very strong response to some types of polar molecules. An evaporative light scattering detector that is sensitive to molecular mass will be purchased during the next funding year. In addition, we will be trapping samples and using a gas chromatograph with a flame ionization to get further information on the molecules that make up coal liquids.

Figure 1

HEAVY GAS OIL ON A DIOL COLUMN

Figure 2

AROMATIC STANDARDS ON A DNAP COLUMN

1. TOLUENE
2. NAPHTHALENE
3. ACENAPHTHENE
4. PHENANTHRENE
5. ANTHRACENE
6. FLUORANTHENE
7. PYRENE
8. BENZO(a)ANTHRACENE
9. CHRYSENE
10. DIBENZO(a,h)ANTHRACENE
11. BENZO(a)PYRENE

Figure 3

Retention Time Correlates with Number of Double Bonds

Name		Double Bonds	Ret. time
Toluene		3	4.0 min.
Naphthalene		5	5.8 min.
Acenaphthene		5	7.2 min.
Fluorene		6	8.6 min.
Phenanthrene		7	12.5 min.
Anthracene		7	13.1 min.
Fluoranthene		8	14.6 min.
Pyrene		8	15.5 min.
Benzo(a)anthracene		9	15.8 min.
Chrysene		9	16.5 min.
Dibenzo(a,h)anthracene		11	19.3 min.
Benzo(a)pyrene		11	19.4 min.

Figure 4a

Trapping Polar Molecules
on Precolumn

Figure 4b

Analyzing Polar Molecules

Figure 4c

Figure 5

OIL FRACTION - DIOL AND DNAP COLUMNS
IRON CATALYZED HUMPHREY MINE COAL

Figure 6

Task III

Novel Coal Liquefaction Concepts

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Project III.1

Bioprocessing of Coal

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Summary

In-situ catalyst formation studies with *Sulfolobus brierleyi* showed the formation of FeOOH crystals. Deposition of molybdenum and iron on outer layers of coal particles increased in biotreated samples. The chemical liquefaction yield of the biotreated coal was dramatically increased from 3 to 25% when the coal sample containing bioformed catalyst was presulfided in the chemical liquefaction reactor. Coal treated with *Thiobacillus ferrooxidans* in the presence of air and CO₂ followed by hydrogen, improved liquefaction yield by 10%.

We have investigated the potential of hydrogenase-containing bacteria in the direct hydrogenation of different untreated coals and coal-related model compounds for improved liquefaction. Hydrogen uptake hydrogenase-possessing thermoacidophilic archaebacterium *Sulfolobus brierleyi* and mesophilic sulfate-reducing bacteria *Desulfovibrio desulfuricans* were used to study the biological hydrogenation of different coals and various model compounds such as diphenyl methane (DPM), 1,2-diquinolyl ethane, α -naphthyl hexane. Hydrogen uptake by the model compounds and various coal types catalyzed by the microbial systems was also determined using G.C. The experiments with the model compounds indeed showed hydrogen uptake ranging from 0.28 μ moles H₂ / μ mole of DPM to 6.55 μ moles H₂ / μ moles of 1,2-diquinolyl ethane in the presence of *S. brierleyi* and *D. desulfuricans* respectively. Chloroform extract of aqueous phase analysis using GC-MS did show that DPM was fragmented into lower parent fragments of M/Z values 73, 95 and 147 depending upon the microorganism used. We also observed significant spectral variation of the liquid phase of medium with coal (KCER # 4677 & 91182) and asphaltenes, when treated with *S. brierleyi* and *D. desulfuricans* under a H₂ atmosphere. Our previous results showed hydrogen uptake by these coals and asphaltenes. Fumarate was reduced (36% conversion) to succinate

in the presence of *D. desulfuricans* under hydrogen atmosphere. Stilbene (1,2-diphenylethylene) was also reduced (~5%) to bibenzyl (1,2-diphenylethane) when treated with *D. desulfuricans* under H₂ gas.

Influence of Bioformed Iron Catalyst on Chemical Liquefaction of Coal:

Coal (KCER # 91182) was treated with *Sulfolobus brierleyi* at 60°C, pH 2.5, in presence of CO₂, air and low concentration (200 ppm) of molybdenum salt. An experiment was conducted with the same parameters but in the absence of *Sulfolobus brierleyi* which is termed the control run. Two sets of experiment with 5% coal were treated with *Sulfolobus brierleyi*. In the shaker setup, about 200 ppm of molybdenum salt was added and the initial pH 3 dropped to 2.4 during the course of the experiment. In the fermenter, 300 ppm of molybdenum salt was added with pH 3 was maintained. Both experiments were conducted at 60°C. Samples were taken every third day, filtered, washed and the coal was dried in an oven at 80°C for about 6 hours. Our previous findings have shown that *Sulfolobus brierleyi* could tolerate different amounts of molybdenum which was present in culture medium. Though, there was an increase in protein content in the culture broth, we observed a sudden decline of growth at the end of 12th day of the experiment.

Mössbauer Spectroscopy and XAFS analysis:

Mössbauer Spectroscopy provided a quantitative measurement of the reactions of pyrite and its transformations in Western Kentucky # 11 coal treated for biodesulfurization by *Sulfolobus brierleyi*. Mössbauer analysis of these biotreated coal samples obtained at the end of the run showed significant changes in the iron forms (Table 1).

XAFS study of biotreated samples obtained, with an increase of time, exhibited prominent increase in the peak between 50-60 eV which represents Mo impregnation on coal (Fig.1).

Elemental analysis on the surface of the biotreated coal (KCER # 91182) using X-ray photoelectron spectroscopic (XPS) technique.

X-ray photoelectron spectroscopic studies were conducted to note the surface characteristics of the biotreated and raw coal (KCER # 91182). By this

technique we determined the elements and chemical information in the outermost 50Å of the exposed coal surface. Here, we are comparing the normalized mass % concentration of elements (C, O, S, Mo and Fe) present on the surface of the control, and biotreated coal samples obtained from two different experiments (Table 2). In the first case, coal was treated with *S. brierleyi* at 60°C and pH 3.0 in the presence of 200 ppm of molybdenum salt in shake flask. The control sample was treated under identical conditions as test, but without bacteria. In the second experiment, coal was treated with *S. brierleyi* at 60°C and pH 3.0 in the presence of 300 ppm of molybdenum salt in fermenter. The concentration of iron and molybdenum are higher in the test runs compared to the control coal samples (Table 2). Raw coal did not show any molybdenum and the concentration of iron on the surface of the raw coal was low compared to the test samples. These observations showed that the biotreatment played a role in increasing the concentration of Fe and Mo on the surface of the coal.

The distinct Fe (2p_{3/2}) peak in the range of binding energy 710-712 eV showed that the iron was in the form of FeOOH (binding energy 710.7 eV) or Fe₃O₄ (binding energy 711.2 eV). Similarly, comparing with the standard peak of MoO₃ (binding energy of 232.6 eV), we concluded that Mo was in the oxide state. The sulfur 2p peaks are visible at the binding energy range of 160-170 eV. Due to the oxygen effect the sulfur peak was shifted from standard binding energy of 161.5 eV to the binding energy of 168.5 eV. Since the fermenter runs were conducted by continuous bubbling of CO₂ and air we found the sulfate peaks were greater in intensity. This also explains the high surface concentration of oxygen.

Liquefaction of bioprocessed coal (KCER # 91182) in the presence of H₂S

Liquefaction was conducted on both the samples of coal. It was conducted at 385°C, 800 p.s.i. for 15 minutes. Excess amount of dimethyl disulfide (1 gram) was added to sulfide the iron and molybdenum present on the surface of the coal. The products of liquefaction contained benzene solubles which constitute the oils and asphaltenes, with benzene insolubles pyridine solubles are the preasphaltenes. Oils and asphaltenes are separated by pentane which dissolves the oils, and thus leaving behind the asphaltenes. The sulfided form of iron and molybdenum acts as catalyst during liquefaction. The total conversion determined as the pyridine solubles showed a

substantial increase of 25% in the test run coal, compared to the control run (Table 3). The experiments were repeated and the results obtained matched the previous result. So far this is the highest liquefaction yield obtained from any of the biotreated coals. Previous liquefaction yield results showed only a 3% increase, without pre-sulfiding the bioprocessed coal. A sudden decrease of protein content of the culture broth might have influenced the formation of the ultra-fine size of the catalyst.

Biotreatment of coal with *Thiobacillus ferrooxidans* in presence of CO₂ plus air followed by hydrogen showed an increase in the chemical liquefaction yield of 10%. Chemical liquefaction yield remained unaffected for the same treatment, if hydrogen gas was not used in the microbial treatment (Table 4). The liquid phase iron analyzed by Atomic Absorption Spectroscopy showed initiation of iron precipitation even before sparging of hydrogen gas (Fig. 2). *T. ferrooxidans* was reported to use hydrogen as an energy source. However, the precise role of *T. ferrooxidans* in increasing the liquefaction yield is not known.

HYDROGENATION OF MODEL COMPOUNDS AND COAL BY DIFFERENT BACTERIA

Hydrogen uptake of hydrogenase-possessing thermoacidophilic archaebacterium *Sulfolobus brierleyi* and the mesophilic sulfate-reducing bacteria *Desulfovibrio desulfuricans* were used to determine the biological hydrogenation of different coals and various model compounds such as diphenyl methane (DPM), 1,2-diquinolyl ethane, fumarate, stilbene and α -naphthyl hexane. Washed cell suspensions were used from the *S. brierleyi* grown chemolithotrophically under aerobic conditions with elemental sulfur as the oxidizable energy source, and *D. desulfuricans* grown anaerobically with lactate as the energy source and sulfate as the final electron acceptor.

Hydrogen uptake measurement by Gas Chromatography

Coal samples were added to 160 ml capacity serum vials containing 50 ml of the mineral salts medium without the growth substrate. The sealed sterile vials were flushed with pure hydrogen gas and incubated at 37°C with *D. desulfuricans* and at 60°C with *S. brierleyi* in the 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-9A (Shimadzu) attached with data processor Chromatopac C-R 1 B. The experiments with model compounds indeed showed hydrogen uptake ranging from 0.28 μ moles H₂ / μ mole of DPM to 6.55 μ moles H₂ / μ moles of 1,2-diquinolyl ethane in presence of *S. brierleyi* and *D. desulfuricans* respectively (Fig. 3 & 4). When 1,2-diquinolyl ethane was dissolved in ethanol, it did not show any hydrogen uptake in the presence of *D. desulfuricans* due to the enzyme inactivation and thus acted as a control. There was a wide variation in the extent of hydrogen uptake even among the model compounds. At present, it is not clear about the pathway of hydrogen incorporation into these compounds. However, chloroform extract of aqueous phase analysis using GC-MS did show that DPM was fragmented into lower parent fragments of M/Z values 73, 95 and 147 depending upon the microorganism used (Fig. 5 & 6). *Rhizobium sp.* also showed hydrogen utilization from the head-space of the reaction vials with different model compounds.

Spectrophotometry

All absorption spectra (UV & Visible) were obtained using Beckman DU-50 Spectrophotometer and HP 8452 Spectrophotometer with appropriate blanks. Our previous results with different coals used for biohydrogenation by *D. desulfuricans*, coal (KCER # 4677) showed the highest hydrogen uptake. Liquefaction of biotreated coal sample (KCER # 4677) showed an increase of approximately 5.5% of liquefaction yield. *Sulfolobus brierleyi* also influenced the hydrogenation of some of the coal samples and of model compounds but it was not as efficient as *Desulfovibrio desulfuricans*. However, the coal samples (KCER # 91182 & 4677) and asphaltenes treated with *D. desulfuricans* and *S. brierleyi* showed increase in ultraviolet absorption when compared to the controls. In the pursuit of observing the direct evidence of hydrogenation, fumarate and 1,2-diphenylethylene were taken as model substrates. We have observed that indeed fumarate was hydrogenated (~36%) to succinate when it was treated with *D. desulfuricans* under continuous bubbling of hydrogen (Fig. 7 & 8). Succinate in the culture supernatant was quantified by enzymatic method (Boehringer Mannheim). Fumarate in culture broth was estimated by colorimetric method using pyridine and acetic anhydride. Besides fumarate, *D. desulfuricans* was able to hydrogenate 1,2-diphenylethylene (~5%) to 1,2-diphenylethane in presence of hydrogen

gas. These compounds (1,2-diphenylethylene and 1,2-diphenylethane) were analyzed by GC-MS. *D. gigas*, another sulfate-reducing bacterium, was also used to reduce fumarate to succinate. It did not show either utilization of fumarate or reduction of fumarate to succinate. We assume that the availability of hydrogen in the aqueous phase may be the limiting factor for the hydrogenation. Therefore, we are now attempting to improve the extent of hydrogenation of model compounds and coal by applying high pressure and by using organic solvents to mediate transport of dissolved hydrogen gas.

Table 1. Composition of iron determined by Mössbauer analysis (12 K) of coal
(KCER # 91182) treated with *Sulfolobus brierleyi*

	% Fe	Phase
Control*	43 %	Pyr. + Fe ³⁺ sulf.
	56 %	Jarosite
Test	61 %	Fe ³⁺ sulf.(+ FeOOH)
	39 %	Jarosite

* - Not treated with *S.brierleyi*

Table 2. X-Ray photoelectron spectroscopic determination of elements present on the surface (50 Å) of Coal when treated with *Sulfolobus brierleyi* at 60°C

Coal Samples (KCER # 91182)	Variation of elements (Mass %)				
	C	O	S	Mo	Fe
Raw Coal	80.69	15.4	3.54	0.00	0.37
Test- Shaker†	62.36	29.47	2.03	4.16	1.98
Control- "	72.98	19.64	2.07	3.79	1.53
Test - Fermentor@	56.96	25.34	2.43	8.94	6.32
Control - "	67.79	20.61	2.33	5.34	3.93

Test - With bacteria

Control - Without bacteria

† - Contains 200 ppm Molybdenum salt. Initial pH is 3 and dropped to 2.4.
Contact time 20 days.

@ - Contains 300 ppm Molybdenum salt. pH maintained at 3. Contact time 21 days.

Table 3: Liquefaction results of the coal(KCER # 91182) treated with *Sulfolobus brierleyi* at 60°C, pH 2.5 and 200 ppm of molybdenum salt

Liquefaction Products Wt. %	KCER # 91182							
	before sulfiding				after sulfiding			
	Control		Test		Control		Test	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Gas	1	1	1	1	1	1	1	1
Oils	9	10	11	12	12	11	13	12
Asphaltenes	18	16	17	17	18	19	29	24
Preasphaltenes	21	25	25	25	25	22	38	41
IOM*	51	48	46	45	44	47	19	22
Conversion	49	52	54	55	56	53	81	78

* - Insoluble organic matter.

Experimental conditions

Temperature	-- 385°C
Pressure	-- 800 p.s.i.
Solvent	-- Tetralin
Time	-- 15 minutes
Sulfiding Compound	-- 1.0 gm of DMDS

Table 4: Liquefaction results of the Coal (KCER # 91182) treated with *Thiobacillus ferrooxidans* at 30°C

Liquefaction products Wt %	Coal (KCER # 91182)*		Coal (KCER # 91182)**		Coal (KCER # 91182)***	
	Control	Test	Control	Test	Control	Test
Gas	1	1	1	1	1	1
Oils	12	14	10	14	10	9
Asphaltenes	18	20	18	18	16	17
Preasphaltenes	28	34	27	27	26	24
IOM†	41	31	44	40	47	49
Conversion	59	69	56	60	53	51

- † Insoluble organic matter
 * Biotreatment at 2.8 (Hydrogen was sparged after 16 days in the absence of air)
 ** Biotreatment at 3.0 (no Hydrogen was sparged during bioprocessing)
 *** Biotreatment at 2.5 (no Hydrogen was sparged during bioprocessing)

Experimental conditions

- Temperature - 385°C
 Pressure - 800 p.s.i H₂
 Solvent - Tetralin
 Time - 15 minutes
 Sulfiding compound - 0.8 g of dimethyl disulfide.

Fig. 1 X-Ray absorption fine structure spectroscopic analysis (sulfur K-edge and Molybdenum L-edge) of coal (KCER # 91182) samples obtained at different time intervals when treated with *Sulfolobus brierleyi* in presence of 200 ppm Molybdenum salt, pH 2.5 and 60°C.

Fig. 2 Variation of liquid phase iron content with time of 5% coal (KCER # 91182) slurry treated with Thiobacillus ferrooxidans at 30°C and pH 2.8

Fig. 3 Hydrogen uptake in presence of *Desulfovibrio desulfuricans* by α -naphthyl hexane

Fig. 4 Hydrogen uptake in presence of *D. desulfuricans* by 1,2-diquinolyl ethane subjected to autoclaving condition

Fig. 5 GC-MS analysis of diphenyl methane extracted chloroform from aqueous medium of test treated with *Desulfovibrio desulfuricans* under hydrogen atmosphere

Fig. 6 GC-MS analysis of diphenyl methane extracted chloro from aqueous medium of test treated with *Sulfolobus brierleyi* under hydrogen atmosphere

Fig. 7 UV absorbance of fumarate medium treated with *Desulfovibrio desulfuricans* under continuous sparging of hydrogen

Fig. 8: Reduction of fumarate to succinate by *Desulfovibrio desulfuricans* under continuous supply of hydrogen

Project III.2

Novel Liquefaction Concepts

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During the past year, we have investigated the bond cleavage mechanisms of naphthylphenyl model compounds in order to better understand catalyst functions. A better understanding of the cleavage mechanisms will assist in the development of new catalysts. Our approach towards understanding the bond cleavage mechanisms of naphthylphenyl model compounds has involved a dual pathway to elaborate the desired information. In the first pathway, independent generation of important reactive intermediates has been attempted in order to accurately assess their reactivity. A second approach has been to develop a new set of compounds which may rigorously establish the location of the cationic species as well as serve as a probe of alternative reaction mechanisms.

The mechanistic problem arises from the products isolated from a series of naphthylated model compounds which were subjected to coal liquefaction conditions with various iron catalysts which have been prepared elsewhere in the Consortium.

Model compound I (i.e., 4-(1-naphthylmethyl)-bibenzyl, **1a**) is shown in Figure 1 and is representative of the reactivity of this set of model compounds in that bond A cleavage is always observed. Bond A is the bond connecting the naphthyl group to the alkyl side chain. The bond A cleavage has been rationalized as originating from a radical cation, based on the observation of catalytic activity,¹ the appearance of a surface charge on the catalyst at the same temperature as the onset of catalytic activity,¹ and theoretical calculations which indicate the least electron density in bond A.² The reactivity of other naphthylated model compounds is similar under catalytic conditions. 1,2-Di-1-naphthylethane is representative in that bond A is the predominate bond being cleaved under catalytic conditions.³ This result is shown in eq (1). While the radical cation explanation of catalyst reactivity is attractive, the results of these naphthylated compounds are in apparent contradiction to the known reactivity of monoaryl systems. Representative of these compounds is 1,1,2,2-tetraphenylethane (**4d**) which is known to cleave bond B when the radical cation is generated by a variety of reagents. This reaction is shown in eq (2). With this apparent contradiction in reactivity in mind, we have endeavored to independently generate the radical cations

of appropriate model compounds and to understand the reactivity of these naphthylated compounds under more controlled conditions.

RESULTS AND DISCUSSIONS

Justification of the Selection of Model Compounds Chosen for This Study: The selection of model compounds is based on two criteria. These criteria are the ease of availability and the relationship between the Farcasiu Model Compound I (i.e., 1a) and known chemistry (either the chemistry of the coal model compound in the presence of the catalyst or from compounds in which the chemistry of the radical cation is known). The first set of compounds is an attempt to incorporate molecular functionality in which the radical cation can be unambiguously identified and its location known. In this category are compounds 1a, 1b, 2a, 2b, 3a, and 3b in which the essential features of polyfunctionality of the Farcasiu Model Compound I are incorporated (Note Figure 1). Although the synthesis of these compounds is somewhat difficult, results obtained from these compounds are expected to be quickly obtained, since their chemical functionality is sufficiently similar to compounds which have been previously studied in the literature as to make for certain bond cleavage reactions in an unambiguous fashion. Further, there will be a clear differentiation between potential radical and radical ion pathways in these compounds. The second set of compounds were chosen because they were commercially available or their synthesis could be accomplished within a short period of time. These compounds contain critical portions of the Farcasiu Model Compound I, but suffer from the disadvantage that results from

experiments on several compounds must be compared to obtain an accurate mechanistic picture of the reaction relative to the catalytic work. These compounds include di-1-naphthylmethane (4a), 1,2-di-1-naphthylethane (4b), 1-naphthylphenylmethane (4c) and 1,1,2,2-tetraphenylethane (4d). These compounds are shown in Figure 2.

Generation of the Radical Cations of 1a, 4a, 4b and 4c Under Degassed Conditions:

Our initial experiments were motivated by the known literature procedures for independent generation of radical cations. These procedures utilized irradiation of an appropriate electron acceptor compound which may then oxidize the substrate. Thus, for this radical cation generation method to work, light must be

Figure 1. Model Compounds Synthesized At West Virginia University

absorbed by the "photosensitizer" which then performs the desired oxidation. Subsequent reactions of the radical cation are usually sufficiently rapid as to compete effectively with the energetically favorable back-electron transfer reaction to generate the initial

substrates. We chose 9,10-dicyanoanthracene (DCA) as our photooxidizer because of its relatively long wavelength absorption (easier to ensure that only the photooxidizer absorbs the light) and its relatively low propensity to undergo side reactions with the substrates.

Irradiation of a freshly distilled acetonitrile solution of **1a** (2.0 mM) and DCA (0.1 mM) at 350 nm for 96 hrs gave no product when the reaction mixture was degassed with N₂ for 15 minutes prior to the irradiation and then sealed with a latex septum. The lack of reaction was initially indicated by the lack of low molecular weight products by GC analysis of the reaction mixture and was confirmed by the use of octyl cyanide as an internal standard. The reactions of **4a**, **4b** and **4c** were similar in that no reactions were detectable after 96 h of irradiation.

To ensure the viability of our laboratory technique, we irradiated DCA in solutions containing **4d** being careful to use

Figure 2. Second Set of Model Compounds Used at WVU

similar reaction conditions. As expected, diphenylmethane and diphenylmethyl methyl ether were produced in quantitative yield in just 24 h of irradiation by using acetonitrile:methanol (3:1) as a solvent. These results are consistent with the results reported in literature and demonstrate that the radical cations of these substrates are being generated under these conditions. The significance of these results is that the radical cations of **4a**, **4b** and **4c** do not cleave readily at room temperature. These results are analogous to those reported for bibenzyl in which a very low quantum efficiency for cleavage has been reported using the photoinitiated electron transfer methodology for radical cation generation. While the lack of bond cleavage from the radical cation of these 1,2-diarylethanes does not rule out the bond cleavage reactions of radical cations under catalytic conditions where higher temperatures may lead to faster reaction from these intermediates, the lack of bond cleavage suggests that these intermediates have higher energy bond dissociation energies which makes their intermediacy more difficult to postulate without further characterization of their reactivity.

Generation of the Radical Cations of 1a, 4a, 4b and 4c in the Presence of O₂: Similar experiments to those above were performed after bubbling of O₂ into the solution for 15 minutes prior to irradiation. In contrast to the lack of reactivity observed under degassed conditions, bond cleavage is observed for **1a**, **4a**, **4b** and **4c** (Figure 3). The aldehydes formed were detected by GC only after 2 h irradiation. In all cases, bond A cleavage is noted in addition to a variety of other products.

O_2 and the $DCA^{\cdot -}$ (formed by electron transfer from the $DCA^{\cdot}$ and the aromatic moiety) to yield $O_2^{\cdot -}$, followed by a H^+ transfer to yield a pair of radicals which initiate a chain reaction may be responsible for the observed reactivity (Figure 4). However, definitive interpretation must await better mass balances and more detailed work to explore the bounds of this reactivity. This work has been published as a preprint paper for the 204th American Chemical Society National Meeting in Washington, DC in August 1992.⁴

Reactions of 1a, 4a and 4b with Fe(III) Complexes at High Temperature: In an attempt to more closely emulate the conditions of catalytic activity, we chose to use $Fe(III)(1,10\text{-phenanthroline})_3$ complexes ($Fe^{III}L_3$) at higher temperatures to generate the radical cations of these coal model compounds. This was predicated on the known catalytic behavior at temperatures as low as $250^{\circ}C$ for some super active catalysts. Our standard procedure was to place an acetonitrile solution of the coal model compound (0.01 M), $Fe^{III}L_3$ (0.02 M), and an appropriate internal standard into base-washed tubes. O_2 was removed from the solution using three freeze-pump-thaw cycles, and the tube was sealed under vacuum. The tubes were then placed in a hot oil-bath ($200^{\circ}C$) for 24 hrs. After this period of time, the color of the solution had changed from blue to red, indicating that the $Fe^{III}L_3$ was completely converted to $Fe^{II}L_3$. The product mixtures were then analyzed directly on the GC.

Although a complete quantitative analysis of these reactions has not been completed, qualitative results detailing some of the

Figure 4. Possible Mechanism for Bond A Cleavage with O₂ in the Solution

products formed in the reaction are available for this report which allow a preliminary analysis of the reactions. Compound **4d** proceeded cleanly to give bond B cleavage in analogy with the low temperature solution phase results (Note eq (2)). This result demonstrates that the radical cations of these model compounds can be generated under these conditions.

Analysis of the reaction solution from compound **4b** and Fe^{III}L₃ showed that naphthalene and 1-naphthylacetamide were formed. The formation of 1-naphthylacetamide is easily rationalized if bond B is broken in the reaction. The production of naphthalene is most easily rationalized from cleavage of bond A. Thus, we make the preliminary conclusion that both bonds A and B were broken under these conditions in a reaction which proceeds via an initial generation of the radical cation of **4b**. Interestingly, both **1a**

and 4a are completely consumed under the reaction conditions, with no identifiable products being detected at the present time. At the current time, we are continuing these studies by attempting to determine mass balances which will allow for a complete mechanistic evaluation of the reactions. In addition, lower temperature studies are being conducted to provide scale-up conditions to obtain more material for analysis of the reaction products.

Synthesis of Polyfunctional Aromatic Compounds 1a-3c: We report here that compounds 1a, 1b, 2a, and 3a of Figure 1 have been synthesized. Complete details of their synthesis is included in the experimental section. Items of particular note in the synthesis of these compounds include the fact that the Dowd synthesis was ineffective in our hands. To get reasonable yields of 1a and 1b, we resorted to the ferric chloride catalyzed reaction of appropriate alkyl chlorides to the appropriate diaryl compounds. Of additional note is the fact that attempted synthesis of compounds 2b and 3b proved more difficult than expected. The synthesis of these compounds requires electrophilic aromatic substitution in unorthodox directions. At the current time, our work has halted in this area in order to elaborate the reactivity of the Fe^{III} oxidation reactions noted above.

Experimental Section

Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model 5890A GC equipped with a 10 m 5% phenylmethylsilicone or a Carbowax 20 m megabore column.

Integration of the signals was performed by a Hewlett-Packard Model 3390A digital integrator. GC-MS were measured with a HP model 5980 mass spectrometer with a 5890 gas chromatograph equipped with a 25-m 5% phenylmethylsilicone column. ^1H NMR spectra δ (ppm) and J (hertz) were measured in the indicated solvent with TMS as an internal standard on a JEOL GX-270 Spectrometer.

Acetonitrile was predried over CaH_2 and then distilled from CaH_2 shortly before use. Unless otherwise specified, all chemicals were purchased from Aldrich. Photochemical reactions were carried out in a Southern New England ultraviolet Rayonet RPR-100 photochemical reactor or a Hanovia 450 W (Medium-Pressure Mercury Lamp). For the reactions with or without oxygen, the sample solutions were degassed by bubbling O_2 or N_2 for 15 min prior to irradiation and then sealed with latex septa. All thermal reactions were carried out in sealed tubes at the temperatures indicated. A solution of diaryl compound and the indicated electron acceptor in 10 mL of freshly distilled acetonitrile was prepared and added to several pyrex tubes. These tubes were degassed by using three freeze-pump-thaw degassing cycles and then sealed under vacuum. The sealed tubes were contained in a Neslab Model EX 250-HT constant temperature bath for the designated time. The product mixtures were then analyzed directly on the GC.

4b was purchased from Lancaster and recrystallized from ethanol. **4a** and **4c** were synthesized by a literature method.⁵ A Grignard reagent was prepared from 1.14 g (0.048 mol) of

magnesium turnings and 9.94 g (0.048 mol) of bromonaphthalene in 20 mL of dry ether. When the reaction was complete, the ether was replaced with dry benzene. To this hot solution was added 5.06 g (0.04 mol) of benzylchloride or 7.06 g (0.04 mol) of 1-(chloromethyl)naphthalene dissolved in 10 mL of dry benzene. The mixture was refluxed for 1 hr, cooled to room temperature, and decomposed with 20 mL of cold 4 N hydrochloric acid. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, concentrated, distilled under vacuum and repeatedly recrystallized from ethanol.

4a: mp 107-108°C; NMR (270 MHz, CDCl₃) δ (ppm) 4.8 (s, 2H), 7.9 (m, 3H), 7.4 (m, 11H).

4c: mp 54-55°C; NMR (270 MHz, CDCl₃) δ (ppm) 4.5 (s, 2H), 7.8 (m, 3H), 7.3 (m, 9H).

4-(1-naphthylmethyl)bibenzyl (1a): Ferric chloride (57 mg, 0.35 mmol) was transferred into a flame dried 50 mL round-bottomed flask in a glove box followed by addition of dry CS₂ (8 mL). The resulting mixture was stirred for 10 minutes and cooled to 0°C. Solid bibenzyl was added and stirred for 10 min. A solution of 1-(chloromethyl)naphthalene (706.6 mg, 4.0 mmol) in dry CS₂ (5 mL) was added dropwise into the reaction flask to bring out excess HCl formed during the reaction. The reaction mixture was poured into ice water (20 mL) containing concentrated HCl (3 mL), diluted with CH₂Cl₂ (20 mL), shaken thoroughly, and transferred into a separatory funnel. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL). The combined organic extracts were decolorized with

activated charcoal, filtered and evaporated in vacuo to give a clear oil (1048 mg). Silica gel column chromatography eluted with 1:4 CH₂Cl₂/hexane was used to recover bibenzyl (802 mg, 80.1%) and the desired naphthylmethylbibenzyl (127 mg, 9.9%)¹ as a colorless solid, mp 64.0-64.5°C (hexane).

Details of the syntheses of 1b, 2a, and 3a have been included in the Quarterly Report on DOE Contract No. DE-FC22-990PC90029 (Period: August 1, 1991- October 31, 1991) and are not included here for the sake of brevity.

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¹When calcium chloride was used as a dispersant and sodium phosphate as a base to neutralize the hydrogen chloride formed in the reaction, the yield (12.1%) may be raised a little at the expense of a longer reaction time.

Better Hydrogen Mass Transfer In Coal Liquefaction

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I. Introduction

Background

During the initial stages of coal liquefaction, it is hypothesized that free radical reactions occur rapidly and that reaction rates increase almost exponentially. These fast reactions involve the thermal disruption of the coal structure to produce free radical fragments. If the free radicals are not stabilized by hydrogen donation, retrogressive reactions and/or catalyst deactivation takes place. Data taken in our laboratory and others indicates that hydrogen starvation in the initial stages of coal liquefaction has a permanent, negative impact on product yields.

Rather than attempting to satisfy the H_2 mass transfer rate requirements of uncontrolled autocatalytic free-radical reactions solely by exceptionally high mass transfer rates, an alternative approach was used. The reactor system detailed in this report was designed and constructed in order to control the rate of free-radical propagation so that only practical, achievable H_2 mass transfer rates would be required. We felt that, with proper reaction rate control, H_2 mass transfer rates could be made sufficiently high so that retrogressive reactions could be kept at a minimum.

The approach taken in developing the reactor system was, therefore, two-fold: (1) a reactant flow pattern was selected which would allow versatility in reaction rate controllability, and (2) a gas-liquid contactor design was sought that provided the highest mass transfer rates per unit volume without significantly affecting reaction rate controllability.

A bang-bang control strategy was implemented in order to regulate reaction rate. A cyclic switching of the coal slurry from high to low reaction temperatures was used to control reaction rate. Physically, this was accomplished using a recycle loop-type reaction in which the temperature in part of the loop was kept high (the reaction zone) and that

in the remainder of the loop was kept low (the quenching zone). This reactor flow arrangement has been commonly used with jet-type reactors which have been utilized commercially when reaction rates are very high (as is the case in the initial stages of coal liquefaction). The frequency of cyclic switching in reactant temperature can be varied simply by changing the reactant recycle flow rate. And by sufficiently increasing the recycle flowrate, the H_2 mass transfer requirements per reaction cycle could be kept low within a range that we felt could be satisfied via practical gas-liquid contactors.

This Year's Activities

The work this past year focused on construction of the new coal liquefaction reactor system. Included in this effort was procuring high temperature and pressure parts, conducting a thorough search for a pump capable of handling slurries under severe conditions, and further developmental work on a gas-liquid contactor. After determining that a mechanical pump was unavailable, this year's work also included developing a unique, gas-charged pumping system.

In searching for a pump capable of handling coal slurries at severe reaction conditions, several major pump manufacturers were contacted. We discovered that suitable pumps for small systems were not available unless they were custom-built at a cost of over \$100,000. Such costs make practical, large-scale coal liquefaction studies economically impossible. This prohibitive cost necessitated the development of a novel, gas-charged pumping system detailed later in this report. The pumping system is unique and has not been tried to this date in coal liquefaction. The system will be capable of circulating a wide range of fluids under severe conditions, it has few moving parts, will be easily serviceable, and is generic in nature.

The pumping system is composed of two modified Autoclave reactors used as stirred tanks, air-operated valves, gas holding tanks, a gas booster, an air compressor, and a programmable logic controller (PLC). Basically, differential pressure between the two stirred tanks is the driving force for fluid transfer. A series of actuated valves, controlled by the PLC, directs the movement of fluid as well as maintaining gas pressures in the system. The fluid flow rate of the pumping system can be changed simply by adjusting valve action and gas pressures. The pumped fluid can range from low viscosity liquids to high viscosity slurries, thereby making the pumping system applicable in a wide range of uses.

A variety of designs for gas-liquid contactors have been evaluated in our previous work including motionless mixers, column packings, high-shearing mechanical agitators, and two types of slot injectors. Each was evaluated not only in terms of its relative effect on gas-liquid mass transfer but also on the feasibility of its use in the new liquefaction process. Of the types tested, the slot-type injector showed the greatest promise for improving gas-liquid mass transfer in coal liquefaction.

A particular type of slot injector, called a jet nozzle, was uncovered this year. Initial testing indicates that the jet nozzle performs better in regard to gas-liquid mass transfer than other types of slot injectors.

II. Novel Coal Liquefaction Reactor System

The system incorporates reaction rate control by allowing modification of two control parameters: (1) reaction zone temperature, and (2) the frequency of cyclic switching. These parameters can be adjusted to regulate the mass transfer requirements per reaction cycle.

Figure 1 is a complete diagram of the new system and Table 1 lists the parts and equipment used in constructing it. The pumping system will be discussed in the next section. Initially, slurry will be charged to Tanks 1 and 2. When system operation begins, slurry will flow out of one of the tanks to the gas-liquid contactor, where gas-liquid mixing occurs, and then through the preheater to the reactor tubes. The reactor tubes contain 5/8 inch stainless steel packing rings to facilitate heat transfer and assist in gas-liquid mass transfer. The temperature of the slurry and the reaction rate is then lowered by passing the slurry through a jacketed cooler using tap water as the cooling medium. Finally, the slurry flows back to either Tank 1 or Tank 2, depending on the current flow cycle, and the entire cycle is repeated.

Product samples will be obtained just after the slurry leaves the reactor tubes. To collect a sample, a valve at the entrance to a collection tank will be briefly opened to admit slurry into the tank. Then an exit valve will be opened to collect the sample into a container. Samples will be taken at specific times during the reaction in order to obtain product profiles with time.

Temperature Control

Heating is provided by the two stirred tanks (incorporating jacketed electrical

heaters), a 3-zone electrical preheater, and the fluidized sand bath. All of the heaters are controlled by PID controllers.

The cooler is primarily responsible for lowering the process temperature. It is constructed of a length of 1/2 inch O.D. tubing inside a 2 inch O.D. tube. Tap water is the cooling medium.

Safety Considerations

Rupture disks are located at strategic points in the system. These will discharge the system should pressures rise too high.

The entire coal liquefaction system is located behind polycarbonate shields and thick walls containing sand bags.

III. Novel Pumping system

In order to affect hydrogen mass transfer, certain flow rates are required in the reactor system. As detailed in the introduction, commercial pumps capable of handling coal slurries under the severe reaction conditions necessary in coal liquefaction are simply not available at reasonable cost. This fact necessitated the development of a novel pumping system.

Figure 1: Coal Liquefaction Reaction System

TABLE 1
EQUIPMENT USED IN THE COAL LIQUEFACTION SYSTEM

IDENTIFICATION	USE	DESCRIPTION
<u>Valves</u>		
VG1, VG2	High Pressure Gas Charge to Holding Tanks	Autoclave Engineers 20SC4071-O1S-TG, 20,000 psi, 340°C, Teflon-Glass Packing, Air-Operated (air-to-open), 1/4 inch ports.
VG3	High Pressure Purge to Tank 1	"
VG4	High Pressure Purge to Tank 2	"
VG5	Tank 1 Gas Return	"
VG6	Tank 2 Gas Return	"
VS1	Slurry Feed to Tank 1	Autoclave Engineers 20SC9072-O1S-TG, 20,000psi, 340°C, 316SS, Teflon-Glass Packing, Air-Operated (air-to-open), 9/16 inch ports.
VS2	Slurry Feed to Tank 2	"
VS3	Slurry Feed From Tank 1	"
VS4	Slurry Feed From Tank 2	"
<u>Tubing</u>		
1/4 inch O.D.	Gas Lines	1/4 inch O.D., 0.035 inch wall, SMLS CD 316SS A269
1/2 inch O.D.	Slurry Lines	1/2 inch O.D., 0.065 inch wall, SMLS CD 316SS A 269
9/16 inch O.D.	For 9/16 in. valve ports	9/16 inch O.D., 0.065 inch wall, SMLS CD 316SS A269
<u>Reactor Tubes</u>		
1 inch O.D.		1 inch O.D., 0.125 inch wall, SMLS CD 304SS A269
<u>Packing</u>		
	Heat transfer; gas-liquid mixing	5/8 inch diameter, 316SS rings
<u>Tube Fittings</u>		
		Swagelok 316SS, pressure rating equal to or greater than that of tubing
<u>Tanks 1 and 2 tank</u>		
	CSTR	Autoclave Engineers stirred reactor, 3500 psi maximum pressure, 1 gallon capacity
<u>Thermocouples</u>		
	Temperature indicators	Type K, chromel-alumel from Omega
<u>Pressure Gauges</u>		
PGC	Pressure indicators	Ash 4 1/2 inch, 1279RS-04L

High and Low Pressure Tanks,
Gas Holding Tanks

Safety, purge

XED, 0-5000 psi, Duragauge
pressure gauge with hi-lo
contact set

3AA3600 gas cylinders, 3600
psi maximum pressure

Solenoids

S

On/off air supply to
air-operated valves

Bürkert 330-C-1/8-F-BR-1/8
solenoids, 120 volt, 8 watts

Checkvalves

Prevent reverse gas flow

Nupro checkvalve, SS-CHS4-10,
6000 psi, 204°C, 10 psi cracking
pressure

Gas Booster

Boosts gas pressure to
3000 psi

Haskel AGD-30-C

Air Compressor

To operate solenoids and
Haskel gas booster

Gardner-Denver model ADR
1014, 15 hp

Fluidized Bath

Process Heating

Techne SBL-2D, 600°C
maximum

Preheater

Process Heating

Applied Test Systems 3210
series, 3-zone heater, 3600
watts, 230 volts, 900°C
maximum

Cooler

To lower temperature of slurry

1/2 inch O.D., 77 inch long
SMLS CD 304SS tube inside
a 2 inch O.D., 64 inch long
SMLS CD 304SS water jacket

Rupture Disk Holder

Safety

Fike, 1.5 inch, stainless steel

Rupture Disks

Safety

Gas-Liquid Separator
with

Collect vapors in gas
recirculation lines

750cc sample cylinder filled
packing rings

Gas-Liquid Contactor

Gas-liquid mixing

Custom-made slot-type injector

Programmable Logic
Controller

Operates system valves

Allen Bradley model SLC 5/02
with OA-16, NIO4V I/O cards

Referring to Figure 1. assume at $t = 0$ that Tank 1 is empty and Tank 2 is full of slurry. At this moment of time, the system valves are in the following states:

VG1 = Open	VG2 = Closed	VG5 = Open
VG3 = Closed	VG4 = Open	VG6 = Closed
VS1 = Open	VS3 = Closed	
VS2 = Closed	VS4 = Open	

The gas holding tank between valves VG2 and VG4 has been previously charged with high pressure gas. For safety purposes, these gas holding tanks are used to feed high pressure gas to the stirred tanks. With valve VG4 open, the high pressure gas will force the slurry out of Tank 2 into the reaction system. As slurry flows into the system from Tank 2, slurry also flows into Tank 1 from the reaction system. Thus, Tank 1 is filling while Tank 2 is emptying.

When Tank 1 is full and Tank 2 is empty, the computer switches the valves to their opposite states. High pressure gas from a holding tank will then force slurry out of Tank 1 into the reaction system while Tank 2 begins filling with slurry from the reaction system. Flow rates and direction can be easily controlled by timing the operation of the system's valves.

When valve VG5 or VG6 is open, the respective stirred tanks are exposed to lower pressure (the suction side of the gas booster). This aids the filling of each tank with slurry.

An Allen Bradley model SLC 5/02 PLC is used to control valve switching in the coal liquefaction system. With the OA-16 and NIO4V I/O cards, it is capable of inputting eight digital and two analog signals simultaneously and outputting sixteen digital and two analog signals. The control program is written in ladder logic format.

Safety Considerations

The high pressure tank and the two stirred tanks incorporate pressure gauges with hi-lo contact sets. The PLC will monitor these contact sets in order to adjust or stop system operation should pressures exceed prescribed limits. The air booster will be set to stop operation when maximum pumping system operating pressure is reached.

IV. Gas-Liquid Contactor

Several gas-liquid contactors have been studied in our laboratory for possible use in our coal liquefaction system. These include slot-type injectors, motionless mixers, and high-shearing mechanical agitators. Of all the types studied, the slot-type injector showed the greatest promise for improving gas-liquid mass transfer in coal liquefaction.

The Jet Nozzle

One type of slot injector, a jet nozzle, was located that appears to perform significantly better in regard to gas-liquid mass transfer than other types of slot injectors we have evaluated. Our initial study involved testing the air suction ability of a conventional slot injector, a modified slot injector, and a jet nozzle. The catalyzed sodium sulphite reaction system shown in Figure 2 was used to evaluate the nozzles. A 2 hp pump circulated water through the nozzle under evaluation. Air flow rates were measured by a rotameter and water flow rates were measured by using a manometer to measure pressure differences across an orifice. Power consumption of the system was calculated from the formula, $P = 1.559 \cdot V \cdot I$ where V refers to the input voltage of the pump motor and I refers to the current consumed by the motor. As indicated in Figure 3, the jet nozzle showed much better air suction ability than the other two types of injectors. There was also an added bonus of less power consumption in the jet nozzle.

Using the sodium sulphite reaction system, we compared the overall gas-liquid mass transfer rates of a conventional slot injector and the jet nozzle. In this test, oxygen is removed from a tank of water by the addition of sodium sulfite and cobalt sulfate. The oxygen-depleted water is then pumped from the tank into the injector where air is mixed with the water. The mixture flows back to the tank where a dissolved oxygen probe measures the dissolved oxygen content of the water.

Results from this test (Figure 4) indicate a mass transfer coefficient of 0.03 sec^{-1} for the jet nozzle or about twice the mass transfer coefficient of a conventional slot injector which measured 0.017 sec^{-1} .

Figure 3: Air flowrate versus liquid flowrate of three injectors

Figure 4: Dissolved Oxygen Test Comparing Different Injectors

Project III.4

Catalytic Hydropyrolysis

Part 1. Catalyst, Coals, and Liquid Product

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Coal catalytic hydropyrolysis has been studied. Blind Canyon coal (Argonne Premium Sample) was used in the first group of experiments performed to investigate the effects of iron, and nickel as catalysts and as promoters for molybdenum at 350°C. The second group of experiments was carried out to study the effects of two different catalyst impregnation methods, ultrasonic and incipient wetness impregnation, in three coals--Blind Canyon, Pittsburgh #8, and Wyodak. Blind Canyon coal was also used in another set of experiments to study the effects of coal pretreatment--demineralization, and pre-extraction. The third group of experiments was designed to study catalyst molybdenum at 400°C. Blind Canyon coal was used.

I. Iron and Nickel as Catalyst Promoters

Catalytic hydropyrolysis of Blind Canyon coal (hvAb, Utah) was studied using either iron, nickel, or molybdenum as catalysts in one-catalyst hydropyrolysis. In co-catalyst runs, iron or nickel was employed as a promoter for molybdenum. The first set of experiments were performed with only molybdenum to examine the effects of ultrasonic impregnation and of coal pre-extraction on liquid yields. The second set was designed to compare catalytic activities of iron and nickel as promoters for activity of molybdenum promoted by iron or nickel.

Blind Canyon coal, obtained from the Argonne Premium Coal Sample Bank, was demineralized with HF, HCl and then with HF again. Iron (III) chloride hexahydrate, nickel (II) nitrate hexahydrate and ammonium tetrathiomolybdate were used as precursors for iron, nickel and molybdenum catalysts, respectively. The molybdenum salt was introduced to coal by either ultrasonic impregnation or incipient wetness impregnation, both in aqueous solution. In all other experiments incipient wetness was used as the impregnation method. In co-catalyst runs, the coal was impregnated with molybdenum salt first, dried, and then impregnated with the iron or nickel salt.

All experiments were conducted in tubing bomb reactors heated by a fluidized sand bath. The reaction time was 1 hour and the reaction pressure was 2000 psig. The reaction temperature was 350°C. The yield of THF solubles and insolubles for the experiments are shown in Table III.4.1.

Table III.4.1.

Yields from Catalytic Hydropyrolysis of Blind Canyon Coal--Effect of Iron, Nickel, and Molybdenum at 350°C

Run	Catalyst		wt% of maf coal	
			THF Insol.	THF Sol.
# 1	-none-	Blind Canyon Coal	76	22
#2	-none-	Pre-extracted Coal	72	28
#3	0.05% Mo	(ultrasonic impreg.)	52	40
#4	0.05% Mo	Pre-extract. (ultr.impreg.)	59	39
#5	0.05% Mo	(incipient wetness impreg.)	52	42
#6	0.05% Mo	Pre-ext. (incipient impreg.)	63	34
#7	1.00% Fe		68	27
#8	0.01% Fe		74	21
#9	1.00% Fe + 0.05% Mo		40	55
#10	0.01% Fe + 0.05% Mo		43	50
#11	1.00% Ni		67	29
#12	0.01% Ni		74	21
#13	1.00% Ni + 0.05% Mo		46	50
#14	0.01% Ni + 0.05% Mo		45	52

For demineralized Blind Canyon coal, the liquid yield from hydropyrolysis with molybdenum obtained from ultrasonic impregnation run was about the same as that obtained from incipient wetness impregnation. Pre-extraction of coal before catalyst impregnation resulted in lower yields of liquids. This indicates the important role of pre-extracts in catalytic hydropyrolysis. From these experiments, molybdenum sulfide was shown to be a good catalyst for coal liquefaction even at low concentrations and relatively low temperatures.

In the iron catalyst runs, iron exhibited some catalytic activities at 1.0 wt% and no activity at 0.01 wt%. However, iron was shown to be a good promoter for molybdenum at these reaction conditions, even at very low concentrations. The amount of char produced was 41% from the 1% Fe/0.05% Mo run and 43% for the 0.01% Fe/0.05% Mo run, compared to 52% from the 0.05% Mo-only run. When used alone, nickel had about the same activity as iron in these hydropyrolysis reactions. Nickel was also a good molybdenum promoter as the char yield indicated - 46% from 1% Ni/0.05% Mo and 45% from 0.01% Ni/0.05% Mo. At this temperature (350°C), iron is better choice as a catalyst promoter than nickel because of its much lower cost and also because it promotes the effect of molybdenum slightly better.

II. Impregnation Method

Three coals, Blind Canyon (hvAb, UT), Pittsburgh #8 (hvBb, PT), and Wyodak (sub, WY), were used in this catalytic hydropyrolysis study to determine the effects of ultrasound on catalyst impregnation in various coals. All coals were Argonne Premium Samples and used without pretreatment prior to impregnation. Two series of experiments were performed: one by ultrasonic impregnation, the other by incipient wetness impregnation. The catalyst used was 1 wt% Fe/1 wt% Mo; iron (III) chloride hexahydrate and ammonium tetrathiomolybdate were used as precursors for iron and molybdenum, respectively. Hydropyrolysis experiments were conducted in shaking tubing bombs heated by a fluidized sand bath. The reaction conditions were 350°C, 2000 psi hydrogen and 1 hour reaction time. Product yields are shown in Table III.4.2.

Blind Canyon coal was also used in another set of experiments designed to assess the effects of coal pretreatment, demineralization and pre-extraction. All catalysts were introduced to coal by incipient wetness impregnation from aqueous solutions of the catalysts' precursor salts. The reaction conditions were same as the above experiments. Results are shown in Table III.4.3.

Table III.4.2. Yields from Catalytic Hydropyrolysis of Coals - Comparison of Ultrasonic and Incipient Wetness Impregnation

Run Coal	Method of Impregnation	wt% of maf coal	
		THF Insol.	THF Sol.
#15 BC	Ultrasonic Impregnation	36	62
#16 BC	Incipient Wetness Impreg.	37	63
#17 WY	Ultrasonic Impregnation	36	63
#18 WY	Incipient Wetness Impreg.	20	68
#19 PT	Ultrasonic Impregnation	45	53
#20 PT	Incipient Wetness Impreg.	42	56

The results show that ultrasound had no apparent beneficial effect on the amount of liquid produced from hydropyrolysis with Fe/Mo catalyst in all coals studied. This agrees with the results shown in last quarterly report (demineralized Blind Canyon coal with 0.05% Mo). Electron probe microanalysis (EPMA) of samples studied earlier indicated that the impregnated hydropyrolysis reaction. Wyodak coal which is a subbituminous coal had a very high degree of conversion. This shows that when an active catalyst is used high liquid yields from a low rank coal can be achieved.

Table III.4.3. Effects of Coal Pretreatment on Hydropyrolysis Yields.

Run	Catalyst	Pretreatment	wt% of maf coal	
			THF Insol.	THF Sol.
#21	0.05% Mo	-none-	62	38
#22	0.05% Mo	Demineralized	52	42
#23	0.05% Mo	Demin. + Pre-extr.	63	34
#24	0.05% Mo	Pre-extr.(added back)	61	39
#25	1% Fe/1% Mo	Demineralized	27	67

After being demineralized with HF, HCL, and HF again, Blind Canyon coal yielded more liquids than when hydropyrolyzed without being demineralized, as shown by run #21 vs. #22 and #16 vs. #25. The liquid yields increased about 4% and the total conversion toward light products increased about 10%. Demineralization caused obvious changes in the coal and could be a good pre-treatment for coal extraction which was performed because it might remove mobile phase components from the coal matrix and open up pores inside the coal particles. Such pretreatment could facilitate better catalyst dispersion. However, pre-extraction (Soxhlet extraction) removed THF solubles from the coal and caused a decrease in the liquid yields in subsequent catalytic hydropyrolysis. Two possible reasons for these decreases are oxidation of coal during the pre-extraction and drying and lack of mobile phase components which could help disperse catalyst and act as a medium for hydrogen transfer during the hydropyrolysis. When the pre-extracts were physically added back to the pre-extracted coal and both were catalytically hydropyrolyzed, the conversion (run #24) was essentially the same as that of a raw (not pretreated) coal (run #21). This suggests that the pre-extracts (mobile phase) played a significant role in catalytic hydropyrolysis because of a lack of solvent in this liquefaction process.

III. Hydropyrolysis at 400°C

Blind Canyon Coal (hvAb, Utah), from the Pennsylvania State University Coal Bank (designated DECS-6) was used in this group of experiments. The objectives, experimental procedures and reaction conditions of these experiments were the same as those for the experiments described under I except for the following: the coal was not demineralized; nickel (II) chloride hexahydrate was used instead of nickel (II) nitrate hexahydrate; only incipient wetness impregnation method was used; and the reaction temperature was 400°C. THF soluble and insoluble yields of these experiments are shown in Table III.4.4.

Table III.4.4. Yields from Catalytic Hydropyrolysis of Blind Canyon Coal Effects of Iron, Nickel, and Molybdenum at 400°C

Run	Catalyst	wt% of maf coal	
		THF Insoluble	THF Soluble
#25	0.01% Mo	39	52
#26	0.03% Mo	27	61
#27	0.05% Mo	14	74
#28	0.10% Mo	9	79
#29	1.00% Fe	56	35
#30	1.00% Fe + 0.03% Mo	47	43
#31	0.01% Fe + 0.03% Mo	26	64
#32	0.01% Ni	50	40
#33	0.05% Ni	34	56
#34	0.20% Ni	26	63
#35	1.00% Ni	14	77
#36	0.005% Ni + 0.03% Mo	15	75
#37	0.01% Ni + 0.03% Mo	15	76
#38	1.00% Ni + 0.03% Mo	11	80

Results from these experiments show that molybdenum was an extremely effective catalyst for catalytic hydropyrolysis of Blind Canyon coal at 400°C. Molybdenum amounts required for high liquid yields were 0.03 wt% of maf coal or higher. At 0.1 wt% Mo, the char (THF insolubles) was only 9 wt% (maf) of the starting coal. When only 0.05 wt% Mo was used, the char amount was still very low (14 wt%). Iron was only slightly active at this temperature even with high loading (35% liquid yields with 1% Fe). Nickel was also a good catalyst for this reaction and helped improve the liquid yields significantly, although higher amounts compared with molybdenum were needed. A very high conversion (14 wt% char) was achieved when 1.0 wt% of Ni was used. At lower concentrations of nickel the conversions were decreased significantly.

When used with molybdenum, iron was not a good promoter for molybdenum in hydropyrolysis of Blind Canyon coal at 400°C. At high loading (1 wt%) of iron with 0.03 wt% Mo, the liquid yield was lower than that of the 0.03 wt% Mo-only run, although it was higher than that of the iron-only run. At low loading (0.01 wt% iron) the conversion was about the same as that for the molybdenum only run. Nickel, however, was a very good promoter for molybdenum at these reaction conditions. Only an extremely small amount of nickel was needed

to promote molybdenum as shown in Table III.4.4. (runs #36 - #38). The char yield decreases from 27 wt% of maf coal in the 0.03% Mo-only run to 15 wt% in the 0.005% Ni + 0.03% Mo run.

Part 2. Energized Coal Liquefaction

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Laboratory experiments were performed to investigate the effect of ultrasonic energy on coal liquefaction at different solvent extraction conditions. In a series of experiments, ultrasonic waves were generated by a Fischer-Sonic Dismemberator with a titanium horn tip, which could generate an ultrasonic frequency of 21 kHz and could give a 300 watt maximum power output. The maximum energy intensity at the horn tip was 98.4 W/cm².

The coal sample used in these experiments was Blind Canyon Coal (PSOC-1503). Solvents such as: THF, THF-water, and pyridine-methanol were used with catalysts or promoter such as: ferric chloride, potassium hydroxide, or TBAH.

From results of the experiments, it was shown that catalysts did not improve the dissolution of coal under these extraction conditions. This was probably due to the low temperature of the extraction. With the help of TBAH in pyridine a significant increase in coal dissolution was observed. Under the coal dissolution conditions used, the application of ultrasonic energy approximately doubled the yield of coal dissolution.

Introduction

Coal liquefaction via solvent extraction assisted by ultrasonic energy has been studied. The dissolution of coal is clearly improved by the application of the ultrasonic energy but the magnitude of improvement depends on the properties of the solvent used.

In earlier studies, a solvent mixture composed of pyridine, methanol and a dissolution promoter, tetra-n-butylammonium hydroxide (TBAH) was found to be very effective in ultrasonic solvent extraction, and gave an extraction yield of 44%. The influence of TBAH on the extraction yield was found to be important. Since the presence of TBAH assists in the coal swelling process, the increase in extraction yield was likely due to property changes in the bituminous coal structure. The distance between coal lamellae could have been increased in the process or the strength of the van der Waals or hydrogen bonds between coal lamellae could have been effected. These changes could have caused the coal to become easier to attack by the ultrasonically energized solvent.

Experimental

Ultrasonic Generator:
Fischer-Sonic Dismemberator
Maximum output: 300 watts
Frequency: 21 kHz

Solvent and Reagents:

Methanol

Tetrahydrofuran

TBAH

FeCl₃

Pyridine

KOH

Coal:

PSOC-1503, Blind Canyon, hvb, -20M, H.V.: 14069 Btu/lb (dry), 14707 Btu/lb (dmmf).

Proximate Analysis	AS RECEIVED	Ultimate Analysis	Dry
% moisture	10.35	% ash	3.91
% ash	3.51	% carbon	77.27
% volatile	41.80	% hydrogen	5.90
% fixed carbon	44.25	% nitrogen	1.48
		% total S	.54
		% oxygen	10.94

Maceral Composition (dry basis):

vitritinite: 86.5%

fusinite: 1.4%

semi-fusinite: 3.8%

macrinite: 0.9%

micrinite: 1.5%

sclerotinite: 0.3%

sporinite: 0.9%

resinite: 0.2%

mineral matter: 4.5%

Sulfur Forms (dry basis): Pyritic: 0.02%, sulfatic: 0.00%, Organic: 0.52%**RESULTS**

1. Figure III.4.1 shows that the best ultrasonic tip intensity for THF coal extraction was close to 90 watt/cm².
2. Figure III.4.2 shows that after 60 minutes the ultrasonic extraction yield from the coal becomes constant.
3. Figure III.4.3 shows that the adding of KOH to the solvent does not increase the coal dissolution.
4. Figure III.4.4 shows that THF/water is a better solvent combination than pure THF.
5. Figure III.4.5 shows how adding TBAH to the pyridine/methanol solvent increases coal dissolution by about 23% after 90 minutes extraction.
7. Table III.4.2 summarizes the results of the solvent extraction of Blind Canyon (Utah) coal in this research.

CONCLUSION

1. Ultrasonic enhancement in low temperature solvent extraction coal is effective for solvent mixtures of pyridine/methanol/TBAH and also THF/methanol/TBAH.
2. Higher yields might be due to the high coal swelling ratio of TBAH, which could assist the ultrasonic energy to rupture the van der Waals and/or hydrogen bonds between bituminous coal lamellae.
3. In order to understand the function of the ultrasonic energy in solvent extraction of coal products analyses need to be completed. SFC and SFC/MS will be used to get more detailed information on the nature of the solvent extracts as a function of solvents used, energy level applied and other variables in the system.

Table 2: Summary of experimental data in ultrasonic coal extraction.

Solvent	Catalyst	Time (min.)	Temp. (°C)	% of coal extracted (dmmf)
THF	—	48 hr	Soxhlet (THF) b.p. 66	14.36 without ultrasonic
THF	—	10	55	14.87
THF	—	30	55	17.39
THF	—	45	55	17.84
THF	—	60	55	18.16
THF	—	60	55	3.80+14.36
THF	KOH (1%)	60	55	3.10+14.36
THF	KOH (5%)	60	55	0+14.36
THF	—	60	55	3.80+14.36
THF	FeCl ₃ (1%)	60	55	3.25+14.36
THF	FeCl ₃ (5%)	60	55	0+14.36
THF/H ₂ O = 1/1	—	60	55	5.97+14.36
THF/H ₂ O = 1/1	FeCl ₃ (1%)	60	55	6.70+14.36
THF/H ₂ O = 1/1	FeCl ₃ (5%)	60	55	4.80+14.36
Pyridine		48 hr	Soxhlet (Pyridine) b.p. 115	17.6 without ultrasonic
Py/MeOH = 2/1		90	60	20.4
Py/H ₂ O/MeOH/TBAH = 67.5/8.5/17.5/6.5		30	60	38.1
Py/H ₂ O/MeOH/TBAH = 67.5/8.5/17.5/6.5		60	60	44.1
Py/H ₂ O/MeOH/TBAH = 67.5/8.5/17.5/6.5		90	60	44.2
Py/H ₂ O/MeOH/TBAH = 67.5/8.5/17.5/6.5		30	60	21.1 without ultrasonic
Py/H ₂ O/MeOH/TBAH = 67.5/8.5/17.5/6.5		60	60	21.3 without ultrasonic
Py/H ₂ O/MeOH/TBAH = 67.5/8.5/17.5/6.5		90	60	21.6 without ultrasonic

Figure III.4.1. The Influence of the Ultrasonic Energy Intensity on Coal Extraction.

Figure III.4.2. Ultrasonic Coal Extraction by THF.

Figure III.4.3. Negative Influence on Coal Dissolution by the Addition of KOH to THF Solvent.

Figure III.4.4.

Negative Influence of Coal Dissolution by Adding Ferric Chloride to THF and THF/water.

Figure III.4.5. Influence of Coal Dissolution by Adding TBAH to Pyridine/Methanol.

Figure III.4.6. Influence of Coal Dissolution by Adding TBAH to THF/Methanol Solvent.

Task IV

Novel Catalysts for Coal Liquefaction

Program Coordinators: Christine Curtis and Dady Dadyburjor

Project IV.1

Catalytic Dehydrogenation of Model Compounds in Relation to Coal Liquefaction

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SUMMARY

It is generally accepted that the main hydrogen sources in coal liquefaction are hydroaromatic structures in added solvents, recycle oils or in coal itself. Efforts have been made to determine the hydroaromatic content in coal and recycle oils by catalytic dehydrogenation of coal ^[1,2]. However, little has been done to elucidate the nature of the dehydrogenation reaction, the ease of removal of hydroaromatic hydrogen from different structural components or the effects of solvents of different boiling points and structure. Our studies have demonstrated that the course of the dehydrogenation of a number of model compounds involves hydrogen transfer to identifiable intermediates, indicating that the determination of the relative rates of hydrogen donation of hydroaromatics in recycle solvents is of particular important in achieving insights into the chemistry of coal liquefaction. There is evidence that the quality of hydroaromatic hydrogen in recycle solvents might be more important than the total hydroaromatic content itself. Catalytic dehydrogenation, in addition to gaining information on hydrogen transfer to coal from hydroaromatic compounds, promises to be a valuable analytical technique to determine the amount and nature of hydroaromatic hydrogen in coal and to be an assessment technique for evaluation of coal liquefaction catalysts.

RESULTS AND DISCUSSION

Reggel et al. have postulated that the reduction potential, the energy required to accept an electron, is of importance in catalytic dehydrogenation. To a certain extent, this is borne out by data obtained from catalytic dehydrogenation of 9,10-dihydroanthracene(DHA) using a reduced Pd/C catalyst with several vehicles. Pyrene, with a high boiling point(393°C) and a comparatively low reduction potential ($-E_{1/2}$ 1.56V) gives 95.1% of the theoretical yield of molecular hydrogen. p-Terphenyl, b.p. 383°C with

a high reduction potential gives only 82.1% of H_2 . On the other hand, phenanthridine and anthracene, with lower boiling points and lower reduction potentials, give high H_2 yields. Results shown in Figure 1 indicate that hydrogen evolution is preferred with the use of lower reduction potential solvents with the boiling point of the solvent exerting a slight effect on hydrogen evolution.

There have been suggestions ^[3] that use of high-boiling solvents could lead to addition and other side reactions. Indeed, it would be advantageous to use low-boiling solvents for the catalytic dehydrogenation of coal, recycle oils and heavy residues. With such solvents, side reactions would be reduced and hydrogen transfer between hydroaromatics and solvent and selective removal of only hydroaromatic hydrogen would be improved.

We have succeeded in carrying out the catalytic dehydrogenation of model compounds using low-boiling solvents in the presence of stilbene, a hydrogen acceptor. These solvents, quinaldine, b.p. 248°C, 2-methylnaphthalene, b.p. 243°C, and biphenyl, b.p. 255°C, are good electron transfer reagents, accepting an electron from zerovalent palladium and transferring it to the solvent. The stilbene accepts two hydrogens to form bibenzyl.

The model hydroaromatic compounds studied included 9,10-dihydroanthracene(DHA); 9,10-dihydrophenanthrene; 1,2,3,4,5,6,7,8-octahydroanthracene(OHA) and 1,4,5,8,9,10-hexahydroanthracene(HHA). The latter compound is neither an aromatic nor a hydroaromatic compound but, with its four isolated double bonds, is rapidly converted to hydroaromatic compounds. Another hydroaromatic compound, 1,2,3,4-tetrahydroanthracene(THA) was formed during these catalytic dehydrogenation reactions. The rates of hydrogen transfer to stilbene of these compounds are quite different, indicating that not all hydroaromatic structures in recycle oils are effective in coal liquefaction. This is in keeping with recent findings of Bate and Harrison ^[4] who found, that for coal dissolution, the type of donor present may be more important than the total hydrogen donor content. The dehydrogenation of a mixture of DHA, HHA and OHA was carried out to compare the hydrogen transfer rates of these model compounds, they are in the following order: HHA>THA>DHA,DHP>OHA (Figure 2). The sequence of hydrogen transfer to stilbene and the mechanism derived for the dehydrogenation of model compounds are in good agreement with the recent findings

based on coal liquefaction ^[5]. In this reference, the hydrogen donation ability of different hydroaromatics to coal were compared. The results indicated that HHA was very active, losing hydrogen even during heating with coal. THA was active, its use would result in an increase in yield of oil. OHA was rather stable and just slightly increased oil yield.

A study of the catalytic dehydrogenation of hydroaromatic model compounds using liquefaction catalysts was performed in an effort to determine the relative activities of these catalysts. Catalysts such as MoS_2 and Fe_7S_8 which are active for coal liquefaction, are also active for catalytic dehydrogenation of the model compounds studied (Figure 3). A comparison of the relative activities of these catalysts can also be obtained. Our studies on catalytic dehydrogenation of model compounds and on direct coal liquefaction indicate a strong parallel between these two as far as the catalyst activity is concerned. It also establishes catalytic dehydrogenation as a novel, rapid technique for assessing and even comparing the activity of different catalysts for direct coal liquefaction.

CONCLUSIONS

For vehicles boiling above 345°C , both boiling point and reduction potential of the solvent employed appear to influence the palladium-catalyzed dehydrogenation of model hydroaromatic compounds. For certain solvents that boil about 245°C (a hundred degrees lower) the dehydrogenation of the same compounds occurs readily in the presence of a good hydrogen acceptor such as stilbene. With lower boiling vehicles, adduction reactions are minimized while the selective removal of hydroaromatic hydrogen is improved. The palladium-catalyzed dehydrogenation involves transfer of an electron from zerovalent palladium to the solvent. The solvent then removes a proton from the hydroaromatic compound. The slow step is the removal of hydrogen from the reduced solvent. The mechanism of removal of different hydroaromatic hydrogen atoms may occur through various intermolecular transfers. There is a need to quantify not only the total hydroaromatic content in coal and recycle solvents but also to determine the contribution from individual types of hydroaromatic compounds. It appears that catalytic dehydrogenation can be developed as a tool for the assessment of the activity of coal liquefaction catalysts.

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Table 1. Dehydrogenation of 9,10-DHA with Pd/C in the Presence of a Hydrogen Acceptor

Catalyst	Vehicle	Feed ^a		H ₂ Removed	
		DHA g	Stilbene g	As Gas %	As Bibenzyl ^b %
Pd/C	Quinaldine 248°C	0.2	0.2	2.7	92.5
Pd/CaCO ₃	Quinaldine 248°C	0.2	0.2	14.5	74.0
Pd/C	2-Methylnaphthalene 243°C	0.2	0.2	5.5	93.4
Pd/CaCO ₃	2-Methylnaphthalene 243°C	0.2	0.2	8.8	90.4
Pd/CaCO ₃	Biphenyl 255°C	0.2	0.2	2.3	87.2
Pd/C	Quinaldine 248°C	0.3	0.15	50	50

a) DHA and stilbene have the same molecular weight
b) formed by addition of hydrogen to stilbene

Figure 1. Dehydrogenation of 9,10-DHA with reduced Pd/C using various solvents.

Figure 2. Dehydrogenation of a mixture of DHA, OHA, and HHA in the presence of a hydrogen acceptor.

Figure 3. Dehydrogenation of 9,10-DHA using liquefaction catalysts.

Project IV.2

Evaluation of Dispersion Methods for Slurry Phase Catalysts

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INTRODUCTION

Slurry phase catalysts have been shown to be very active for coal liquefaction. Pellegrino and Curtis (1989) compared the activity of three different types of molybdenum catalysts: an oil-soluble molybdenum naphthenate, a presulfided molybdenum on alumina, and a precipitated MoS_2 catalyst. The catalyst generated *in situ* from molybdenum naphthenate was the most active in terms of hydrogenation and heteroatom removal as well as showing the highest coal conversion and product upgrading. Kim and Curtis (1990) evaluated catalyst precursors of molybdenum, nickel, and vanadium for their activity in coprocessing of coal with resid. The activity of the molybdenum and nickel precursors for coal conversion and oil production was high while that for the vanadium was low. The research undertaken in this project was to evaluate the activity of slurry phase iron catalysts for pyrene hydrogenation and compare their activity to that of molybdenum naphthenate. Different methods of dispersion were evaluated.

The objectives of this research were (1) to establish the activity of slurry phase iron catalysts for pyrene hydrogenation; (2) to compare the activity of the slurry phase iron catalysts to MoS_2 generated *in situ* from molybdenum naphthenate; and (3) to evaluate the effect of different methods of dispersion on the activity of iron-based catalysts in comparison to their effect on the activity of finely divided MoS_2 from molybdenum naphthenate. Three different methods of catalyst dispersion were tested. These methods were (1) *in situ* where the catalyst precursor was added directly to the pyrene/hexadecane system and was reacted in the presence or absence of sulfur; (2) *ex situ* where the catalyst precursor reacted in the presence of pyrene in hexadecane was reclaimed and used in a second pyrene hydrogenation reaction and (3) two stages where

the catalyst precursor was added to hexadecane, hydrogen, and sulfur and reacted for 3 min. After reaction, the pyrene was introduced into the reactor along with hydrogen and reacted for 30 min. The product distribution from each method of dispersion was determined and compared. Since the observed activities of the iron catalyst precursor and the molybdenum naphthenate were substantially different, a procedure was developed using UV-visible spectroscopy to determine the stability of the slurry phase iron catalysts at liquefaction conditions. The amount of organometallic complex remaining after different reaction times was determined and compared.

BACKGROUND

Comparisons of the catalytic activities of iron and molybdenum catalysts used in reactions of model coal molecules showed high catalytic activity for $\text{Fe}(\text{CO})_5$ or $\text{Fe}(\text{CO})_5\text{-S}$ for hydrogenation of aromatic species (Suzuki et al., 1989). However, $\text{Mo}(\text{CO})_6\text{-S}$ more strongly promoted hydrogenation of polyaromatic compounds as well as hydrogenation of some phenyl carbon bonds. The effect of dispersion methods had also been examined using iron catalysts in which an iron oxide (FeOOH) precursor was dispersed onto the solid coal matrix (Cugini et al., 1991). Other iron systems, such as Fe_2O_3 dispersed on carbon black, iron incorporated into coal by impregnating with FeCl_3 and to lignite by cation exchange and a sulfated Fe_2O_3 , have been used as finely dispersed catalysts for coal liquefaction and characterized by Mossbauer and XAFS spectroscopy (Huffman et al., 1991). The relation between chemical structure and reactivity has not yet been established.

Ikari and Hayakawa (1990) have developed a process for catalytic hydroliquefaction which involved mixing coal with petroleum heavy ends and iron containing catalysts which was followed by first-stage liquefaction at temperature between 400 to 470°C and 150 to 200 atm for 30 to 90 min. The first stage was followed by second-stage processing of a distillation cut obtained from the first stage using a $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst. Bacaud (1991) developed a multistage coal liquefaction process in which unsupported high-surface-area iron oxides were used as catalysts to prevent retrograde reactions. The catalysts were promoted by the incorporation of a small amount of molybdenum.

Finely divided iron (III) oxides and iron oxyhydroxides modified with either (SO_4^{2-}

or molybdate (MoO_4^{2-}) anions used in coal liquefaction have shown increased coal conversion and selectivities to n-pentane soluble products (Pradhan et al., 1991). A bimetallic catalyst, $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4^{2-}$ that consisted of 50 ppm Mo and 3500 ppm Fe, was active for coal conversion with a selectivity for oil. The effect of the pyrite to pyrrhotite ratio produced from ferric sulfide as a precursor on coal liquefaction has also been studied. A definite effect of intermediate stoichiometry of the ratio is observed on the selectivity to lighter products at higher liquefaction temperatures (Stansberry et al., 1991).

EXPERIMENTAL

Pyrene hydrogenation reactions with slurry phase iron catalysts and molybdenum naphthenate performed using three different experimental procedures of generating the catalysts: *in situ*, *ex situ*, and two stage. The catalyst obtained *in situ* was generated by introducing the catalyst precursor at a level of 900 to 1100 ppm metal directly into the reaction system of 2 wt % pyrene in hexadecane. The reactants were charged into a 20 cm^3 stainless steel tubular microreactor. The reactions were conducted at 380 or 425°C for 30 or 60 minutes with a hydrogen pressure of 1250 psig at ambient temperature and an agitation rate of 550 rpm. Reactions were performed both with and without sulfur. When sulfur was present, it was introduced as elemental sulfur in a stoichiometric ratio of 3:1 sulfur to metal.

The catalysts precursors used in the *in situ* experiments were iron (III) naphthenate, iron (III) acetylacetonate, iron (III) citrate hydrate, iron (III) 2-ethyl hexanoate, and molybdenum naphthenate for comparison. Iron (III) acetylacetonate (99% purity) was obtained from Eastman Kodak Company; iron (III) citrate hydrate (98% purity) was obtained from Aldrich Chemical Company; iron (III) 2-ethylhexanoate (8 to 11.5% Fe) and iron (III) acetylacetonate (99% purity) were obtained from Strem; and the molybdenum naphthenate was obtained from Shepherd Chemical. All of the catalyst precursors were used as received.

Several sets of experiments were performed with naphthalene using selected slurry phase iron catalysts or molybdenum naphthenate using the *in situ* method. The effect of sulfur on the activity of iron acetylacetonate catalyst for naphthalene hydrogenation was evaluated by introducing sulfur in sulfur to iron ratios ranging from 3:1, 1:1, 0.33:1,

0.2:1, to 0:1. The effect of time and temperature on catalyst activity was evaluated reacting naphthalene in the presence of iron acetylacetonate at two reaction times, and 60 min, and two reaction temperatures, 380 and 425°C.

The *ex situ* catalyst was generated by collecting the catalyst solids produced during an *in situ* reaction and then drying the solids for 72 hours in a vacuum oven at 60°C. The dried solids were then introduced into the reactor containing pyrene in hexadecane solution at a level of 900-1100 ppm active metal.

Two-stage pyrene hydrogenation reactions were performed by producing the catalyst in the first stage using a system of catalyst precursor, excess sulfur, hexadecane and a hydrogen pressure of 1250 psig at ambient temperature. After 30 min of reaction the reactors were removed from the sandbaths, cooled, and then charged with pyrene and 1250 psig hydrogen introduced at ambient temperature. The pyrene hydrogenation reaction was then performed at 380°C for 30 min.

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

The product slates were determined for each reaction and the amount of hydrogenation of the aromatic determined. The percent hydrogenation is defined as the moles of hydrogen required to produce the product slate as a percentage of the moles of hydrogen required to produce the most hydrogenated liquid product. The most hydrogenated liquid product from naphthalene was considered to be decalin and from pyrene, perhydropyrene.

An analysis procedure for measuring the amount of organometallic complex that reacted under liquefaction conditions was developed using UV-visible spectroscopy. The procedure used iron naphthenate in hexadecane as the reaction system and monitored the concentration of iron naphthenate present in the liquid phase after different reaction times. A calibration curve of absorbance versus iron naphthenate concentration was developed using a Varian Model DMS 200 UV-visible spectrometer. The reaction of iron

naphthenate at 380°C in 1250 psig hydrogen introduced at ambient temperature was conducted at times of 2, 5, 15, and 30 min. The liquids present after reaction were evaluated at two absorbance wavelengths to determine amount of organometallic complex remaining.

RESULTS AND DISCUSSION

Naphthalene Hydrogenation Reactions. The activity of slurry phase iron and molybdenum catalysts for naphthalene hydrogenation was evaluated in the presence and absence of sulfur. Molybdenum naphthenate (MoNaph) was used as the Mo catalyst precursor and iron acetylacetonate (FeAcAc) as the Fe precursor. MoNaph with sulfur converted the most naphthalene to tetralin and gave the highest percent hydrogenation (% HYD) as shown in Table 1. MoNaph without sulfur converted nearly 30% of naphthalene to tetralin while FeAcAc showed little activity with sulfur and none without. The effect of sulfur on the activity of the Fe catalyst generated from FeAcAc was also examined (Table 2). The highest S to Fe ratio of 3:1 gave the highest amount of conversion of naphthalene to tetralin, ~6%. Sulfur present at a 1:1 S to Fe ratio showed slight activity while S to Fe ratios of 0.33:1 and lower showed no activity.

The effect of increased temperature and reaction time on the activity of FeAcAc was evaluated as presented in Table 3. Increased reaction time at 380°C in reactions with and without sulfur showed no effect on the reaction product produced. A higher reaction temperature of 425°C and time at 60 min yielded higher conversion of naphthalene and higher % HYD than any of the other reactions.

Pyrene Hydrogenation. Four slurry phase iron catalysts were tested for their activity for pyrene hydrogenation at two temperatures, 380 and 425°C, in the presence and absence of sulfur as described in Table 4. Iron naphthenate (FeNaph) produced the most pyrene hydrogenation of any of the slurry phase iron catalysts. At 380°C with sulfur 12% HYD of pyrene occurred while at 425°C with sulfur 11.5% HYD occurred. In both cases, dihydropyrene (DHP) was the primary product, hexahydropyrene isomers were the secondary products while a small amount of tetrahydropyrene (THP) was formed. Of the other three slurry phase iron catalysts tested with sulfur, FeAcAc reacted at 425°C was the only one which showed substantial hydrogenation of 9.3% and yielded the same products as FeNaph. All of the other systems with sulfur, Fe Citrate-Hydrate

(FeCH) and Fe 2-ethylhexanoate (Fe 2-EH) showed limited activity for pyrene hydrogenation.

The reactions with the slurry phase iron catalysts without sulfur resulted in low conversion of pyrene at 380°C and somewhat higher conversion of pyrene at 425°C. Hence, although these catalyst precursors were all treated under equivalent reaction conditions, they exhibited different activities for pyrene hydrogenation. Two primary reasons for this behavior have been hypothesized: (1) the organometallic complexes broke down at different rates at liquefaction conditions and (2) the reaction rates and possible composition of the active catalytic species, iron sulfide, are different for each of the different complexes.

A comparison of the activity of FeNaph at 380 and 425°C, in the presence and absence of sulfur, and for times of 30 and 60 min is given in Table 5. The presence of sulfur at a 3:1 stoichiometric ratio of sulfur to iron greatly influenced the activity of FeNaph since similar product slates were observed at both reaction temperatures and reaction times when sulfur was added. The reactions without sulfur showed much less activity but were affected positively by both increased temperature and reaction time.

Reactions were also performed with MoNaph with and without sulfur at 380 and 425°C for 30 min. The presence of sulfur in the reactor allowed the Mo released from MoNaph to form finely divided MoS₂ which was an active catalyst for pyrene hydrogenation (Kim et al., 1989). At 380°C, without sulfur, the reaction with MoNaph yielded 11.7% HYD with DHP as the primary product and THP as the secondary product. At 380°C, with sulfur, the reaction with MoNaph yielded 34.6% HYD of pyrene with HH isomers being the primary products and a substantial amount of decahydropyrene (DCHP) being formed.

At 425°C, the reaction of MoNaph without sulfur showed less activity for pyrene hydrogenation than did the system with sulfur. Without sulfur the % HYD of pyrene was somewhat higher at 13.8% than at 380°C which yielded 11.7%. But the reaction at a higher temperature, 425°C, with sulfur gave less activity than at 380°C with sulfur. At 425°C, thermodynamics are limiting the amount of pyrene conversion allowed and, hence, lowers the amounts of partially saturated compounds produced in the reaction (Ting et al., 1992).

Comparison of Methods of Dispersion on the Activity of Catalysts. Three

methods were used to test the effect of dispersion on the catalytic activity of the generated catalysts. The catalysts were generated *in situ*, *ex situ*, and in a two-stage batch process as presented in Table 6. The reaction conditions were 2 wt % pyrene in hexadecane with 900-1100 ppm Fe or Mo, introduced as FeNaph or MoNaph, reacted for 30 min with a 3:1 sulfur to metal ratio and 1250 psig hydrogen introduced at ambient conditions. Comparison of FeNaph and MoNaph activity for pyrene hydrogenation using the *in situ* method revealed that MoNaph resulted in nearly three times as much hydrogenation as FeNaph. HHP was the primary product for MoNaph while DHP was the primary product for FeNaph. The *ex situ* method, in which the catalyst produced in an *in situ* experiment was added to pyrene hydrogenation reaction system resulted in less activity for both FeNaph and MoNaph. FeNaph did not convert any pyrene while MoNaph yielded about half the amount of hydrogenation observed in the *in situ* reaction.

Two-stage batch reactions were performed in which the catalyst precursor was introduced into hexadecane in the first stage and then reacted in the presence of sulfur and hydrogen for 30 min at 380°C. At that point, the reaction was quenched, gas released and pyrene and a new charge of hydrogen added. The system, including pyrene, was then reacted again for 30 min. The two-stage reaction with FeNaph yielded about 6% conversion of pyrene to DHP so that its activity was much less than that of the *in situ* generated catalyst. By contrast, the two-stage reaction with MoNaph yielded higher pyrene hydrogenation, 40.7% for the two-stage compared 34.6% for the *in situ* single-stage. Hence, the catalytic activity of MoNaph appeared to increase with the two-stage treatment while FeNaph did not.

Concentration of Iron Naphthenate at Liquefaction Conditions. FeNaph in hexadecane with an initial concentration of 1000 ppm Fe was reacted at 380°C with a hydrogen charge of 1250 psig hydrogen at ambient temperature. The amount of FeNaph remaining in the solution after 2, 5, 15, and 30 min was monitored at 450 nm. The amount of FeNaph present after 2 min was 470 ppm which was less than half of the amount of FeNaph present prior to reaction. After 5 min of reaction only 20 ppm FeNaph remained, while after 30 min of reaction only 4 ppm of FeNaph remained. This procedure will be used on the other slurry phase catalysts to determine the reactivity of the iron and molybdenum complexes at liquefaction conditions.

SUMMARY

The slurry phase iron catalysts showed a small amount of activity for hydrogenation of naphthalene. The higher temperature of 425°C and a 3:1 addition of sulfur to iron increased the activity of the slurry phase iron catalyst; however, the activity of the iron sulfide catalyst formed was substantially less than that observed from the slurry phase MoS₂ catalyst generated from molybdenum naphthenate and excess sulfur.

The activity of the slurry phase iron catalysts for pyrene hydrogenation depended upon the ligand, reaction temperature, and the addition of sulfur. Iron naphthenate was the most active of the iron precursors. The higher reaction temperature of 425°C and a longer reaction time of 60 min were also beneficial for pyrene hydrogenation.

The method by which the catalyst was dispersed in the pyrene/hexadecane system made a substantial difference in the activity of the catalyst. Iron naphthenate showed the greatest activity using the *in situ* dispersion method and the least using the *ex situ* method. Molybdenum naphthenate also showed less activity with the *ex situ* method compared to the *in situ* method but showed the most activity with the two-stage method.

Analysis of the stability of iron naphthenate at liquefaction conditions revealed that the iron complex broke down quickly, making the Fe available for further reaction with sulfur. The other iron and molybdenum complexes are currently being tested to evaluate their stability.

NOMENCLATURE

FeNaph	=	iron naphthenate
FeCH	=	iron citrate hydrate
FeAcAc	=	iron acetylacetonate
Fe 2-EH	=	iron 2-ethylhexanoate
PYR	=	pyrene
% HYD	=	percent hydrogenation
DHP	=	dihdropyrene
THP	=	tetrahydropyrene
HHP	=	hexahydropyrene
DCHP	=	decahydropyrene

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Table 1. Product Distributions from Naphthalene Hydrogenation Reactions Using Different Catalysts

Product Distribution (mol %)	Catalysts				
	No Catalyst	Mo Naphthenate	Mo Naphthenate with S ^a	Iron Acetylacetonate	Iron Acetylacetonate with Sulfur ^a
Naphthalene	99.6	70.4 ± 1.1	37.3 ± 1.9	100.0 ± 0.0	94.2 ± 0.5
Tetralin	0.4	29.6 ± 1.1	62.4 ± 1.9	0.0	5.8 ± 0.5
Decalin	0.0	0.0	0.3 ± 0.02	0.0	0.0
Butylbenzene	0.0	0.0	0.0	0.0	0.0
% Hydrogenation		11.6 ± 0.5	24.6 ± 0.7	0.0	2.5 ± 0.2

a. S to Fe ratio is 3:1.

Table 2. Product Distributions from Naphthalene Hydrogenation Reactions Using Iron Acetylacetonate and Different Amounts of Sulfur

Product Distribution (mol %)	Sulfur to Iron Ratio				
	3:1	1:1	0.33:1	0.2:1	0:1
Naphthalene	94.2 ± 0.5	98.7 ± 0.5	100	100	100.0 ± 0.0
Tetralin	5.8 ± 0.5	1.3 ± 0.5	trace	0.0	0.0
Decalin	0.0	0.0	0.0	0.0	0.0
Butylbenzene	0.0	0.0	0.0	0.0	0.0
% Hydrogenation	2.3 ± 0.2	0.5 ± 0.2	0.0	0.0	0.0

Reaction Conditions: 900-1100 ppm Fe, 2 wt % naphthalene in hexadecane, 1250 psig hydrogen at ambient conditions, 380°C, 30 min.

Table 3. Effect of Time and Temperature on Catalytic Activity of Iron Acetylacetonate for Naphthalene Hydrogenation

	380°C		380°C		425°C		425°C	
	No Sulfur		3:1 S to Fe		No Sulfur		3:1 S to Fe	
Products (mol %)	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min
Naphthalene	100±0.0	100±0.0	94.2±0.5	96.4±0.8	NP	99.8±0.3	NP	83.7±2.2
Tetralin	0	0	5.8±0.5	3.6±0.8	NP	0.2±0.3	NP	16.3±0.4
% HYD	0	0	2.3±0.2	1.5±0.3	NP	0±0.0	NP	6.5±0.9

Table 4. Effect of Temperature on the Activity of Iron Complexes for Pyrene Hydrogenation

Product Distribution (mol %)	Fe Naphthenate		Fe Citrate-Hydrate		Fe Acetylacetonate		Fe 2-ethyl-Hexanoate	
	380°C	425°C	380°C	425°C	380°C	425°C	380°C	425°C
3:1 S to Fe Ratio								
PYR	49.7±1.0	52.9±1.9	93.3±0.7	NP	95.6±0.7	61.6±0.6	100	90.5±0.7
DHP	32.1±0.5	29.1±0.5	6.7±0.7	NP	4.4±0.7	24.0±0.5	0	9.5±0.7
THP	2.9±0.1	3.2±0.3	0	NP	0	2.2±0.1	0	0
HHP1	7.3±0.2	7.1±0.5	0	NP	0	5.7±0.1	0	0
HHP2	8.1±0.3	7.8±0.6	0	NP	0	6.6±0.2	0	0
% HYD	12.0±0.3	11.5±0.6	1.0±0.1	NP	0.6±0.1	9.3±0.1	0.0	1.4±0.1
No Sulfur								
PYR	98.2±0.1	87.9±0.2	100.0±0	NP	98.8±0.8	93.1±0.5	100	94.2±0.2
DHP	1.8±0.1	12.1±0.2	0	NP	1.2±0.8	6.9±0.5	0	5.8±0.2
% HYD	0.3±0.0	1.7±0.0	0	NP	0.2±0.0	1.0±0.1	0.0	0.8±0.0

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

PYR = pyrene DHP = dihydroxyrene THP = tetrahydroxyrene NP = not performed
HHP1 = hexahydroxyrene HHP2 = hexahydroxyrene % HYD = percent hydrogenation

Table 5. Effect of Time, Temperature, and Sulfur on the Activity of Fe Naphthenate and Mo Naphthenate for Pyrene Hydrogenation

Product Distribution (mol %)	Fe Naphthenate				Fe Naphthenate				Mo Naphthenate			
	380°C				425°C				380°C		425°C	
	No Sulfur		3:1 S to Fe		No Sulfur		3:1 S to Fe		No Sulfur	3:1 S to Mo	No Sulfur	3:1 S to Mo
	30 min	60 min	30 min	60 min	30 min	60 min	30 min	60 min	30 min	30 min	30 min	30 min
PYR	98.2±0.1	95.7±0.3	49.7±1.0	51.2±0.5	87.9±0.2	81.3±0.2	52.9±1.9	51.0±0.3	39.3±1.4	14.7±1.4	45.5±1.5	33.1±0.5
DHP	1.8±0.1	4.3±0.3	32.1±0.5	28.8±0.4	12.1±0.2	18.7±0.2	29.1±0.5	27.6±0.8	44.7±1.5	18.7±1.5	30.5±1.2	22.1±0.1
THP	0	0	2.9±0.1	3.1±0.1	0	0	3.2±0.3	3.2±0.3	11.9±0.9	7.5±0.6	5.9±0.3	4.5±0.2
HHP1	0	0	7.3±0.2	7.6±0.1	0	0	7.1±0.5	8.8±0.2	1.5±0.2	17.1±0.7	7.6±1.2	14.2±0.2
HHP2	0	0	8.1±0.3	9.4±0.2	0	0	7.8±0.6	9.4±0.2	2.6±0.2	26.4±1.0	10.7±1.8	18.1±0.1
DCHP1	0	0	0	0	0	0	0	0	0	3.3±0.4	0	1.5±0.9
DCHP2	0	0	0	0	0	0	0	0	0	5.1±0.7	0	2.3±0.5
DCHP3	0	0	0	0	0	0	0	0	0	7.3±0.8	0	3.8±0.9
% HYD	0.3±0.0	0.6±0.0	12.0±0.3	12.3±0.1	1.7±0.0	2.7±0.1	11.5±0.6	12.7±0.1	11.7±0.4	34.6±1.7	13.8±1.0	23.7±0.6

Reaction Conditions: 900-1100 ppm Fe, 1250 psig hydrogen pressure at ambient conditions, 2 wt % pyrene in hexadecane.

PYR = pyrene DHP = dihydroxyrene THP = tetrahydroxyrene % HYD = percent hydrogenation
HHP1, HHP2 = isomers of hexahydroxyrene DCHP1, DCHP2, DCHP3 = isomers of decahydroxyrene

Table 6. Comparison of Methods of Dispersion of Iron and Molybdenum Precursors on the Hydrogenation of Pyrene

Product Distribution (mol %)	Fe Naphthenate			Mo Naphthenate		
	In Situ	Ex Situ	Two Stage	In Situ	Ex Situ	Two Stage
PYR	49.7±1.0	100.0±0.0	94.2±1.0	14.7±1.4	33.3	10.2±1.0
DHP	32.1±0.5	trace	5.8±1.0	18.7±1.5	32.3	14.2±0.5
THP	2.9±0.1	0	0	7.5±0.6	9.1	6.1±0.3
HHP1	7.3±0.2	0	0	17.1±0.7	10.1	17.7±0.6
HHP2	8.1±0.3	0	0	26.4±1.0	15.4	27.7±1.0
DCHP1	0	0	0	3.3±0.4	trace	4.9±0.9
DCHP2	0	0	0	5.1±0.7	0	7.5±0.6
DCHP3	0	0	0	7.3±0.8	0	10.8±1.0
PHP	0	0	0	trace	0	0.9±0.8
% HYD	12.0±0.3	0	0.8±0.1	34.6±1.7	18.1	40.7±0.6

Reaction Conditions: 900-1100 ppm Fe or Mo, 380°C, 30 min, 3:1 S to metal ratio, 1250 psig hydrogen at ambient conditions, 2 wt % pyrene hexadecane.

PYR = pyrene DHP = dihydropyrene THP = tetrahydropyrene PHP = perhydropyrene
HHP1 = hexahydropyrene HHP2 = hexahydropyrene % HYD = percent hydrogenation

Table 7. Change in Iron Naphthenate Concentration on Heating at Liquefaction Conditions

Reaction Time (min)	Fe Naphthenate Concentration (ppm)*
0	996
2	470
5	20
15	10
30	4

Reaction Conditions: 1000 ppm Fe in iron naphthenate in hexadecane, 380°C, 1250 psig hydrogen at ambient conditions.

* Monitored at 450 nm.

Project IV.3

Improved Catalysts for Coal Liquefaction and Co-Processing: New Initiative in Dispersed Slurry Phase Catalysis

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1. INTRODUCTION

This year we began a new initiative dealing with slurry phase catalysts. These catalysts are being tested in a trickle flow reactor system using a fixed bed of small (powdered) particles and a tubing bomb microreactor. We are performing model compound experiments using iron based catalysts. Our idea was to find an active catalyst for the model compound reaction first, and then to apply this catalyst to coal liquefaction. Our coal runs are now just beginning and so the results reported herein deal mainly with the model system. Our objective is to determine conditions which maximize the activity for hydrogenation and cracking reactions. This should provide insight into how iron based catalysts function in coal liquefaction and how to pretreat the catalysts for maximum activity and desired selectivity.

2. EXPERIMENTAL SECTION

Except for the tubing bomb batch reactions which will be discussed later, most of the reaction experiments were carried out in a CDS 900 trickle bed reactor system which has been described in detail elsewhere^[3]. Three kinds of catalyst tested were Ni-Mo/Al₂O₃

(Shell 324, 1/16"), Fe-1 (Harshaw Chemical Co, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, 35-60 mesh), and Fe-2 (Strecher Chemicals Inc, unsupported Fe_2O_3 powder). The catalyst was packed in the central 6 inch section of the tube reactor, which is 18 inches long. Different structures of reactor tube were designed to hold the catalysts. For Ni-Mo/ Al_2O_3 , the catalyst was preceded in the reactor by 6 inches of 3 mm glass beads and followed by 6 inches of 3 mm glass beads which was supported on glass wool. Fe-1 catalyst was held in a basket made of 400 mesh stainless steel screen and the glass beads were the same as that for Ni-Mo. A 0.5 μm stainless steel frit was used to hold Fe-2 catalyst with the glass beads of 0.1-0.12 mm preceding the catalyst and nothing following.

In all the experiments, the reactor was operated at about 1000 psi at a hydrogen flow rate of 100 ml/min (STP) which was in large stoichiometric excess. Nitrogen was used to purge and pressurize the reactor before starting the reaction. The reactant feed solution contained 2 wt % naphthalene (Fisher, >99%) in mineral oil (Humco) in most of the experimental runs except for the vapor phase reactions, in which cases toluene and cyclohexane were used as solvents. The product samples were sampled periodically from the reactor effluent and analyzed with a Varian 3300 gas chromatograph. Temperature programming was used to improve peak resolution and decane was used as an internal standard.

3. RESULTS AND DISCUSSION

I. Hydrogenation Activity of Iron Catalysts

In the first part of the experiment when the catalyst activity was of interest, the liquid

feedstock flow rate was 0.2 ml/min except for the Ni-Mo catalyst, in which case different flow rates were tested. Temperature was varied from 200°C to 425°C to examine the dependence of activity on the reaction conditions. A relative activity A_H and a cracking activity A_C were defined as follows to characterize the extent of the hydrogenation and cracking reactions, respectively.

$$A_H = \frac{2 * M_T + 5 * M_D}{5 * (M_N + M_T + M_D)} \quad (1)$$

$$A_C = 1 - \frac{(M_D + M_T + M_N)}{M_{N0}} \quad (2)$$

Where, M_N : moles of naphthalene (NAPH) in 100 g liquid product

M_T : moles of tetralin (TET) in 100 g liquid product

M_D : moles of decalin (DEC) in 100 g liquid product

M_{N0} : moles of NAPH in 100 g liquid feed

Ten experimental runs with catalysts were carried out in this part: one with Ni-Mo, two with Fe-1 and the other seven with Fe-2. In addition, a blank test was performed at temperatures up to 400°C and showed that the reactor filled with glass beads alone had negligible activity for naphthalene hydrogenation. In many of the experiments, especially at high temperature, the total moles of NAPH, TET and DEC were less than the moles of NAPH feed. We suggest that the missing material probably results from (1) undetected reactions giving volatile gaseous products and coke deposits on the catalyst, (2) unidentified products which were mixed with the cracking products of mineral oil at high temperature. This is the basis for our definition of cracking activity A_C in equation (2).

Ni-Mo (Run #1) This reaction was used to test the equipment and as a basis of comparison for later runs. Ten different reaction conditions were selected for Ni-Mo catalyst in a total run of 864 hrs. No obvious deactivation was observed even though a fairly severe condition (425°C) was employed. Cracking activity was fairly low except at the upper temperature 400°C where it was about 10 % of the NAPH feed. It can be seen from Figure 1 in which we have plotted the A_H vs. temperature at the liquid flow rate of 0.2 ml/min, that an optimum temperature existed (~310°C). We suggest that this results from the thermodynamics of the reactions. Low temperature favors the exothermic hydrogenation reactions, but at too low a temperature, the reaction rate is slower. At 300°C, A_H decreased with the increase of liquid flow rate (Figure 2). This phenomenon can be attributed to the decrease of residence time as the flow rate is increased.

Fe-1 (Harshaw, Runs #2, #3) This catalyst was a low surface area Fe_2O_3 on Al_2O_3 with particle size of 35-60 mesh. The reaction run #2 with Fe-1 catalyst was begun first at 400°C (Run #2). Low A_H was observed and it kept decreasing although the temperature had been changed to 300°C. Therefore, the reaction was repeated with 300°C as the starting temperature (Run #3). The relative activity was so high that neither unreacted naphthalene nor tetralin was detected. When the temperature was increased to 400°C, A_H decreased to about zero again and activity could not be restored upon returning the temperature to 300°C. These results obviously show that, in both runs, the catalyst has undergone a rapid deactivation probably by coking from the cracking of naphthalene. About half of the naphthalene products was not found and a number of unidentified lighter components appeared on GC output. As for the activity decrease at 300°C in the Run #2, it was

Figure 1. The dependence of A_H on temperature

Figure 2. The dependence of A_H on liquid flow rate

probable that during the preceding 96 hrs at 400°C, the catalyst was coked, resulting in the activity loss. In both runs the cracking activity was high at 400°C (30-50 %), especially in Run #2 with the fresh catalyst.

Fe-2 (Strem, Runs #4-#10) Seven runs were performed with Fe₂O₃ catalyst powder from Strem Chemical Inc. The different reaction conditions are shown in Table 1. Run #4 showed evidence of catalyst deactivation throughout the run, while Run #5 had approximately constant activity. Both runs showed little activity in the first 5 to 6 hours indicating an activation of the catalyst by H₂ reduction. This view was supported by the results of Runs #6, #7 when the catalysts were H₂ pre-reduced before reaction and Run #8 (Fig 3) in which the temperature was held constant at 250°C and samples taken every two hours during the first 24 hours. Since the main difference in Run #4 and Run #5 was only the initial temperature, the results indicated that this initial activation temperature may be important for subsequent catalyst performance.

Table 1. Reaction Conditions with Fe-2 Catalyst

Run No	Initial Temp. (°C)	Temp. Range (°C)	Cat.wt. (g)	H ₂ Pre-Reduction	CS ₂ in Feed
4	250	250--400	22.81	No	No
5	300	300--400	21.84	No	No
6	250	250--400	22.13	Yes	No
7	200	200--350	22.84	Yes	No
8	250	const. 250	22.85	No	last 32 hrs
9	250	const. 250	22.59	No	first 92 hrs
10	250	const. 250	22.64	No	first 48 hrs

In order to further investigate the effect of pre-reduction of the iron catalyst, two experimental runs (Runs #6, #7) were carried out with catalyst being partially reduced in a H_2 atmosphere for 24 hrs before starting the liquid feed. The reduction conditions were 1000 psi, 400°C, with H_2 flow rate 100 ml/min (STP). Catalyst in Run #7 was cooled down in the same H_2 atmosphere at 200°C for 1 hr while catalyst in Run #6 wasn't. The results showed that the partial reduction of catalyst generally yielded higher relative activity, although the temperature causing significant cracking was moved up to 350°C rather than 400°C observed before. Comparing the behavior of catalyst with and without pre-reduction, it was concluded that unsupported iron oxide in the ferric state would probably have very small hydrogenation activity. Proper reduction to its metallic or ferrous state is required to activate its surface. Experiments are underway to test the implications of these results with coal.

The test results with sulfur in the feed are shown in Fig 3. The source of sulfur is in the form of carbon disulfide which converts to H_2S extremely fast under the reaction condition^[2]. The amount of CS_2 in the feed was 2.375 wt% to give a concentration of sulfur of 2 wt%. The liquid feed without CS_2 was charged in Run #8 for the first 72 hrs and then switched to the feed with CS_2 , when the relative activity reached a relatively stable level. The A_H dropped continuously to about zero after 32 hrs during this process indicating that the hydrogenation reactions have been inhibited by the presence of CS_2 . Two more runs were performed by charging the feed with CS_2 in the first 92 hrs (Run #9) and 48 hrs (Run #10) respectively, and normal feed was then provided after that. The results showed no reaction at all once there was CS_2 in the feed, and A_H could not be restored to its normal

Figure 3. Relative activity A_H vs. time at 250°C

level. This obviously indicates that H_2S has poisoned the iron catalyst permanently for the hydrogenation reaction and/or that the sulfide form of the iron is much less active than the reduced form, because both runs showed very small, but stable A_H although the residual H_2S concentration in the reactor has become less and less. This inhibition effect of H_2S is consistent with the earlier works by Rhee et al.^[1] with naphthalene hydrogenation in batch reactor using Ni-Mo/ Al_2O_3 catalyst and Sapre^[2] with biphenyl hydrogenation in the continuous reactor using Co-Mo/ Al_2O_3 catalyst.

II. Continuous Slurry Phase Iron Catalyst Reaction

As part of this research, we modified the CDS reactor system to allow pumping of a dispersed slurry phase catalyst feed with a model compound. A feed containing a dispersed

iron particle catalyst was charged to our CDS 900 reactor system using a Beckman 110B pump. The feed contained 2 wt% naphthalene and 0.05 wt% iron (Nanocat Superfine Iron Oxide, MACH I Inc.) in mineral oil. According to the product specification, the iron is α - Fe_2O_3 with high surface area of $282 \text{ m}^2/\text{g}$, and the particle size is about 30 Å and approximately one-half of the atoms reside on the particle surface. The feed solution was prepared by dispersing the iron particles in the mineral oil with an ultra-sonicator (Branson Sonifier W350) for 1 hr. A magnetic stirrer was employed to keep iron particles suspended in the solution while charging the feed to the reactor. The 0.515 inch I.D. reactor tube of 18 inch length was packed with 0.1-0.12 mm glass beads supported on glass wool.

The analysis of the products from this experiment showed no apparent conversion of the naphthalene. In addition, the reactor effluent appeared to contain no iron particles indicating probable accumulation of iron particles somewhere in the reactor system. After 60 hours of feeding the dispersed catalyst feed, the outlet check valve on the liquid feed pump failed and the run was terminated. Examination of the reactor packing revealed iron and coke accumulation in the glass packing.

III. Tubing Bomb Experiments with Dispersed Catalysts

During this year a large number of tubing bomb experiments were run. The experiments involved the hydrogenation of the model compound naphthalene at a concentration of 2 wt% in mineral oil, generally at 350°C . The exact conditions for these experiments are given in Table 2, and the product distributions are given in Table 3. Most of the iron catalysts were not effective for the hydrogenation of naphthalene, however runs

Table 2. Experimental Conditions for Tubing Bomb Reactions

1. No catalyst, 350°C, 6 g, 2% Naph/Min. Oil, 1000 psi H₂, 1 Hr
2. 0.3 g Iron (III) Oxide, red (Hematite), 99.8%, (Strem)
3. same as (2), 1% CS₂
4. 0.3 g Iron (III) Oxide, 99.98%, (Aldrich)
5. 0.3 g Fe₃O₄, Iron (II,III) Oxide, black (magnetite) 97%, (Strem)
6. 0.3 g Fe₂O₃·H₂O, Iron(III) Oxide monohydrate, yellow, (Strem)
7. same as (6), 1% CS₂
8. 0.3 g MagNox NP-411, 23.71 m²/g
9. same as (8), 1% CS₂
10. 2.0 g 12% Iron NEO-NAP, (Mooney)
11. same as (10), 1% CS₂
12. 1.3 g Ferric Acetylacetonate, 99%, F30-0, (Aldrich)
13. same as (12), 1% CS₂
14. same as (13), 0.1 g fumed amorphous Silica (Aerosil 300)
15. same as (14), 425°C
16. 0.1 g Fe₂O₃ (Mach-I), Superfine Iron Oxide (SFIO)
17. same as (16), 2% CS₂
18. same as (16), 1% CS₂
19. 0.1 g 1% Pd on CaCO₃ powder (Engelhard) 150°C 100 psi H₂, 15 min
20. same as (19), 0.2 g, 1% Pd on CaCO₃, 200 psi H₂, 1 Hr
21. same as (20), 0.4 g, 1% Pd on CaCO₃
22. same as (20), 400 psi H₂
23. same as (19), 1.0 g, 1% Pd on CaCO₃, 300 psi H₂, 1 Hr
24. same as (23), 200°C, horizontal motion
25. same as (24), 1% CS₂

Note: Unless otherwise noted, all runs were performed using 6 g of 2 wt% Naph/Min. Oil at 350°C, 1000 psi H₂ (ambient), and 1 Hr.

Table 3. Results of Tubing Bomb Reactions with Dispersed Catalysts

RUN NO	NAPH (wt%)	TET (wt%)	DEC (wt%)
1	1.96	0.01	0
2	1.73	0.24	0
3	1.93	0.02	0
4	1.89	0.07	0
5	1.94	0.01	0
6	1.91	0.03	0
7	1.90	0.04	0
8	1.93	0.03	0
9	1.94	0.03	0
10	0.86	0.02	0
11	0.98	0.04	0
12	1.69	0	0
13	1.72	0	0
14	1.61	0	0
15	1.59	0	0
16	1.82	0.08	0
17	1.04	0.88	0
18	1.05	0.92	0
19	1.45	0.52	0
20	0.18	2.02	0
21	0	2.02	0.13
22	0.32	1.80	0
23	0	1.36	0.87
24	0	0.03	2.02
25	1.83	0	0

17 and 18 with a superfine iron oxide in the presence of CS_2 were effective in producing about 50 percent conversion of the naphthalene to tetralin. This was the most effective iron catalyst tested. It is interesting that no conversion is obtained with this catalyst in the absence of sulfur.

An organometallic compound, ferric acetylacetonate, was not effective in the presence or absence of CS_2 . In addition, the presence of a high surface area silica as support for particle precipitation did not aid the reaction as shown by runs 14 and 15.

For reference purposes only a few runs were made with a Pd on CaCO_3 catalyst (runs 19-25). Complete hydrogenation is obtained with this catalyst at mild conditions, however the catalyst is poisoned by sulfur (run 25). At the standard conditions of 350°C , 1000 psi H_2 and 1% CS_2 , the Pd catalyst does perform about the same as the Mach I Fe_2O_3 powder.

We are now in the process of performing coal liquefaction runs with certain of the catalysts used in these experiments. Preliminary runs show that the addition of the SF16 iron catalyst does promote the formation of pentane and THF solubles from coal.

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