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Cooperative Research Program in Coal Liquefaction

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

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

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University of Pittsburgh
University of Utah
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Auburn University**

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TABLE OF CONTENTS

TASK I - Iron Based Catalysts for Coal Liquefaction	1
Project I.1 - Sulfated Iron Oxides and Related Catalysts in Direct Coal Liquefaction and Model Compound Reactions (I. Wender and J. Tierney)	2
Project I.2 - Low Temperature Depolymerization and Liquefaction of Premium U.S. Coal Samples (J. Shabtai, K. Chary and J. Hu)	3
Project I.3 - Generic Structural Characterization Studies of Fe-Based and Related Catalysts (G. Huffman, F. Huggins, N. Shah)	4
Project I.4 - Catalyst Dispersion in Three Argonne Coals (E. Eyring, D. Sommerfeld, and Y.-H. Huang)	5
Project I.5 - In-Situ TEM Studies of Metal Sulfide Catalysts (N. Rodriguez and R.T.K. Baker)	6
Project I.6 - Novel Test Reactors for Coal Liquefaction (J. Zondlo, A. Stiller, J.P. Wann, W. Stewart)	7
Project I.7 - Ferric Sulfide as a Precursor for Coal Liquefaction Catalysts (D. Dadyburjor, A. Stiller, J. Zondlo, P. Stansberry, C. Stinespring)	9
Project I.8 - Laser Pyrolysis of Ultrafine Particle Catalysts for Coal Liquefaction (P. Eklund)	10
TASK II - Exploratory Research On Coal Conversion	12
Project II.1 - Coal Structure/Liquefaction Yield Correlation by Means of Advanced NMR Techniques (R. Pugmire)	13
Project II.2 - Mass Spectrometric Studies of Liquefaction Mechanisms (H. Meuzelaar and H. Huai)	14

Project II.3 - Catalytic Cracking/Hydrogenation and Catalysts Characterization (M. Seehra and M. Ibrahim)	15
Project II.4 - ESR and ENDOR Investigation of the Role of Free Radicals in Coal Liquefaction Under Mild Conditions (N. Dalal and J. DeLooze)	16
Project II.5 - Surface Characterization of Coal Liquefaction Catalysts and Catalyst Impregnated Coals (P. Reucroft and J. Kim)	20
Project II.6 - Computational Chemistry of Model Compounds (K. Subbaswamy)	21
Project II.7 - Chemical Characterization and Hydrogenation Reactions of Single Coal Particles (A. Ray)	25
Project II.8 - Liquefaction Pathways (B. Davis and R. Keogh)	26
Project II.9 - Development of Advanced Methods of Coal Liquefaction Product Analysis (E. Kugler)	27
TASK III - Novel Coal Liquefaction Concepts	28
Project III.1 - Bioprocessing of Coal (D. Bhattacharyya, M. Aleem, R. Kermode, M. Murty, M. Venkatachalam)	29
Project III.2 - Distinguishing Chemical Reaction Mechanisms in Coal Liquefaction (J. Penn, J. Wang, Y. Liu)	30
Project III.3 - Better Hydrogen Transfer in Coal Liquefaction (A. Tarrer, J. Guin, C. Curtis)	31
Project III.4 - Catalytic Hydropyrolysis (L. Anderson, J. Jumpol)	38

TASK IV - Novel Catalysts for Coal Liquefaction	40
Project IV.1 - Catalytic Dehydrogenation of Model Compounds in Relation to Coal Liquefaction (I. Wender, J. Tierney)	41
Project IV.2 - Evaluation of Dispersion Methods for Slurry Phase Catalysts (Y. Tang and C. Curtis)	42
Project IV.3 - Improved Catalysts for Coal Liquefaction and Co-Processing: New Initiative in Dispersed Slurry Phase Catalysts (J. Guin, A. Tarrer, C. Curtis)	44

Task I

Iron-based Catalysts for Coal Liquefaction

Program Coordinators: Irving Wender and Gerald P. Huffman

Project I.1

Sulfated Iron Oxides and Related Catalysts in Direct Coal Liquefaction and Model Compound Reactions

**I. Wender and J. Tierney
University of Pittsburgh**

The activity of small amounts of iron and molybdenum added as finely divided sulfated oxide/oxyhydroxide catalysts (FeOOH/SO_4 , $\text{Fe}_2\text{O}_3/\text{SO}_4$ and $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$) for the direct liquefaction of low pyrite bituminous (Blind Canyon) and subbituminous Wyodak coals was determined. Measurement of dispersion and composition of these catalysts before and after coal liquefaction reactions was also carried out. Measures of dispersion (such as surface area and particulate size) were obtained for the oxides and oxyhydroxides of iron containing 3-4 wt% of sulfate anion as such and after their transformation from the oxide phase to sulfides during coal liquefaction. The rates of these transformations were studied at 400°C and the size and composition of the resulting sulfide particles were obtained. It was found that all of the added sulfated iron oxides were completely converted to pyrrhotite, Fe_{1-x}S , after five minutes of reaction at 400°C . Fe_7S_8 , prepared by treating sulfated iron oxide with sulfur in the presence of tetralin, was also used as a catalyst for coal liquefaction and was found to be almost as effective as the sulfated iron oxides. 1000-5000 ppm of iron and 20-100 ppm of molybdenum with respect to coal were used in our catalytic systems. Molybdenum, used in small amounts, was more effective when used with the calcined form of the sulfated iron oxyhydroxide than with its uncalcined form, FeOOH/SO_4 .

Project I.2

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

J.S. Shabtai, K.V.R. Chary and J. Hu
University of Utah

The main research activities under this project during the November 1, 1991-January 31, 1992 period were as follows:

1. Continuation of systematic low-temperature coal depolymerization-liquefaction studies with special emphasis on the optimization of a Fe-containing catalyst in the first stage of the procedure.
2. Hydrogenolysis studies of thioethers, including diaryl thioethers, e.g., diphenyl sulfide, showed that such compounds are easily susceptible to acid-catalyzed cleavage with elimination of hydrogen sulfide. Protonic aqua complexes, e.g., $\text{Fe}(\text{H}_2\text{O})_6^3+$, are effective catalysts at 325-350°C.
3. Work on the detailed structural analysis of depolymerized coal products was continued. A paper on the GC/MS analysis of hydrocarbon fractions of such products was published (M. Lee, J. Shabtai, et al., Fuel, 1992, 71, 19-29).
4. Work on the construction of a flow reactor for testing the unified HT-BCD procedure was continued.

Project I.3

Generic Structural Characterization Studies of Fe-Based and Related Catalysts

G.P. Huffman, F.E. Huggins, and N. Shah
University of Kentucky

During the third quarter of the current contract year, in situ XAFS studies were conducted on a 3 nm Fe_2O_3 catalyst from Mach I and a 10 nm $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst prepared by the Pitt CFFLS group. The measurements were carried out at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The experiments were conducted using an XAFS compatible furnace at temperatures of 100 to 400°C with the catalysts immersed in a hydrogen donor (dihydrophenanthrene or hexahydrophenanthrene) containing elemental sulfur. Both the sulfur and iron K-edge x-ray absorption spectra were obtained. The data, which clearly show transformation of the catalysts to sulfide phases, are now being analyzed.

A renovation of the Mossbauer laboratory is nearing completion. A second Mossbauer spectrometer system has been installed and tested. Routine use of this system will begin when a second radioactive source is delivered, which should occur within the next few weeks. Our cryogenic system has also been renovated by replacement of the old vacuum system, installation of a new heater and temperature controller, and overhaul of the compressor system. The system is now performing much more efficiently than previously and low temperature Mossbauer studies of catalysts from a number of CFFLS investigators are in progress.

A new run was made with the in situ probe - stirred autoclave system, designed to allow the rapid extraction of samples from the autoclave during liquefaction under a hydrogen or nitrogen atmosphere. An $\text{Fe}_2\text{O}_3/\text{SO}_4$ catalyst was used with a very low pyrite Blind Canyon coal (PSU DECS-6) in the presence of added sulfur. The samples are being analyzed by XAFS and Mossbauer spectroscopy.

A new postdoctoral fellow has initiated scanning transmission electron microscopy (STEM) studies on a number of ultrafine iron-based catalysts.

Project I.4

Catalyst Dispersion in Three Argonne Coals

Edward M. Eyring*, David A. Sommerfeld and Yo-Hsin Huang
University of Utah

During the quarter ending January 31, 1992, three coals from the Argonne Premium Coal Sample Program (Blind Canyon, Wyodak and Pittsburgh #8) were impregnated with Fe/Mo and Ni/Mo bimetallic catalysts using both ultrasound and the incipient wetness techniques. Coal samples were then hydrotreated at 350°C and 2000 psig H₂. The dispersion of the catalysts was followed through the use of electron probe microanalysis (EPMA). The effectiveness of the catalyst systems was measured by tetrahydrofuran solubles produced.

Regardless of the impregnation technique used, EPMA micrographs show the two metals present on the exterior of the coal particles before hydrotreatment. After hydrotreatment the metals occupy the interior of the coal particles. The iron has a uniform dispersion, whereas both the nickel and molybdenum species aggregate in random clumps inside the coal particles. From these results it seems evident that catalyst mobility occurs during hydrotreatment.

The best yield of THF solubles was obtained from Wyodak coal followed by Blind Canyon coal. Pittsburgh #8 had the lowest yield of THF solubles. These results track the amount of carbon and oxygen in the three coals. Wyodak coal has a comparatively low carbon content and a comparatively high oxygen content versus Pittsburgh #8 which has a high carbon content and low oxygen content.

A possible explanation for these results would be that during hydrotreatment the pore structure of low rank coals (e.g. Wyodak) is preserved permitting better catalyst dispersion and better yields. In higher rank coals more graphitization occurs and catalyst dispersion and yields of THF solubles suffer.

Project I.5

In-Situ TEM Studies of Metal Sulfide Catalysts

N.M. Rodriguez and R.T.K. Baker
Auburn University

From a consideration of the interaction of atomic hydrogen species with coals 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 characteristics.

In-situ electron microscopy studies of the dynamic behavior of certain metal sulfides supported on single crystal graphite shows that when such specimens are treated in 0.2 Torr hydrogen, pitting of the carbonaceous support at edges, steps and defect regions of the basal plane occurs. In the absence of a catalyst attack of graphite by molecular hydrogen is not observed until the temperature is raised to above 1000°C. In contrast, when a metal sulfide is present gasification of the graphite takes place at very low temperatures. We believe that this unusual behavior, which is quite different to that observed in the presence of metal catalysts, is the result of attack by atomic hydrogen which is produced from the interaction of molecular hydrogen with the metal sulfide particles. These observations are consistent with those of other workers who have studied the interaction of microwave generated atomic hydrogen species with graphite.

FUTURE STUDIES

Experiments are underway to determine whether it is necessary for the catalyst to be in direct contact with the carbonaceous solid in order to promote hydro-gasification, if it is possible for the active species to be transported through the gas phase.

In other experiments, we are using in-situ electron diffraction techniques to ascertain the chemical nature of the active catalyst at various stages of the reaction.

Project I.6

Novel Test Reactors for Coal Liquefaction

J. Zondlo, A. Stiller, J.P. Wann, W. Stewart
West Virginia University

During the past quarter, the shaken batch reactor has been thoroughly evaluated and tested. It is becoming the work horse for the catalyst testing program here at West Virginia University. An extensive evaluation of the Blind Canyon Coal (DECS-17) has been completed. In these studies, the Blind Canyon Coal has been liquefied in tetralin at 1000 psi hydrogen pressure (cold) and at various reaction temperatures. Several formulations of the WVU iron-based catalyst have been prepared. These include samples with pyrrhotite to pyrite ratios in the range of 1 to 6. Some representative examples for tests performed at 350 and 400°C are shown in Tables 1 and 2.

Work continues on the hydrogen-purged semi-batch liquefaction reactor. The reactor itself along with its agitation mechanism has been completed. Currently the system is being assembled with its associated control and data acquisition systems.

Summary of Future Tasks

Work will continue with the agitated batch reactor on the evaluation of additional catalyst formulations with DECS-17 coal as well as other candidate coal samples. Of particular interest is the Illinois Coal Sample No. 109 (supplied by Illinois State Geological Survey) which is a bituminous coal representative of those found in the eastern and central United States. Its pyrite content, though not zero, is very low (approximately 0.4%). In addition to catalyst testing, an evaluation of various techniques currently in use for the analysis of coal liquefaction products will be investigated. It is hoped that through this work, a unified standard procedure for product work-up can be developed for use by all consortium workers.

Work on the hydrogen-purged reactor will continue. Within the next quarter all instrumentation and piping will be completed and a preliminary shake down of the reactor itself will occur.

Table 1. Liquefaction Yields from DECS-17 at 350°C

<u>talysts</u>	<u>CS₂</u>	<u>Conversion</u>	<u>Yields (daf basis)</u> <u>Asphaltene</u>	<u>Oil+Gas</u>
ne	N	58.1	49.1	9.0
ne	Y	60.1	47.2	12.9
A	N	71.0	53.0	18.0
A	Y	72.0	55.4	16.6
B	N	70.4	54.2	16.2
B	Y	70.7	55.7	15.0
C	N	70.9	54.8	16.1
C	Y	80.5	59.4	21.1

Table 2. Liquefaction Yields from DECS-17 at 400°C

<u>talysts</u>	<u>CS₂</u>	<u>Conversion</u>	<u>Yields (daf basis)</u> <u>Asphaltene</u>	<u>Oil+Gas</u>
ne	N	89.8	55.6	34.2
ne	Y	91.8	55.4	36.4
A	N	95.7	53.4	42.3
A	Y	94.9	49.6	45.3
B	N	95.5	54.8	40.7
B	Y	96.6	53.4	43.2
C	N	95.2	55.4	39.8
C	Y	95.1	53.0	42.1

 = room temperature disproportionation, PH/P=6
 = 100°C disproportionation, 1 hour, PH/P=2
 = 200°C disproportionation, 1 hour, PH/P=1

ere: PH = pyrrohtite
 P = pyrite

Project I.7

Ferric Sulfide as a Precursor for Coal Liquefaction Catalysts

**D. Dadyburjor, A. Stiller, J. Zondlo,
P. Stansberry, C. Stinespring
West Virginia University**

We have, during the reporting period, attempted to demonstrate the effectiveness of iron sulfide catalysts that were synthesized to have specific pyrrhotite/pyrite (PH/PY) ratios for the liquefaction of DECS-17 coal. The prepared catalysts were characterized with x-ray diffraction to identify the crystalline species in the mixtures. Auger Electron Spectroscopy (AES) analyses were initiated to compare the catalysts with mineral standards and to identify surface species on the iron sulfide catalysts. We have sent a representative catalyst along with its liquefaction reactants and products to Brookhaven National Laboratory for characterization analyses by G. Huffman's group. We are also investigating the role played by sodium chloride produced during the synthesis of ferric sulfide precursor.

Summary of Future Tasks

For our future work, we will test the modes of in-situ catalyst dispersion on the DECS-17 coal. We also plan to investigate the relationship between catalyst loading and liquefaction conversion as well as product selectivity. We will study thermal stability and reactivity of the catalysts using AES analyses, which involve characterization of the iron sulfide stoichiometry, chemical state, and structure as functions of temperature and exposure to O_2 and H_2S .

Project I.8

Laser Pyrolysis of Ultrafine Particle Catalysts for Coal Liquefaction

P.C. Eklund

Center for Applied Energy Research
University of Kentucky

In this quarter we worked on improving the production rate of ultrafine particle (UFP) iron carbide catalysts. We investigated the effect of increased nozzle diameter. Higher mass flow rates were then possible for the reactant gas (ethylene & Fe-carbonyl). Production rates for the Fe_7C_3 and Fe_3C catalysts particles (dia. ~ 20 nm) are now 0.8 g/hr and 1.5 g/hr, respectively, an improvement by a factor of 2-3 over previous production rates. We should emphasize that Fe_7C_3 is ready to use without further chemical treatment. For Fe_3C , passivation in a 10% O_2 / 90% He mixture is required, if this catalyst is to be exposed to an oxidizing atmosphere prior to the liquefaction reaction. Our previous report (2nd quarter) documents the observation that Fe_7C_3 shows some promise as a coal liquefaction catalyst when dimethyl disulfide (DMDS) is added. The presence of DMDS allows the transformation of our UFP carbide catalysts to pyrrhotite in the tubing bomb reactor.

Furthermore, we have carried out initial studies of the possibility of using laser pyrolysis to synthesize an Fe-sulfide catalyst. I am happy to report that our initial attempts have been successful. We have prepared ~ 20 nm dia particles of pyrrhotite. The reaction was carried out mixing ethylene, H_2S & Fe-carbonyl. The ethylene is used as an absorber gas, coupling to the CO_2 laser. We were not sure before our attempts, whether or not ethylene would be a passive spectator, or would react to form oxy-sulfides. Apparently, the ethylene is acting chemically as a spectator, simply transferring the heat from the laser to the other gases in the mixture.

X-ray diffraction on the resulting powders indicate that the ultrafine $\text{Fe}_x\text{S}_y\text{C}_z$ powders are indeed the pyrrhotite phase and we infer that $z \sim 0$. Shown below in Fig. 1 is a powder diffraction pattern for the Fe-S catalyst (.....) as compared with the sulfided Fe_7C_3 catalyst (____). The standard pyrrhotite powder ($\text{Fe}_{1.8}\text{S}$) pattern diffraction file is indicated by the thin vertical lines whose intensities are proportional to the respective integrated intensity. Thus, it is very interesting that the final (sulfided) form of the carbide Fe_7C_3 catalyst and the initial form of the Fe-S catalyst are the same. We can then use the new Fe-S catalyst to address questions regarding the active phase in the Fe-based catalysts used with added sulfur. Work in our micro-auto clave reactors will be carried out to address this important issue. Also, we are now investigating the reaction conditions required to produce other Fe-S phase catalysts.

Figure 1.

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

Ronald J. Pugmire
University of Utah

During the past quarter the work on the combination of slow spinning at the magic angle¹ with selective excitation² and dipolar dephasing³ techniques (discussed in the last Progress Report) has produced enough results for a publication. The method, which extends the more typical selective excitation of only a single resonance to a method of exciting (either saturation or inversion) a larger number of resonances, is demonstrated on 1,2,3,-trimethoxybenzene (TMB) and on a Lewiston-Stockton coal sample. The measured tensor components on TMB are in good agreement with those obtained in single crystal experiments.⁴ In addition, several different experiments performed under slightly different conditions gave similar results, indicating that the results are reproducible. These multiple experiments have allowed for an estimation of errors of ± 6 ppm for the aromatic carbon tensor components and ± 3 ppm for the components of the methoxy carbons, well within the range expected for the analysis of slow spinning sideband patterns. Therefore, the use of selective excitation does not affect the side band intensities to any measurable extent. The paper, which should be ready for submission to *Analytical Chemistry* within the month, presents the experimental details of this new multiple resonance DANTE and of a more efficient method for selective signal saturation (dephased DANTE), along with the results on the above mentioned compounds. Efforts to study more complicated polycyclic aromatic compounds (i.e., compounds with both more resonances and more overlap between resonances) to determine the possible limitations of these techniques are currently underway and will continue in the next quarter.

In addition, the installation of the new Chemagnetics CMX-100 console has been completed and the personnel on the CFFLS project have started to learn its operation. The pulse sequences for the multiple resonance DANTE experiments have recently been implemented on this system in order to continue testing of the sequences. Bench testing of the dynamic angle spinning (DAS)⁵ equipment has been successful, and in the next quarter we will hopefully obtain a 2-D DAS spectrum on a polycyclic aromatic compound.

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Project II.2

Mass Spectrometric Studies of Liquefaction Mechanisms

H.L.C. Meuzelaar and H. Huai
University of Utah

The Cahn TG 151 model high pressure thermogravimetry system was installed and a series of simple pyrolysis tests on selected Argonne National Laboratory coals was initiated to determine key instrumental parameters (repeatability, sensitivity, signal-to-noise ratio, optimum flow configuration) as well as the effects of pressure on char yield. Upon completion of these tests the high pressure TG system will be interfaced directly to our ion trap MS system, by means of a "transfer line" GC coupling similar to the technique developed in our laboratory for on-line monitoring of high pressure conversion reactions (paper to be presented at the spring 1992 ACS meeting in San Francisco). Among the high pressure TG/GC/MS experiments planned for the coming year are comparisons of thermally and catalytically controlled pyrolysis and hydrolysis reactions as well as the effects of reactive vapor atmospheres ranging from H₂O to methanol. Special attention is being paid to safety aspects. Furthermore, potential arrangements with industrial co-sponsors are being explored in order to enable operation and maintenance of the very demanding and sensitive high pressure TG system by a full time, dedicated operator/technician.

An AABSPEC Corporation Model 4000 high pressure flow-through infrared cell (specially modified for operation at temperatures up to 400 C) was delivered and is being readied for on-line FTIR monitoring of high pressure conversion reactions using a Perkin Elmer 1760 X FTIR system.

Molecular weight distribution determinations of low temperature coal liquefaction fractions by means of a novel, combined short column GC/CIMS and vacuum thermogravimetry method were completed. This work will also be reported at the San Francisco ACS meeting. Extension of these MW distribution studies to nonvolatile coal liquid fractions by means of supercritical fluid chromatography (in collaboration with Dr. Larry Anderson) is being considered.

Project II.3

Catalytic Cracking/Hydrogenation and Catalyst Characterization

**M.S. Seehra and M.M. Ibrahim
West Virginia University**

Much of our effort during the past quarter was devoted to the investigation of the hydrogenation of Blind Canyon coal using in-situ high temperature/high pressure ESR spectroscopy of free radicals. The experiments were carried out from room temperature to 530°C, in H₂ pressures up to 600 psi, and with and without the Shell 324 presulfided catalyst. The concentration of free radicals, N, was monitored in these experiments. Of significant interest are the experiments carried out at a fixed temperature of 440°C where N was monitored as a function of H₂ pressure up to 600 psi, in steps of 25 to 50 psi. Without the catalyst, N decreases monotonically as H₂ pressure increases. This is likely due to capping of the thermally induced free radicals by H₂ gas. On the other hand, in the presence of the Shell 324 catalyst, there is a slight initial increase in N for pressures up to about 150 psi followed by a monotonic decrease as pressure is increased further. In addition, in the presence of the catalyst, N is about 50% higher at all pressures compared to the case of N without the catalyst. Thus it appears that in the presence of the catalyst, an additional process namely hydrogenolysis is taking place, in addition to capping of the free radicals by H₂. At lower pressures (<150 psi) of H₂, hydrogenolysis appears to dominate in the presence of the catalyst whereas at the higher pressures, the capping process is dominant. The concentration of the catalysts in these experiments was about 2% of the coal by weight.

During the next quarter, these experiments will be brought to a conclusion and an interpretation of the results will be sought. We are also planning to analyze the products of different experiments so as to provide further insights into the process of hydrogenation/hydrogenolysis. Results of these experiments will be written up for a publication.

Project II.4

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

N. Dalal and J. DeLooze
West Virginia University

As originally proposed, during this quarter we continued our EPR and ENDOR measurements of the role of free radicals in the mechanism of coal liquefaction via homogeneous catalysis. 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 the charge on the radicals involved in the liquefaction reactions because some experimental studies by Farcasiu and Smith has indicated that the radical involved must be cations. This conclusion has been supported by molecular orbital calculations by Swamy at the University of Kentucky, as discussed at the recent CFFLS Technical Meeting hold at Lexington and the recent CFFLS meeting held at Pittsburgh. We have, therefore, initiated a program of assembling an atlas of EPR spectra of different free radical species generated from aromatic compounds that are considered as model compounds for coal liquefaction reactions.

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 EPR spectra of pentacene cation as well enion 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 in the EPR spectra. The same procedures will be utilized to analyze the EPR spectra from the anion and cation species from 21 other compounds. These results will be finally utilized in identifying the complex spectra expected from the radical species from coal.

Some represented EPR spectra are attached herewith.

anthracene, 9-carboxylic acid

1,3-dihydroxynaphthalene

Project II.5

Surface Characterization of Coal Liquefaction Catalysts and Catalyst Impregnated Coals

P.J. Reucroft and J.Y. Kim
University of Kentucky

In previous reports, surface characterization studies on six catalysts and catalyst impregnated Illinois #6 coal were described.¹ Peak synthesis and depth profiling studies were carried out using model compound data from the literature.² Due to the limited literature information that is available on the characteristics of model compounds (FeOOH, Fe₂O₃ and MoO₃, etc.), the results have not been fully interpreted, to date.

During the next quarter, XPS characteristics on model compounds will be carried out in order that the analysis of the catalyst data may be further extended.

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Project II.6

Computational Chemistry of Model Compounds

K. Subbaswamy
University of Kentucky

1. Further tests of Radical Cation hypothesis for liquefaction reactions in the presence of carbon black.

A. Thermal and catalytic conversion of n-propyl phenanthrene:

Bond Dissociation Energy (eV)

Bond	ASED	
	Neutral	+1 on ring
a	4.16	2.81
b	3.95	3.15
c	4.07	3.29

B. Test of Radical Hydrogen Transfer mechanism for catalytic decomposition of Model I.

All energies in eV

	ΔE_1	ΔE_2	Q_{CH}	ΔE_3	ΔE_4	BDE	%
1	0.57	2.15	1.58	1.30	0.71	0.59	7
2	0.51	1.91	1.40	1.21	0.73	0.48	19
3	0.44	1.86	1.42	1.36	0.84	0.52	64
4	0.55	1.90	1.35	1.29	0.78	0.51	10

Work in Progress

1. Catalytic mechanism in a series of model compounds.
2. Further development of ab initio molecular dynamics technique for reactions involving model compounds.
3. Development of electronic structure calculations for iron-based catalysts: bulk and surface.

Project II.7

Chemical Characterization and Hydrogenation Reactions of Single Coal Particles

**Asit Ray
University of Kentucky**

Dr. Asit Ray is on sabbatical leave this report period.

Project II.8

Liquefaction Pathways

**B.H. Davis and R.A. Keogh
Center for Applied Energy Research
University of Kentucky**

During the past quarter, the preasphaltene intermediate was liquefied using a number of different reactor temperatures and residence times. The solubility class distributions were determined on the reactor products to determine their thermal liquefaction pathway. Several of the experiments were repeated using a presulfided Ni/Mo (Shell 324) catalyst and an oil soluble catalyst (molybdenum naphthenate) to determine the catalytic pathway of the preasphaltenes. As expected, the preasphaltene thermal pathway was different from the asphaltene thermal pathway. However, the production of oils during the conversion of the preasphaltenes was slightly higher than predicted. The preasphaltene thermal and catalytic liquefaction pathways were similar.

Project II.9

Development of Advanced Methods of Coal Liquefaction Product Analysis

**E.L. Kugler
West Virginia University**

During the past quarter, we have trained a new graduate student for this project. He has reproduced the data obtained with an undergraduate summer student and has started work on quantitating HPLC data.

During the next quarter, we plan to continue work on quantitating HPLC data. We expect to obtain enough data to evaluate our approach using internal standards in the oil fraction of coal liquids.

Task III

Novel Coal Liquefaction Concepts

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

Project III.1

Bioprocessing of Coal

D. Bhattacharyya, M.I.H. Aleem, R.I. Kermode, M.V.S. Murty, M. Venkatachalam
University of Kentucky

In-situ catalyst formation studies with *Sulfolobus brierleyi* showed the formation of FeOOH crystals as well as impregnation of molybdenum on coal particles by various physical techniques. Our previous chemical liquefaction yield of the coal treated with *Sulfolobus brierleyi* was dramatically increased by 26% when the coal sample containing bioformed catalyst (FeOOH) was presulfided with dimethyl sulfide in the liquefaction reactor. Present study for in-situ iron catalyst formation by chemolithotrophic, mesophilic (30°C) acidophile, *Thiobacillus ferrooxidans* under different conditions showed precipitation of jarosite or FeOOH/Fe³⁺ on surface of coal (KCER #91182). The nature and quantity of iron released/precipitated was dependent on pH of the culture medium. Rapid rate of aqueous phase iron precipitation took place at pH 2.8 and 3.0 which are very close to the optimum temperature of the microorganism. Depth profile by XPS of the biotreated coal sample also showed that the amount of iron precipitated on outer layer of 0-50 Å was predominantly more than the following inner layers. The quantity of iron precipitated was decreased as the depth increased in both test and control coal samples. Mossbauer Spectroscopy also revealed that jarosite formation at pH 2.5 was more than that of FeOOH/Fe³⁺. However, the percent of FeOOH/Fe³⁺ formed at pH 3.0 appeared more than at pH 2.5. The liquefaction yield of the biotreated coal at pH 2.8 was also increased by 10% over the control coal sample.

Our previous results showed decrease of H₂ from the head space of the vials containing bacteria and different model compounds. Present work on hydrogenation of model compounds such as methyl naphthalene and ethyl naphthalene in the presence of *Desulfovibrio desulfuricans* under continuous sparging of H₂ to avoid hydrogen limitation is in progress. During then next quarter several of the biogenerated coal samples have to be liquefied and find out possible route of hydrogenation of the model compounds.

PROJECT III.2

DISTINGUISHING CHEMICAL REACTION MECHANISMS IN COAL LIQUEFACTION

John H. Penn, Jin-hai Wang, and You-quan Liu
West Virginia University

During the past quarter, we have generated the radical cations of 4-(1-naphthylmethyl)-bibenzyl by photochemical electron transfer. Bond cleavage is observed in the naphthylmethyl bonds, similar to the results reported earlier by Farcasiu.

Similar reactivity has been observed in 1-naphthylphenylmethane. During the next quarter, we plan to obtain good mass balances for these reactions and to run control experiments which will prove that we have generated the radical cation that we claim to have generated.

Project III.3

Better Hydrogen Transfer in Coal Liquefaction

A. R. Tarrer, J. A. Guin, C. W. Curtis
Auburn University

Introduction

During the past quarter, construction has continued on the coal liquefaction reactor system. Once completed, the reactor system should demonstrate improvements in mass transfer techniques applicable to coal liquefaction and offer versatility in reaction rate controllability.

An Allen Bradley SLC 500 programmable logic controller (PLC) will be used to develop the ladder logic programming necessary to operate the reactor system and will also be used in the testing and start-up phases. A much more powerful computer system, the Texas Instruments Model 545, will later be employed to operate the completed reactor system. The Allen Bradley PLC is being temporarily utilized because of delays in acquiring the Texas Instruments unit. We are also experiencing delays in acquiring the remaining number of valves to be used in the reactor system because of manufacturing changes by the supplier.

Last quarter, we also discovered and began testing a new type of gas-liquid contactor (referred to as a jet nozzle in this report) that is similar to the modified slot injectors mentioned in previous reports. In preliminary testing using a catalyzed sodium sulphite system, the jet nozzle is showing much improved mass transfer rates in relation to previous contactors we have examined.

Another aspect of our work last quarter concerned developing a unique pumping system for use in the coal liquefaction reactor system. A thorough search for a commercial pump capable of handling coal slurries under the severe reaction conditions inherent in coal liquefaction at the required flow rates revealed that no pump was available unless it was custom built at a cost of \$120,000. This prohibitive cost necessitated the development of the pumping system detailed in the following section.

A Novel Pumping System For Use in Coal Liquefaction

In order to affect hydrogen mass transfer, certain flow rates are required in the reactor system. Commercial pumps with the capability to handle coal slurries under the severe reaction conditions necessary in liquefaction and at the required flow rates are simply not available. The pumping system under development 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, it will be easily serviceable, and is generic in nature.

The system will be composed of two modified Autoclave Engineers reactors used as stirred tanks, valving, gas holding tanks, 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 a PLC, directs the movement of fluid as well as gas pressures in the system. For safety reasons, gas holding tanks are used to feed gas to the stirred tanks. The fluid flow rate of the pumping system can be changed simply by adjusting gas pressures and valve action. 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.

The basic pumping system is shown in Figure 1. While tank 1 is filling with fluid, tank 2 is emptying of fluid and vice versa. Fluid enters the pumping system through valve VS1 and is directed to either tank 1 or tank 2, depending on the computer program being used.

Assume tank 1 is empty and tank 2 is full of fluid. Valve VG3 is open to the low pressure regulator. This allows fluid to enter tank 1 via valve VS1. At the same time, fluid in tank 2 is being forced out by opening valves VG2 and VG4, subjecting the tank to high gas pressure. The fluid coming out of tank 2 flows through valve VS2 to the external system.

Eventually, tank 1 fills with liquid while tank 2 becomes empty. At this point, the PLC switches the pumping systems' valves in order to accept fluid from the external system into tank 2. Valves VG2 and VG3 are switched to provide high pressure to tank 1 in order to begin forcing fluid out of the tank. Valve VS2 is also switched to allow the fluid to flow into the external system. Also, valve VG4 is switched to the low pressure regulator, allowing the gas pressure in tank 2 to drop. This action allows fluid to flow into the tank from the external system via valve VS1.

The pumping system can be constructed using a wide variety of commonly available materials and parts, depending on the operating parameters of the system in which it is used. The pump is generic in nature and can be applied to several different processes.

Gas-Liquid Contactors

A variety of designs for gas-liquid contactors have been evaluated in our previous work including gas-liquid jet injectors, 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.

As mentioned in the introduction, a jet nozzle was discovered that initial testing indicates performs significantly better in regard to gas-liquid mass transfer than other types of slot injectors we have evaluated. We first tested the air suction ability of a conventional slot injector, a modified slot injector, and the jet nozzle. The results are shown in Figure 2 and Figure 3. As indicated, the jet nozzle showed much better air suction ability than the other two types of injectors and with the added bonus of less power consumption.

Using a catalyzed sodium sulphite reaction system, we compared the overall gas-liquid mass transfer rates of a conventional slot injector and the jet nozzle. The results are shown in Figure 4. In this test, oxygen is removed from a tank of water by the addition of sodium

FIGURE 1: NOVEL PUMPING SYSTEM

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.

The results indicate a mass transfer coefficient of 0.03 sec^{-1} for the jet nozzle and 0.017 sec^{-1} for a conventional slot injector, which is about one half the mass transfer coefficient of the jet nozzle. Evaluation of the jet nozzle will continue during this work quarter and it is anticipated that it will be used in the coal liquefaction reactor system now under construction.

Fig. 2 Air flowrate versus liquid flowrate of three injectors

Fig. 3 Air flowrate versus power consumption of three injectors

Fig. 4 Dissolved oxygen rate of three injectors

Project III.4

Catalytic Hydropyrolysis

Larry L. Anderson and J. Jumpol
University of Utah

Three coals, namely Blind Canyon (hvB, UT), Pittsburgh #8 (hvB, PT), and Wyodak (subbi, WY), were used in catalytic hydropyrolysis studies 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 accompanied by ultrasonic, the other using incipient wetness impregnation. Hydropyrolysis experiments were conducted in shaking tubing bombs heated by a fluidized sand bath. Product yields are shown in Table 1.

Blind Canyon coal was also used in another set of experiments designed to assess effects of coal pretreatment, demineralization and pre-extraction. All catalysts were introduced to coal by incipient wetness impregnation in aqueous solution of the catalysts' precursor salts. The reaction conditions were same as the above experiments. Results are shown in Table 2.

Table 1. Yields from Catalytic Hydropyrolysis of Coals

Catalyst: 1% F/1% Mo; T=350°C; P=2000 psi, H₂; Reaction time=1 hr

Run	Coal	Method of Impregnation	% of maf coal	
			THF Insoluble	THF Soluble
#1	BC	Ultrasonic Impregnation	36	62
#2	BC	Incipient Wetness Impreg.	37	63
#3	WY	Ultrasonic Impregnation	36	55
#4	WY	Incipient Wetness Impreg.	20	68
#5	PT	Ultrasonic Impregnation	45	53
#6	PT	Incipient Wetness Impreg.	42	56

Our results show that ultrasound had no apparent beneficial effect on the amount of liquid produced from hydropyrolysis with Fe/Mo catalyst in all the coals experimented.

Table 2. Effects of Coal Pretreatment on Hydropyrolysis Yields

Run	Catalyst	Pretreatment	% of maf coal	
			THF Insoluble	THF Soluble
#7	0.05% Mo	- none -	62	38
#8	0.05% Mo	Demineralized	52	42
#9	0.05% Mo	Demin. + Pre-extract.	63	34
#10	0.05% Mo	Pre-extract. (added back)	61	39
#11	1% Fe/1% Mo	Demineralized	27	67

After being demineralized with HF, HCL, and HF again, Blind Canyon coal yielded more liquids when hydropyrolyzed than without being demineralized, as shown by run #7 vs. #8, and #2 vs. #11.

Continued work will follow on the evaluation of electron probe microanalysis (EPMA) studies on the mobility of the catalyst during liquefaction. We are also in the process of installing an advanced analytical technique using supercritical fluid chromatography (SFC) combined with an atmospheric pressure inlet and time of flight mass spectrometer. This instrument will be used to analyze and characterize liquid products from this and other consortium projects. This will be a considerable advancement in our analytical ability and the instrument is the first of its kind. Preliminary testing has encouraged the manufacturer to order parts for two additional such instruments.

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 Direct Coal Liquefaction

**I. Wender and J. Tierney
University of Pittsburgh**

Catalytic dehydrogenation of model compounds was carried out at the boiling point of vehicles under atmospheric pressure in a glass flask with 5 wt% reduced Pd on CaCO_3 or on active carbon as catalysts. It was shown that under these conditions, the evolved hydrogen came solely from hydroaromatic compounds. Effects of the oxidation state of the palladium catalyst and the reduction potential of the vehicle on hydrogen evolution were investigated. Interrelations among these factors were not investigated in early published studies of the dehydrogenation of coal. The low oxidation state of palladium plays a key role in mechanistic interpretation of catalytic dehydrogenation studies. All experiments were conducted using stilbene as a hydrogen acceptor; only hydroaromatic hydrogen was transferred to stilbene rather than evolved as molecular hydrogen. In addition, stilbene was used in the dehydrogenation of mixtures of model compounds in an effort to elucidate the catalytic dehydrogenation pathway. It is proposed that catalytic dehydrogenation has potential for estimating the amount of transferable hydrogen, a quantity difficult to measure by other methods, in coals, recycle solvents, and heavy oils.

Project IV.2

Evaluation of Dispersion Methods for Slurry Phase Catalysts

Ying Tang and Christine W. Curtis
Auburn University

During the past quarter, the activity of slurry-phase iron-based catalysts in model compound systems was compared to that of slurry-phase molybdenum catalysts. The iron-based catalysts precursors used were iron naphthenate, iron acetylacetonate, and iron (III) 2-ethyl hexanoate; the molybdenum slurry phase catalyst precursor used was molybdenum naphthenate. The two model systems, naphthalene and pyrene, were introduced at two weight percent in hexadecane. The catalyst level was 1000 ppm active metal of either iron or molybdenum which was reacted in the presence or absence of excess sulfur. Reactions were conducted at 380 and 425°C for thirty minutes in a well-agitated stainless steel microtubular reactor.

The initial reactions were performed with naphthalene which was reacted in the presence of either iron acetylacetonate or molybdenum naphthenate with and without sulfur. Molybdenum naphthenate with sulfur yielded more than 62% tetralin while without sulfur less than 30% was produced. The opposite result was obtained with iron acetylacetate where only 6% tetralin was formed with sulfur present but more than 90% was formed without sulfur. Lesser amounts of sulfur in the naphthalene and iron acetylacetonate system had adverse effects on the hydrogenation of naphthalene.

The reaction of pyrene in the presence of iron-based catalysts has been performed in the absence and presence of sulfur. The reaction of pyrene with iron naphthenate without sulfur at 380°C showed practically no reaction but the addition of sulfur yielded more than 50% conversion of pyrene, forming dihydropyrene as the predominant product and hexahydropyrene as the most hydrogenated product. By contrast, iron acetylacetonate with sulfur only produced a small increase in pyrene conversion compared to the system without added sulfur, while pyrene in the presence of iron (III) 2-ethylhexanoate showed no reaction either with or without sulfur.

For comparison, reactions of pyrene were performed with molybdenum naphthenate at 380°C. Without sulfur present, more than 60% pyrene conversion occurred. The primary reaction product was dihydropyrene, with hexahydropyrene being the most hydrogenated product. The addition of sulfur to molybdenum naphthenate resulted in substantially more

conversion of pyrene, yielding hexahydropyrene as the primary product and decahydropyrene as the most hydrogenated product.

Currently, reactions with iron (III) citrate pentahydrate are underway. The effect of the reaction temperature on the reactivity of the organic iron complex is under investigation. Each of these iron systems will be reacted with pyrene at 425°C as will molybdenum naphthenate for comparison. As active iron species are produced, they will be collected and analyzed for their chemical structure and reactivity. Further research will employ coal in liquefaction reactions with iron-based catalysts. These reactions will evaluate the activity of the iron-based catalysts in coal systems as well as the effect of different dispersion methods.

Project IV.3

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

**J.A. Guin, A.R. Tarrer, C.W. Curtis
Auburn University**

During the past quarter, we investigated the effect of several activation conditions including H_2 reduction and sulfidation on the hydrogenation reaction of naphthalene using iron oxide powder as a catalyst. The results showed that the initial activity of the catalyst was strongly dependent on the activation conditions. Proper reduction of unsupported iron oxide in the ferric state to its metallic or ferrous state was required to activate its surface. Hydrogen sulfide appears to be a poison for the iron catalyzed hydrogenation reaction.

During the next quarter, we plan to compare the selectivity and activity performance of different iron catalysts with or without a sulfur source in the feed. The reaction will be carried out in a trickle bed reactor or in a fixed bed reactor with vapor phase reaction. We also plan to try to pump a dispersed phase small particle (30 Å) iron catalyst in our continuous reactor.

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