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Abstracts and Research Accomplishments of University Coal Research Projects

Managed by:
Pittsburgh Energy Technology Center
Advanced Power Generation and Fundamental Research Division
P.O. Box 10940
Pittsburgh, Pennsylvania 15236

Supported by:
U.S. Department of Energy
Fossil Energy Program

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FOREWARD

The Principal Investigators of the grants supported by the University Coal Research Program (B&R #AA1525050) were requested to submit abstracts and highlight accomplishments of their projects in time for distribution at a grantees conference on June 25-27, 1991 at the Vista International Hotel, Pittsburgh, PA. This book is a compilation of the material received in response to the request. The grants reported in this book are managed by the Advanced Power Generation and Fundamental Research Division of the Pittsburgh Energy Technology Center.

For convenience, the grants reported in this book are sorted into seven technical areas, coal science, coal surface science, reaction chemistry, advanced process concepts, engineering fundamentals and thermodynamics, environmental science, and high temperature phenomena as outlined in the Table of Contents. Indexes are provided for locating projects by subjects, principal investigators, and contracting organizations.

Copies of this compilation will be available to interested parties while supplies last.

Advanced Power Generation and
Fundamental Research Division

DISCLAIMER

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COAL SCIENCE

TITLE: COALIFICATION BY CLAY-CATALYZED OLIGOMERIZATION OF PLANT MONOMERS.

P.I.'s: MILTON ORCHIN AND R. MARSHALL WILSON

STUDENTS AND DEGREE FOR WHICH THEY ARE REGISTERED:
JULIANNE GREEN, Ph.D.
STEFFAN ASSMANN, M.S.
MANCHAO XIAO, Post Doc

INSTITUTION/ORGANIZATION: DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI

GRANT NO.: DE-FG22-88PC88931

PERIOD OF PERFORMANCE: OCTOBER 1,1988-SEPTEMBER 30, 1991

I. ABSTRACT

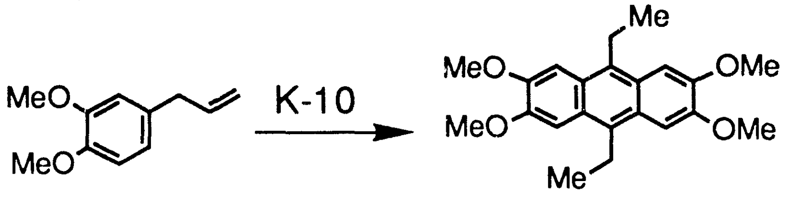
OBJECTIVE: To demonstrate that structures shown to be characteristic of low rank coals can be generated from C_3-C_6 units (e.g., essential plant oils, etc.) by radical-cation and acid catalysed reactions promoted by smectic clays such as montmorillonite.

WORK DONE AND CONCLUSIONS: It has been demonstrated that polycyclic compounds and several naturally occuring and important lignan structures (e.g. galbulin and podophylloyoxin) can be generated from C_3-C_6 precursors such as eugenol, isoeugenol, and cinnamates.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Our work may shed considerable light on the biogeogenesis of low rank coals. There is increasing evidence that coal has a macromolecular structure. It is useful therefore to (l) identify possible monomeric units (2) demonstrate the kinds of organic chemical reactions that convert these monomers to polycyclic oligomers (3) identify possible naturally occuring catalysts that may be responsible for such reactions. Finally if one can understand the nature of the oligomerization it is possible to find new ways of depolymerizing the coal macromolecule.

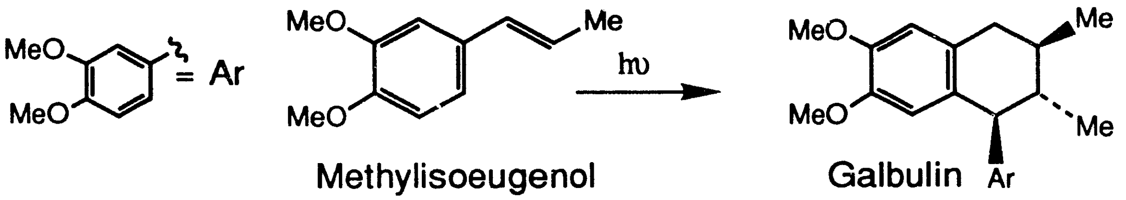
II. HIGHLIGHT ACCOMPLISHMENTS

1) It has been demonstrated that polycyclic aromatic hydrocarbons are formed when simple plant monomers such as methyleugenol are treated with the montmorillonite clay K-10.

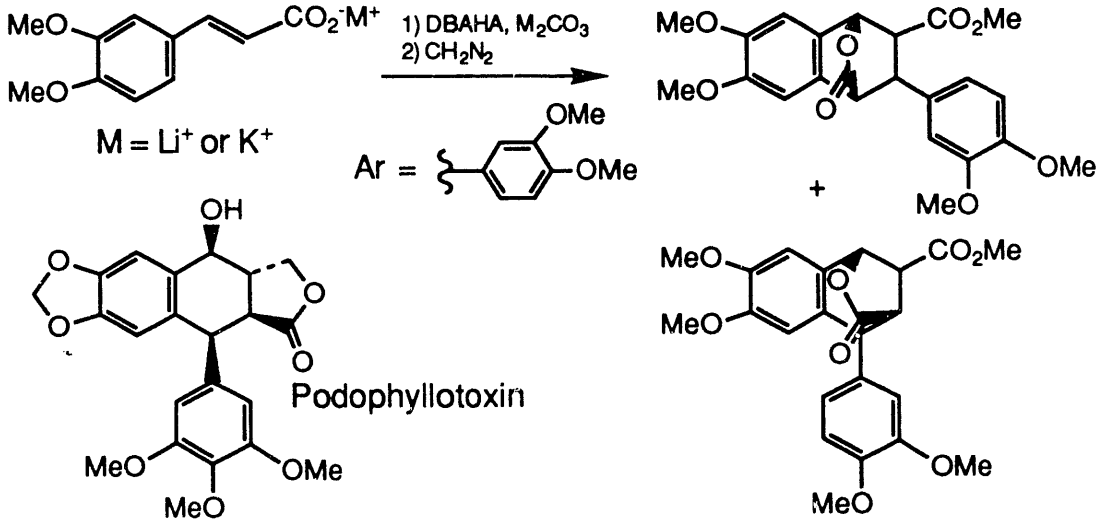


Methyleugenol Anthracene Derivative

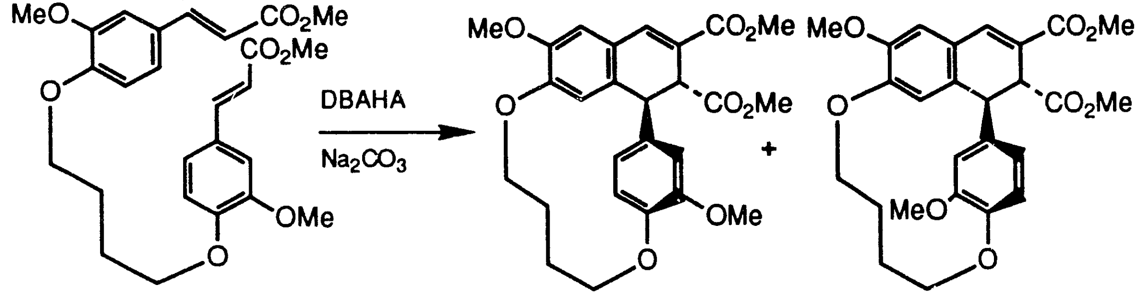
2) The natural product galbulin is formed when the simple plant monomer methyl isoeugenol is irradiated.



3) Radical cation dimerization of cinnamic acid salts has been found to produce lignan natural products including the lactones shown below. These lactones are particularly significant, since their formation suggests that the plant may use a similar radical cation dimerization in the formation of important natural lignans such as podophyllotoxin.



4) Radical cation cyclization of tethered cinnamates has been shown to reduce drastically the number of isomers formed, and to restrict the stereo- and regiochemistry of the isomers to those that occur naturally.



III. ARTICLES AND PRESENTATIONS

1. Radical Cation-Initiated and Acid-Catalyzed Dimerization of 3,4-Dimethoxycinnamic and Acid and Related Cinnamate Esters Using the Radical Cation Salt Tris-(2,4-Dibromophenyl) aminium Hexachloroantimonate (DBAHA), J. G. Dietz, R. M. Wilson, M. Spahr, D. M. Ho.

2. Clay-Catalyzed Organic Reactions: The Dimerization of 3,4-Dimethoxypropenylbenzene with K-10 Montmorillonite Clay. R. M. Wilson, M. Orchin, J. V. Green, J. G. Dietz.

These papers were presented at the 199th American Chemical Society Meeting, Boston, Massachusetts, April 1990.

TITLE: SPIN-MAPPING OF COAL STRUCTURES WITH ESE AND ENDOR DATE: 4/9/91

P.I.s: R. Linn Belford and Robert B. Clarkson

STUDENTS AND THE DEGREES FOR WHICH THEY ARE REGISTERED: D. R. Brown (Ph.D.); H. C. Crookham (Ph.D.); K. J. Mattson (Ph.D.); W-J. Shi (Ph.D.); F-S. Jiang (Ph.D.); D. Youn (Ph.D.); J.-H. Hwang (Ph.D.); W. Wang (Ph.D.); S. Boyer (B.S.); S. Hoffman (B.S.)

INSTITUTION/ORGANIZATION: University of Illinois
Department of Chemistry and Illinois ESR Research Center
367 Noyes Laboratory
505 S. Mathews Street
Urbana, Illinois 61801
(217) 333-2553 or (217) 244-1375

GRANT NO: DE-FG22-88PC88921

PERIOD OF PERFORMANCE: 9-1-88 through 8-30-91

I. ABSTRACT

OBJECTIVE: The goal of this work is to develop nondestructive methods to determine the atomic and molecular structures present in the organic (maceral) components of whole coal and coal products.

WORK DONE AND CONCLUSIONS: The naturally occurring unpaired electrons in coal are being used as "observation posts" from which to survey neighboring atoms through electron-nuclear hyperfine interactions and g-anisotropy. The approach has been termed ELECTRON SPIN MAPPING of coal structure. Newer techniques – 2-dimensional ENDOR, ESE, and very high frequency EPR – are being developed in the context of the research. During the entire grant period we have focused on these questions: (i) can we distinguish spectroscopically between purely hydrocarbon structures in coal and those containing heteroatoms? (ii) can we account for the spectral effects of heteroatoms in terms of g-anisotropy and hyperfine interactions? We have proceeded with comparisons between 2-dimensional ENDOR spectra of coal at X-band (9.5 Ghz) and EPR measurements made at much higher fields and frequencies (W-band, 96 Ghz; UHF, 250 GHz). With support from this DOE grant, supplemented by additional funding from the Illinois Center for Research on Sulfur in Coal, the Petroleum Research Fund (ACS) and the National Institutes of Health, we have developed a very high frequency electron paramagnetic resonance (EPR) spectrometer operating at the W-band of microwave frequencies (96 GHz), one of only three such instruments in the world, and the only one in the U.S.A. Conclusions: This instrument is exhibiting unique sensitivity to heteroatoms in coal, and we believe the technique can be successfully applied for the non-destructive, direct determination of organic sulfur in coal. Preliminary data from Illinois coals and separated macerals indicate that the method also may be able to distinguish aromatic from aliphatic sulfur, and may be useful in assessing the extent of conjugation in aromatic portions of the coal.

Through work on model compounds such as benzothiophene, dibenzothiophene and thianthrene, we have developed an interpretation for the ENDOR spectra of heteroatomic

conjugated aromatic radicals including both the g-anisotropy and hyperfine interactions. This analysis makes use of the concept of orientation selection in the ENDOR spectra, and applies the 2-dimensional ENDOR technique with simulation analysis to disordered aromatic systems.

Finally, we have started two exploratory extensions - (1) the combination of high-frequency EPR and ENDOR and the utility of this combination for the study of fossil fuels, and (2) the use of ESE-determined relaxation times and EPR-determined signal strengths, linewidths, and line shapes to study surface properties of coals and chars, in particular their response to oxygen. Conclusion from (2): certain types of coal particle surfaces exhibit exquisite sensitivity to oxygen, the mechanism(s) being complex and requiring further study.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: 2-dimensional ENDOR and very high frequency EPR measurements of coal provide much better spectral resolution for the identification of structure. Our progress in these two areas, together with advances in our theoretical understanding of the structural origins of the effects, means that we are advancing toward our goal of the nondestructive determination of coal structure. In the short term, it means that we may now be able to quantitatively determine the hydrocarbon/heteroatom ratios in coals and separated macerals in a quick, nondestructive test.

PLANS FOR THE COMING YEAR: This is the final year of the current grant; the final effort on this grant will concentrate on (1) continuation of the very-high-frequency spectral measurements of sulfur-containing aromatic model compounds and their analysis, (2) comparative high-frequency, ENDOR, and ESE analyses of coal macerals before and after low-temperature pyrolysis, and (3) continuing exploration of the surface properties of coal particles under treatment by oxygen and similar gases, as examined by EPR and ESE.

II. HIGHLIGHT ACCOMPLISHMENTS

The probe of coal structure in our nondestructive spectroscopic approach is the unpaired electron. This electronic spin 1/2 particle allows us to perform various EPR, ENDOR (electron-nuclear double resonance), and pulsed EPR experiments (electron spin echo or ESE, and 2D-FT EPR) that are designed to explore the atomic and molecular environments of the unpaired electron. In the third year of this grant, the most intense concentration has been upon resolution of organic heteroatomic regions in coal by VHF EPR spectroscopy, and we highlight this aspect of the work.

Very-high-frequency (W-band and G-band) EPR spectra acquired on several Argonne Premium Coal Samples, upon density-gradient-separated maceral components and treatment products from Illinois # 6 coal, and upon sulfur-containing heterocyclic model compounds revealed a wide range of behaviors. The common characteristic of these spectra is extraordinary resolution. A low-magnetic-field feature in the spectrum is always present, and it correlates strongly with sulfur content. The simulations which we have performed strongly suggest that each signal arises from more than one chemical component in the coal and that it is a mixture of nearly-isotropic spectra of homocyclic aromatic molecules and anisotropic spectra associated with sulfur-containing heterocyclic rings. A systematic study of thiophenes fused to aromatic rings is starting to suggest that the position of the low-field feature can be used to determine effective heterocyclic fused-ring system size while its shape and width provide clues to site strain and dispersion of sizes.

III. ARTICLES AND PRESENTATIONS

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G. B. Rattinger, R. L. Belford, H. Walker, and T. L. Brown, "EPR-Derived Electronic Characteristics of Zerovalent Manganese," Inorg. Chem. 28, 1059, 1989.

J. B. Cornelius, J. McCracken, R. L. Belford, R. B. Clarkson, and J. Peisach, "ESEEM Angle Selection Studies," J. Phys. Chem., 94, 6977, 1990.

R. B. Clarkson, R. L. Belford, D. R. Brown, H. C. Crookham, K. J. Mattson, M. J. Nilges, Wei Wang, and D. J. Youn, "Magnetic and Molecular Structure in Coal," invited keynote paper, 12th International Symposium on EPR, Denver, August, 1989.

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D. J. Youn, K. J. Mattson, R. L. Belford, and R. B. Clarkson, "ENDOR Spectra of Aromatic Radical Ions in Disordered Solids: Spectra and Analysis", 12th International Symposium on EPR, Denver, August, 1989.

M. J. Nilges, M. D. Timken, W. Wang, R. B. Clarkson, P. H. Davis, J. Forrer, and R. L. Belford, "High-Field EPR: W-Band (95 GHz) Spectroscopy", 12th International Symposium on EPR, Denver, August, 1989.

R. B. Clarkson, "Influence of Organic Sulfur in Very High Frequency EPR of Coal", Third Processing and Utilization of High-Sulfur Coals, Ames, November, 1989; Clarkson, R. B., Wang, W., Nilges, M. J., and Belford, R. L. In Processing and Utilization of High-Sulfur Coals III; Markuszewski, R. and Wheelock, T. D., Eds; Elsevier: New York, pp. 67-79, 1990.

D. L. Brown, H. C. Crookham, R. L. Belford, and R. B. Clarkson, "Electron Magnetic Resonance Studies of Argonne Sample Bank Coals", invited paper, International Chemical Congress of Pacific Basin Societies, Honolulu, December, 1989.

Clarkson, R. B., Timken, M. D., Brown, D. R., Crookham, H. C., and Belford, R. L. "Enhancement of Nuclear Modulation in Electron Spin Echoes at Low Magnetic Fields: S-Band ESE Spectrometer," Chem. Phys. Letters, 163, 277-281, 1989.

R. B. Clarkson, R. L. Belford, and C. Reiner, "A SAW Oscillator-Based Modulator/Mixer for Frequency-Modulated ENDOR," Rev. Sci. Instrum., 61, 3356, 1990.

Dennis J. Youn, "Anisotropic EPR Spectra of Heterocyclic Sulfur Compounds," PhD Thesis, University of Illinois, Urbana, IL (1989).

R. B. Clarkson, Wei Wang, D. L. Brown, H. C. Crookham, and R. L. Belford, └o"Multi-Frequency EPR Studies of Argonne and Illinois Sample Bank Coals," FUEL, 69, 1405 (1990).

R. B. Clarkson, W. Wang, D. L. Brown, H. C. Crookham, and R. L. Belford, "Multi-Frequency EMR Studies of Argonne Premium Coal Samples," in Techniques in Magnetic Resonance for Carbonaceous Solids, R. Botto and Y. Sanada, eds., ACS Advances in Chemistry Series, American Chemical Society, Washington, 1991 (in press).

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H. C. Crookham, "X-Band ENDOR and S-Band ESEEM of Paramagnetic Disordered Solids," Ph.D. Thesis, University of Illinois, Urbana, IL, 1990.

D. R. Brown, "S-Band ESE and Multifrequency EPR Studies of Some Disordered Solids," Ph.D. Thesis, University of Illinois, Urbana, IL, 1990.

K. J. Mattson, "Computer-Assisted Analysis of EMR Spectra and ENDOR of Isolated Perylene Cations," Ph.D. Thesis, University of Illinois, Urbana, IL, 1990.

W. Wang, R. B. Clarkson, R. L. Belford, and M. J. Nilges, "W-Band EPR Spectra of Coal Models: Aromatic Radicals with Sulfur Atoms," 14th International Symposium on EPR, Denver, July, 1991.

DATE: April 22, 1991

TITLE: ^{31}P NMR Analysis of Coal Moieties Bearing -OH, -NH and -SH Functions

PI: John G. Verkade

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED: Dr. R. V. Davis (Ph.D.); Dr. A. Wroblewski (postdoctoral); Dr. M. C. Ye (postdoctoral)

INSTITUTION: Department of Chemistry
Iowa State University
Ames, IA 50011-3111
(515) 294-5023

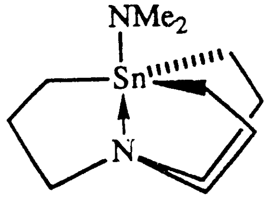
GRANT NO.: DE-FG22-88PC88923

PERIOD OF PERFORMANCE: September 1, 1988 to August 31, 1991

I. ABSTRACT

OBJECTIVE: To develop heteronuclear NMR reagents for the identification and quantitation of labile hydrogen functional groups in liquid and solid coal materials.

WORK DONE AND CONCLUSIONS: Two chlorophospholanes ($ClP(OCMe_2)_2$ and $ClP(SCH_2)_2$ have been synthesized as ^{31}P-containing NMR reagents and we have demonstrated them to be useful in the identification and quantitation of phenols in coal pyrolysates. These reagents afford considerably better chemical shift dispersions than phosphorus reagents used heretofore by others. A serendipitous discovery made during the course of this work led to the development of $Ph_2(O)PCl$ as an advantageous ^{31}P NMR tagging reagent for the analysis of moisture in coals (and other pyridine-extractable solids). A variety of ^{119}Sn NMR tagging reagents of the type $R_3SnNR'_2$, $RC(O)NR'SnR_3$, $RC(O)N(SnR_3)_2$ and $(R_3Sn)_2NR'$ have been evaluated for their efficacy in identifying and quantitating labile hydrogen functional groups found in coal materials. While several of these reagents appear promising in that they provide significantly better chemical shift dispersions than any of our ^{31}P reagents, there is a persisting problem with concentration dependence of the ^{119}Sn chemical shifts of the derivatized species, owing to equilibria involving coordination of a solvent molecule to the tin (to render it five-coordinate) and dimerization of the derivatized species. We anticipate that this problem will be solved by the robustly chelated five-coordinate tin reagent shown which we have recently synthesized. Mössbauer data on an Illinois No. 6 coal derivatized with $O(SnBu_3)_2$ were previously interpreted by Larsen and co-workers to be consistent with tin nuclei rendered five-coordinate in the coal matrix by coordination of a neighboring heteroatom. Although our ^{119}Sn NMR data seem to suggest the presence of four-coordinate tin, our independently obtained Mössbauer data are essentially consistent with those of Larsen and co-workers. Further CPMAS ^{119}Sn NMR studies are clearly indicated to resolve the apparent discrepancy between the two spectroscopic techniques. Since platinum(II) readily coordinates organosulfur molecules, complexes of this metal ion are being investigated for their utility in identifying organosulfur forms in coal materials. Numerous model organosulfur compounds including thiophenes have been coordinated to several platinum(II) reagents, and their ^{195}Pt chemical shifts have been measured.



SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM: An accurate knowledge of the content and chemical environment of oxygen- and sulfur-bearing organic functional groups in coal and coal-derived materials is required for today's and the future's increasingly sophisticated coal processing technologies.

PLANS FOR THE COMING YEAR: 1) We plan to utilize our ^{31}P, ^{119}Sn and ^{195}Pt methodologies as a valuable adjunct to HPLC/MS techniques for identifying and quantitating heteroatom organic molecules in coal liquids, including heavy liquefaction fractions. 2) In order to shed further light on the manner in which water is bound in solid coals, we will follow the extraction of water over time with solvents of varying swelling capability. Preliminary results indicate that even for solvents of the same swelling ability, the rate of water extraction is not the same for some coals. 3) We will carry out reactions of the novel ^{119}Sn reagent whose structure was shown earlier in this abstract, with model labile hydrogen functional compounds to verify the anticipated invariance of the ^{119}Sn chemical shift with solution concentration. We will then proceed to the analysis of a variety of coal liquids. We will also derivatize solid coals with this rigid already five-coordinate tin reagent in an effort to resolve the apparent discrepancy between the NMR and Mössbauer data described earlier in this abstract. 4) We wish to clarify the nature of a reaction of PBu_3 with solid Illinois No. 6 coal to give a CPMAS ^{31}P NMR peak at ca. 3 ppm. This chemical shift does not correspond to $OPBu_3$ or to $SPBu_3$. When we find the origin of this peak, this reaction may constitute the basis for a valuable NMR probe of solid coal structure.

II. HIGHLIGHT ACCOMPLISHMENTS

1) Sixty percent of the phenols in an Illinois No. 6 condensate have been identified and quantitated using the ^{31}P NMR tagging reagents $ClP(SCH_2)_2$ and $ClP(OCMe_2)_2$. 2) Moisture contents in six Argonne Premium Coal samples have been measured with the superior ^{31}P NMR tagging reagent for this purpose $Cl(O)PPh_2$ and the values compared with other methods. 3) Platinum(II) and tin(IV) reagents have been developed as NMR tagging reagents for the analysis of organosulfur and organic labile hydrogen functional groups, respectively.

III. ARTICLES AND PRESENTATIONS

1. C. Lensink and J. G. Verkade, *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.*, 33, 906, (1988).
2. A. E. Wroblewski, C. Lensink, R. Markuszewski and J. G. Verkade, *Energy and Fuels*, 2, 765, (1988).
3. K. Reinartz and J. G. Verkade, *Meeting Abstracts, Coal Characterization Symposium, 1989 International Chemical Congress of Pacific Basin Societies*, INOR 596, Honolulu (1989).
4. C. Lensink and J. G. Verkade, *Energy and Fuels*, 4, 197, (1990).
5. J. G. Verkade, M. C. Ye, *Abstracts, 200th Meeting, American Chemical Society, Washington D.C.*, INOR 30 (1990).
6. A. E. Wroblewski, C. Lensink and J. G. Verkade, *Energy and Fuels*, accepted.
7. J. G. Verkade, invited lecture, The Pennsylvania State University, scheduled for fall semester, 1991.

Date: April 9, 1991

TITLE: FORMATION AND RETENTION OF METHANE IN COAL

P.I.S.: V. Joseph Hucka and David M. Bodily

STUDENT AND DEGREE FOR
WHICH HE IS REGISTERED: He Huang, Ph.D. in Fuels Engineering

GRANT No.: DE-FG22-88PC88939

PERIOD OF PERFORMANCE: September 15, 1988 to September 14, 1991

I. ABSTRACT

OBJECTIVE:

The methane content of coal seams in Utah and Colorado will be measured in situ as well as in the laboratory and correlated with the geological and geochemical history of the seams and surrounding strata. Chemical and physical properties will be measured in the laboratory for coals that contain methane and coals of similar rank which do not contain methane. Methane yields on pyrolysis will be used to measure the propensity of coals to form additional methane. Methane formation and retention will be interpreted in terms of the physical and chemical properties of the coal and the chemical and geological history of the coal seam.

WORK DONE AND CONCLUSIONS:

The methane content was measured in situ in the Lower Sunnyside seam of the Sunnyside Coal Mine (2.5 to 5.00 m^3/mt), in the Synnyside seam of the Soldier Creek Mine (1.2 m^3/mt), and in the Castlegate A seam of the Beaver Creek Mine No. 8 (no methane was detected). Field measurements on cleats in coal and joints in the surrounding rocks were also performed in these seams.

Eleven coal samples have been collected, 8 from the Book Cliffs and 2 from the Wasatch Plateau fields of Utah and 1 from Colorado. All of the samples come from gassy seams, except for the two from the Wasatch Plateau field. Ultimate, proximate and other analysis has been performed for each of these coals. Helium densities were also measured. Permeabilities have been measured for selected samples.

Dipolar dephasing carbon-13 nuclear magnetic resonance spectroscopy measurements have been performed on each of these samples. Types of aliphatic and aromatic carbons were determined for each sample.

The coal samples have been pyrolyzed at 12°C/min up to 900°C to determine the propensity for additional methane formation. The formation of carbon dioxide, carbon monoxide, hydrogen, ethane and ethylene were also measured during pyrolysis. The pyrolysis behavior of these coals has been compared with that of coals from the Argonne Coal Sample Bank.

Equipment has been designed and constructed for the measurement of the adsorption, desorption, heat of adsorption, and diffusion behavior of methane and other gases in these coals.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Coalbed methane represents a valuable energy resource, with estimates of up to 800 trillion cubic feet. Mining in the presence of methane presents safety hazards and adds to mining costs. This study will provide information on the interaction of methane and coal that will be useful in the design of methane recovery schemes.

PLANS FOR THE COMING YEAR:

This project ends in September 1991. The pyrolysis data will be used to evaluate models for gas formation during pyrolysis, with special emphasis on methane formation. The gas adsorption and desorption properties of various gases and coal will be determined. These studies will include measurements of heats of adsorption and diffusion characteristics. The results of the methane adsorption studies, the pyrolysis studies, the nuclear magnetic resonance studies, and the characterization of the coals will be correlated to determine the relationships between chemical and physical structure and methane formation and retention. Methane retention will also be correlated with geological conditions and history.

II. HIGHLIGHTS OF ACCOMPLISHMENTS

In situ measurements on methane content were performed. A collection of samples from gassy seams in Utah has almost been completed. The laboratory analysis of these samples was performed, including carbon-13 nuclear magnetic resonance. The pyrolysis of the 11 coal samples from this study and 8 Argonne Coal Sample Bank coals was completed. Equipment has been constructed to measure the adsorption and desorption properties of the coals.

III. ARTICLES AND PRESENTATIONS

"Methane Drainage from Gassy Western U.S. Coal Seams," V. J. Hucka and D. M. Bodily, Today's Technology for the Mining and Metallurgy Industries, MMIJ/IMM Joint Symposium, Volume of Papers, 1989, Kyoto, Japan, p. 453.

"Correlation of Chemical Structure of Coals in the Book Cliffs and Wasatch Plateau fields with Methane Formation and Retention," David M. Bodily, He Huang and V. Joseph Hucka, accepted for publication in Geology of East-Central Utah, Thomas C. Chidsey, Ed., Utah Geological Association, Salt Lake City, 1991.

"Formation of Methane during Coalification and Pyrolysis" He Huang, D. M. Bodily and V. J. Hucka, accepted for poster session, 1991 International Conference on Coal Science, Newcastle on Tyme, September 16-20, 1991.

"In Situ Determination of Desorbable Methane Content by Use of Three Different Decay Functions," R. R. Plaizier and V. H. Hucka, Prepared for 1991 RMAG Guidebook (Coalbed Methane of Western North America, organized by Colorado School of Mines.

April 15, 1991

TITLE: Permeability Changes in Coal Resulting from Gas Desorption

PIs: Jeffrey R. Levine, Department of Geology, The University of Alabama
Philip M. Johnson, Department of Mineral Engineering,
The University of Alabama

STUDENTS AND THE DEGREES FOR WHICH THEY ARE REGISTERED:

Gopalakrishna Prakash: Master of Science, Mineral Engineering
Michael McCollum: Bachelor of Science, Chemical Engineering

INSTITUTION/ORGANIZATION: The Univ. of Alabama, Tuscaloosa, AL 35487
General Phone #: 205-348-6010

GRANT NO.: DE-FG22-89PC89764

PERIOD OF PERFORMANCE: August 15, 1989 - August 14, 1991

I. ABSTRACT

OBJECTIVE: The principal objective of this research is to test the hypothesis that volumetric shrinkage of coal during desorption of occluded gases (particularly CH_4) can result in a net increase in the permeability through natural fractures underground. Testing of this hypothesis for a variety of U.S. coal basins involves four tasks: 1) characterization of coal composition, 2) estimation of mechanical strength and elasticity, 3) measurement of sorption/desorption isotherms, and 4) determination of volume changes during sorption/desorption.

WORK DONE AND CONCLUSIONS: Samples have been collected at field localities in Illinois basin (Illinois), Black Warrior basin (Alabama), and San Juan basin (Colorado). Additional coals selected from the DESC sample bank at Penn State, represent the Northern and Central Appalachian basins. Specimen preparation procedures involve slabbing, polishing, and grinding to provide suitable representative samples controlling for variations in petrographic composition.

Equilibrium gas storage capacity of the coal must be accurately measured in order to interpret sorption-related swelling and shrinkage. Traditionally these measurements have been made via "constant volume" experiments. In an effort to develop an alternative methodology that is both more rapid and usable with smaller samples (e.g. concentrated kerogen or drill cuttings), a high pressure microbalance sorption apparatus has been assembled to precisely measure weight changes of coal during gas sorption. The present configuration is capable of 1200 psi and allows resolution of weight changes as small as 1 microgram on a sample as large as 100 mg. Measurement noise arises from turbulence, due in part to adiabatic heating or cooling of gas during changes in pressure.

Changes in sample weight pressure represent the combined influence of changes in mass of sorbed gases plus changes in buoyancy of the ambient gases. Changes in buoyancy represent the combined effects of changes in displacement volume of the specimen plus changes in density of the ambient gas. Instantaneous weight changes of the sample can theoretically be used to measure changes in displacement volume of the sample; however, sorption of gases occurs too quickly to enable this measurement to be made accurately. Re-equilibration is faster with increasing pressure. Notwithstanding the experimental difficulties, precise sorption isotherms are now being obtained using this approach.

Sorption-related swelling and shrinkage is being measured with strain gages affixed to thin wafers of coal. Small gages enable relatively homogeneous lithotype bands to be isolated. Pairs of gages are mounted parallel and perpendicular to banding. Samples are placed in a large sorption chamber, evacuated to provide a base line value, then exposed incrementally to gas pressures up to 1200 psi. Specimen elongation occurring with changes in pressure represents the combined influence of sorption-related strain plus mechanical compression by the ambient gases. Mechanical response is instantaneous, followed by slow re-equilibration due to sorption. CO_2 sorption produces greater swelling than CH_4. Observed relationships to lithotype banding and bedding anisotropy have been inconsistent.

Preliminary results show that sorption capacity and swelling both decrease with rank, passing through a minimum around high volatile A bituminous rank, before increasing again.

<u>SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:</u> As a consequence of their abnormally high gas concentrations at shallow depths, coal bed gas reservoirs constitute a potentially attractive energy resource. Economic production of gas from coal is hampered in many cases, however, by low permeabilities, which severely limit the flow rates of gas through the reservoir. Development could expand into other regions if reservoir permeability limitations can be overcome. Desorption-related may have important implications regarding producibility of natural gas from coal bed reservoirs. Coals having insufficient shrinkage will become "self-sealing" during production, while coals having sufficient shrinkage will develop progressively higher absolute permeabilities. This research will help to elucidate target areas in basins having the highest potential for economic productivity. Moreover, if permeability can be shown to increase significantly during production, this information will help to refine reservoir models and to develop more accurate economic evaluations and production estimates.

The research is providing an improved understanding of gas sorption in coal and its relationship to coal composition. Information on swelling during sorption may find additional applicability in solvent swelling studies of coal. An additional benefit is the development of high pressure microgravimetric sorption techniques.

<u>PLANS FOR THE COMING YEAR:</u> After overcoming initial difficulties with equipment, data collection is well underway. Additional coals must be studied before conclusions can be drawn regarding the controls of rank and petrographic composition on desorption-related shrinkage. Theoretical changes in permeability will be assessed using Gray's (1987) approach.

II. HIGHLIGHT ACCOMPLISHMENTS

Development of novel methodology for gas sorption studies using high pressure microbalance technology. Preliminary identification of window of minimum sorption capacity/swelling characteristics around high volatile A bituminous rank.

III. ARTICLES AND PRESENTATIONS

Levine, J.R., Thompson, D.A., and Telle, W.R., 1990, Coalbed gas resources of Upper Pottsville Fm. near Duncanville, AL: Geol. Soc. of America Abstracts with Programs, v. 22, p. 23.

Levine, J.R., in press, The impact of oil formed during coalification on generation and storage of natural gas in coal bed reservoir systems: 3rd Coalbed Methane Symposium, Tuscaloosa, AL, May 13-16, 1991, 9 p.

March 12, 1991

TITLE: BASIC PROPERTIES OF COALS AND OTHER SOLIDS

PI: Edward M. Arnett

STUDENT: Tanweer Ahsan, Postdoctoral
Graduate Student, Steven Truckenbrod, Ph.D. Candidate

UNIVERSITY: Department of Chemistry
Duke University
Durham, North Carolina 27706

GRANT NO.: DE-FG22-89PC89780

PERIOD OF PERFORMANCE:

I. ABSTRACT

OBJECTIVE: To make a rigorous thermodynamic evaluation of the physical/chemical interactions of a variety of acids with several clearly defined solid bases as a means towards characterizing complex solids such as coals in terms of their acid-base properties.

WORK DONE AND CONCLUSIONS: The first eighteen months of the project have concentrated on interactions of the following solids with a variety of acids covering a wide range of strengths from acetic to trifluoromethanesulfonic acid and also boron trichloride. Slurries of polyvinylpyridine in acetonitrile were compared with corresponding solutions of pyridine as a homogeneous analog. An excellent correlation of the heats of interaction for the two systems with thirteen of the acids described above demonstrated the feasibility of comparing solid bases with carefully chosen homogeneous analogs. A similar comparison was made under a previous grant (DE-FG22-85PC80521) for which an excellent correlation was obtained comparing slurries of a polysulfonic acid resin with solutions of p-toluenesulfonic acid through their interactions with twenty-nine bases.

An attempt to study the behavior of silica as a solid base through its interaction with the above series of acids led to the unexpected and surprising conclusion that silica is such a powerful hydrogen bond donor that it actually interacts with the whole series of carboxylic and sulfonic acid resins as though they were bases.

With this background the heats of interaction of samples of Exxon Rawhide subbituminous coal and Illinois #6 subbituminous (Argonne Coal Bank) were compared using twelve carboxylic and sulfonic acids. Although no general correlation was obtained, fairly good correlations were found for the interactions of a series of aliphatic acids, and another for a series of aromatic acids implying differential behavior involving π-π interactions. Again good correlations were found between the behavior of the acids with polyvinylpyridine and with the two coal systems.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Many of the processes for refining coal or extracting it depend upon disrupting the hydrogen

bonding and acid-base interactions which hold the coal macromolecules together into an extended framework. Since coals are both acids and bases and are also dispersion force adsorbents it should be useful to provide a classification of different types of coals in terms of these properties and to relate them to other types of simple solids. The present project should provide a quantitative thermodynamic basis for analyzing these types of interactions.

PLANS FOR THE COMING YEAR: With the methodology for comparing basic solids with each other and with homogeneous analogs demonstrated we shall extend it to a wider series of coals many of which we have already studied as solid acids in order to develop multiparameter equations for characterizing them in terms of their overall acid-base behavior. The results will be compared with those for a series of coal liquids derived by various processes as homogeneous analogs to the solid coals.

II. HIGHLIGHT ACCOMPLISHMENTS

The principal accomplishment has been to establish the thermochemical method for comparing solid bases (e.g., polyvinylpyridine) with homogeneous analogs (pyridine solutions). Our demonstration of the extraordinarily powerful hydrogen-bonding ability of silica with carboxylic and sulfonic acids is significant in view of the importance of silicas and related solids as adsorbents and catalysts for a wide variety of processes in the fossil fuel industries.

III. ARTICLES AND PRESENTATIONS

Two articles have been submitted for publication. Two invited lecture presentations at meetings of the American Chemical Society, a) at Boston on April 24, 1990, b) at the Southeast Regional Meeting, New Orleans, December 7, 1990.

TITLE: Single Electron Chemistry of Coals DATE: 3/26/91

P. I.: John W. Larsen

STUDENT AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Robert A. Flowers, PhD., Tom Eskay, PhD.

INSTITUTION: Department of Chemistry, Lehigh University,
Bethlehem, PA 18015, 215 758-3489

GRANT NO.: DE-PS22-89-PC89785

PERIOD OF PERFORMANCE: 10/1/89 to 9/30/92

I. ABSTRACT

OBJECTIVE: There are two objectives concerning the native free radicals in coal. They are: (1) To determine whether the native free radicals in the Argonne coals are sufficiently reactive to initiate the polymerization of 4-vinyl pyridine. (2) To attempt to remove the native radicals from coal by their reaction with N, N′-Diphenyl-p-phenylene diamine (DPPD). Another objective, which does not involve coals' native radicals, is to determine the ability of coals to participate in charge transfer interactions. This will be done by depositing tetracyanoquinodimethane(TCNQ) and tetracyanoethylene (TCE) in the coals and studying their IR spectra. The ESR spectra of the resulting coal-electron acceptor system will also be obtained and evaluated.

WORK DONE AND CONCLUSIONS: 4-vinyl pyridine has been deposited in coals. All of it cannot be removed under vacuum. FTIR difference spectra reveal that it has polymerized in the coals. ESR spectra of the coals have been obtained before and after this polymerization. In all cases, the ESR peak associated with inertinite radicals either disappears or is significantly diminished. Few, if any, changes occur in the ESR signal from the vitrinite macerals. It seems that the radicals associated with vitrinite are sufficiently delocalized so that they are not capable of initiating the polymerization of this styrene analog. The reasons for the disappearance of the inertinite radicals are not entirely clear. It is likely they are involved in the polymerization of the 4-vinyl pyridine.

N, N′-Diphenyl-p-phenylene diamine (DPPD) has been reacted with several coals. Our attempts to detect its oxidation product using FTIR failed. ESR studies reveal about a 30% decrease in the population of radicals in the coal.

TCNQ and TCNE have been deposited in the coals. The changes in the CN stretching frequency of both molecules have been carefully measured and used to determine the extent of electron transfer to them. In both cases, an electron transferred to them must enter the lowest unoccupied molecular orbital. For Illinois #6 coal at a variety of TCNE loadings up to 1 TCNE molecule per aromatic unit in the coal; the TCNQ LUMO is 50% occupied. The corresponding value for TCNE is 30%. ESR spectra demonstrate that the TCNQ radical anion has not formed and that the increase in radical population of the doped coals is up to two orders of magnitude less than

that required for formation of the TCNQ radical anion. IR studies on a large number of aromatic systems demonstrate that none of them can transfer more than about 10% of an electron to TCNQ. We conclude that TCNQ participates in the formation of valence electronic band structures in coal and that the one of these bands is approximately 50% occupied. Consistent with this, many TCNQ coal complexes are bright blue.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The potential role of coals' native free radicals in conversion processes is often discussed. Our data suggests that these radicals are so delocalized that they are essentially unreactive and are not capable either of initiating widespread chemical reactions or even dimerizing. There are in coals extensive stacks of cooperatively interacting aromatics and these can be extended significantly in the presence of electron acceptors. Facile single electron transfer within the coals raises the possibility that this process may be in a variety of chemical reactions of coals. Cooperative aromatic-aromatic interactions are certainly important in the overall structure of the coals.

PLANS FOR THE COMING YEAR: Our plans for the coming year involve two major thrusts. One is to continue to explore the electronic structure coal-TCNQ complexes and extend this work other electron acceptors. As part of this, we will initiate a study of the electronic band structure of bituminous coals. The other main thrust will be the consideration of coal reactions which are induced by single electron transfer processes.

II. HIGHLIGHT ACCOMPLISHMENTS

It has been demonstrated that the native free radicals in coal are essentially unreactive and need not be considered as active participants in most reactions of coals. Coals readily form extended electronic valence band structures when good electron acceptors are added.

III. ARTICLES AND PRESENTATIONS

Flowers II, Robert A; Gebhard, Layce A.; Larsen, John W.; Silbernagel, Bernard G.; Energy & Fuels, 3 762 1989

Flowers II, Robert A.; Gebhard, Layce A.; Larsen, John W.; Silbernagel, Bernard G.; Demineralization Effects on the EPR Properties of Argonne Premium Coals, Energy & Fuels (accepted for publication).

Invited lecturers at the 1990 Gordon Conference, Argonne National Laboratory, University of Southern Illinois, Exxon Research and Engineering Co., University of Southern Mississippi, Colgate University

TITLE: Chemistry of Coal-Related Microparticles DATE: 6 April, 1991

PIs: Professors E. James Davis and Barbara Krieger-Brockett

STUDENTS:
Theresa M. Allen, Ph.D. Candidate in Chemical Engineering
Scot D. Rassat, Ph.D. Candidate in Chemical Engineering
Mark F. Buehler, Ph.D. Candidate in Chemical Engineering (part support)

INSTITUTION:
Department of Chemical Engineering, BF-10
University of Washington
Seattle, WA 98195
(206) 543-2250 and FAX 206 543 3778

GRANT NO.: DE-FG22-89PC89790

PERIOD OF PERFORMANCE: 01 September, 1989 to 31 August, 1992

I. ABSTRACT

OBJECTIVE:

Develop and apply novel single microparticle techniques to perform simultaneously thermogravimetric analysis and Raman/fluorescence spectroscopies on microparticles of coal (macerals) and sorbents (CaO) used for coal desulfurization. The combination electrodynamic balance/spectrometer system will be used to chemically characterize macerals from different ranks of coal and to explore the chemistry and chemical reaction rates associated with processes involving such microparticles. Rate processes will be examined at elevated temperatures by heating the particles electromagnetically.

WORK DONE AND CONCLUSIONS:

A new type of electrodynamic balance has been built and coupled to a Raman spectrometer. With this device a single electrically charged microparticle is suspended in one or more laser beams by means of superposed ac and dc electrical fields. The new apparatus is equipped to permit gas flow through the chamber so that gas-solid and gas-liquid chemical reactions can be carried out. Studies of single microparticles have been performed to explore the laser intensities and optics needed to obtain Raman spectra with a minimum of background noise. In addition, the interaction between a high-intensity laser beam and the microparticle has been studied to determine the energy absorption characteristics of the microparticle. This information is needed to design a laser-based particle heating system to permit reactions to be carried out at elevated temperatures and to control the heating rate of the levitated particle.

Measurements of fluorescence and Raman spectra of coal macerals supplied by Argonne National Laboratories have been made to examine differences between particles of the same maceral type but of different size and to measure the major differences between liptinite, inertinite and vitrinite macerals as evidenced by their fluorescence and Raman spectra. The liptinites examined show a broad fluorescence spectrum which masks the Raman spectrum. Thusfar, this has been done at room temperature, but the work will be extended to macerals at elevated temperatures. Preliminary studies of the chemical reaction between calcium oxide and sulfur dioxide have also been performed to work out a suitable technique for following the reaction rate via Raman spectroscopy. We shall be able to follow the formation of calcium sulfate, the product, by Raman measurements.

Equipment development has proceeded in parallel with spectroscopic studies. An infrared laser heating system has been designed and built to measure and control the particle

temperature and heating rate. This required the design and construction of a new electrodynamic balance chamber with several optical ports for the installation of infrared and visible light detectors. The infrared detectors are used to measure the particle temperature by three-color pyrometery, and an argon-ion laser is used to provide the excitation source for Raman and fluorescence spectroscopy.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

The experimental facility which has been developed through this research project and the facilities currently under construction are unique tools for the study of coal macerals, fuel droplet combustion, and sorbent particle reactions with SO_2 and H_2S. Reactions which occur in fluidized bed coal combustors and other processes can be explored at the level of the single particle under carefully-controlled conditions which closely match the temperatures and heating rates of interest in commercial installations. The spectroscopic probes provide chemical information that cannot be obtained by other methods.

PLANS FOR THE COMING YEAR:

Spectroscopic measurements with macerals will be continued in order to explore a wider range of coal types. Using the apparatus currently under construction, the measurements will be carried out at elevated temperatures. In the first two months of the next year the infrared heating and temperature control system will be installed and tested. Measurements of maceral devolatilization kinetics and of sorbent/SO_2 reactions will also be performed at elevated temperatures to examine the effects of pore-plugging on the effectiveness of the sorbent(s).

II. HIGHLIGHT OF ACCOMPLISHMENTS

Techniques and apparatus have been developed for chemically characterizing macerals and coal-related microparticles with dimensions in the range 1-100 μm. Raman spectra and fluorescence spectra of coal macerals and other carbonaceous microparticles have been obtained to characterize such materials. Spectroscopic studies of calcium sulfate have also been carried out for use in the study of the reaction between calcium oxide sorbent particles and sulfur dioxide. In addition, energy transfer between a high-intensity laser beam and a microparticle has been studied experimentally and theoretically to provide information needed to design apparatus for heating microparticles for studies of devolatilization kinetics and processing characteristics of macerals and sorbent particles at elevated temperatures. The apparatus to be used for measurements at elevated temperatures is currently under construction.

III. ARTICLES AND PRESENTATIONS

Davis, E. J., Buehler, M. F., and Ward, T. L., "The Double-Ring Electrodynamic Balance for Microparticle Characterization," *Rev. Sci. Instrum.* **61**, 1281-1288 (1990).

Allen, T. M., Buehler, M. F., and Davis, E. J., "Radiometric Effects on Absorbing Microspheres," *J. Colloid Interface Sci.* **142**, 343-356 (1991).

Davis, E. J., Allen, T. M., and Buehler, M. F., "Radiant Energy Absorption by Microparticles of Fuel," presented at the 1990 Gordon Research Conference in Fuel Science, July 2-6, 1990.

Davis, E. J., Allen, T. M., and Buehler, M. F., "Laser Heating of Microparticles and Microdroplets," presented in the symposium "Fundamental Research in Heat and Mass Transfer" at the AIChE Annual Meeting in November, 1990.

Davis, E. J., "Optical Measurements of Electrodynamically Levitated Microparticles," *SPIE Proc. Intl. Symp. on Laser Spectros.*, in press (1991).

TITLE: Novel technique for Coal Pyrolysis and Hydrogenation Product Analysis

PI: Lisa D. Pfefferle, Assoc. Professor

STUDENT:
James Boyle, Ph.D.

INSTITUTION/ORGANIZATION: Yale University, Department of Chemical Engineering,
P.O. Box 2159 Yale Station, New Haven, CT 06520.
Phone number of PI: (203) 432-2460

GRANT NO.: DE-FG22-89PC89767

PERIOD OF PERFORMANCE: 9/1/89 - 8/1/92

ABSTRACT FOR 1991 ANNUAL MEETING

The overall objective of this study is to establish vacuum ultraviolet photoionization-MS and VUV pulsed EI-MS as useful tools for a simpler and more accurate direct mass spectrometric measurement of a broad range of hydrocarbon compounds in complex mixtures for ultimate application to the study of the kinetics of coal hydrogenation and pyrolysis processes. The VUV-MS technique allows ionization of a broad range of species with minimal fragmentation. Many compounds of interest can be detected with the 118 nm wavelength, but additional compound selectivity is achievable by tuning the wavelength of the photo-ionization source in the VUV.

The microjet reactor coupled to a VUV photoionization time-of-flight mass spectrometer has been used to obtain species measurements for high temperature pyrolysis of ethyl acetylene, butadiene, cyclohexane, benzene and toluene. Using this technique, intermediate species profiles of both stable and labile product masses were obtained for analysis of the pyrolysis pathway. Fragmentation was minimized due to the nature of the ionization, yielding predominantly molecular ions. This allows the study of reaction pathways in complex high temperature systems where both sampling and detection challenges are severe. This was true even for the worst case of cyclohexane where fragmentation of the parent fuel was appreciable.because fragmentation of the reaction products was so low In our presentation we will discuss the results from benzene and cyclohexane pyrolysis and our work with development of correlations for VUV photoionization yields based on PES data.

Boyle, J., Pfefferle, L., Lobue, J., Colson*, S., *Combust. Sci. and Tech.*, 70, (1990),187.

Boyle, J., and Pfefferle, L., Presentation at the AIChE Annual Meeting, San Fransisco, CA, Nov. 1989.

Boyle, J., Pfefferle, L.,Gulcicek., Colson*, S., Rev. *Sci. Insts.*, 62 (2), (1991), 323.

*Currently at DOE-Battelle Pacific Laboratory

DATE: April 4, 1991

TITLE: MOLECULAR ACCESSIBILITY IN SOLVENT SWELLED COAL

P.I. (AUTHORS): Lowell D. Kispert (PI), Ross Spears and Lidia Piekara-Sady

STUDENT AND THE DEGREE FOR WHICH HE IS REGISTERED:
D. Ross Spears, Ph.D.

INSTITUTION: The University of Alabama, Chemistry Department, Tuscaloosa, AL 35487-0336, Telephone: (205) 348-7134

GRANT NO.: DE-FG22-90PC90284

PERIOD OF PERFORMANCE: 8/3/90 - 8/2/93

I. ABSTRACT

OBJECTIVE: It is the objective of this research to determine catalyst accessibility in Argonne Premium Coal Samples (APCS) upon swelling in polar, basic solvents before and after moisture loss. This can be obtained using an EPR technique that we have developed [S-K. Wuu and L. D. Kispert, *Fuel*, **64**, 1681 (1985)] involving various nitroxide spin probes of different shapes or sizes diffused into coal samples. The results are consistent with SANS, DRIFT and NMR relaxation measurements of pore structure as a function of swelling solvents. The advantage of the EPR method is that it permits molecules of selected shape and size to be used as probes of accessible regions of the coal, thus providing information on the importance of molecular shape.

WORK DONE AND CONCLUSIONS: The EPR spin-probe method was utilized to measure the changes in pore accessibility in all eight Argonne Premium Coal Samples (APCS) as a function of swelling solvent, temperature of swelling solvent and coal rank. The structures of the spin probes varied from I which was spherical to XIII and V which were elongated and differed in length. The coals were swelled with nonpolar toluene or nitrobenzene or polar pyridine, at various temperatures.

At room temperature, the spin concentration of spherical TEMPOL in the swelled coals decreased with rank for coals swelled with either toluene or nitrobenzene. For coals below about 85% carbon content (dmmf) swelled in nitrobenzene contained a higher spin probe concentration than coals swelled in toluene. For coals with greater than 85% carbon content (dmmf), there was no significant difference in spin probe concentration regardless of rank or swelling solvent. Coals (< 85%) swelled with pyridine did not retain TEMPOL to any significant degree.

Coal has been shown by SANS (Gehner or Winans) experiments to contain spherically shaped pores. Coal swelled in a mild swelling solvent like toluene at room temperature still retains a significant quantity of spherical pores. At room temperature, nitrobenzene, a moderately polar swelling solvent, caused an increase in the number of the spherically shaped pores and a subsequent increase in the number of trapped smaller spherical shaped probe I. However, when coal underwent more severe swelling, such as in pyridine, pores lost their sphericity and became enlarged and elongated or cylindrical in shape. As a result, the spherical TEMPOL molecules are not retained when the coals were washed with cyclohexane.

The severity of swelling is not only affected by solvent polarity, but also by temperature. An increase in swelling temperature from 288 K to 333 K, while small, had a significant effect on the pore structure of coal. For higher ranked coals (above 85% carbon content), spin probe concentration did not vary significantly regardless of rank or swelling solvent.

For lower ranked coals, toluene-swelled coals retained a significant number of spherically shaped pores, while coals swelled in pyridine did not. Interestingly, at 333 K, coals swelled in nitrobenzene no longer contain significant quantities of spherically shaped pores.

The swelling process using nitrobenzene and pyridine result in a break-up of the hydrogen bonding system, causing an elongation of the pore structure. For nitrobenzene this was most noticeable using spin probe XIII at 298 K and at 333 K. Spin probe XIII is long and cylindrical in shape. When the APCS coals were swelled in nitrobenzene at room temperature, a significant number of cylindrical pores were present, as were numerous spherical pores. When the swelling temperature was increased to 333 K, the spherical pores all but disappeared, and the number of cylindrical pores increased significantly.

Due to limited space we will only briefly discuss the effect of temperature on the optimal elongation length deduced using several different spin probes for each solvent as a function of coal rank. Elongated probe V shows that almost no detectable spin probes of the size for which probe V would be trapped occurred at room temperature for toluene, or nitrobenzene or pyridine. However, at 333 K, pyridine exhibited significant and measurable concentration of elongated pores similar to that of probe V while none were observed for toluene or nitrobenzene solvents.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The conversion of coal by an economically feasible catalytic method requires the catalyst to diffuse into the coal sample so that hydrogenation catalysis can occur from within as well as the normal surface catalysis. Thus an estimate of the size and shape of the pores in the coal before and after swelling with different solvents is needed so that an optimum sized catalyst will be used.

PLANS FOR THE COMING YEAR: We plan to study the change in pore structure with swelling solvents after dehydration of the samples at various elevated temperatures. Studies of the swelling properties of gels and polymer beads are now underway to gain insight into the coal swelling process using our spin probe method.

II. HIGHLIGHT ACCOMPLISHMENTS

The use of nitroxide spin probes with swelling solvents is a simple way in which to gain an understanding of the pore structure of coals and how it changes in the presence of swelling solvents. Coal contains significant quantities of spherically shaped pores increasing with decreasing rank. If coal is mildly swelled with nitrobenzene, the number of spherically shaped pores increases. As solvent polarity increases, such as with pyridine or as swelling temperature increases pores become elongated as evidenced by a decrease in the number of spherically shaped pores and a similar increase in the number of elongated pores. Finally, regardless of the swelling conditions, the pore structure of high rank coals changes very little.

III. ARTICLES AND PRESENTATIONS

1. J. Goslar and L. D. Kispert, "EPR and ENDOR Studies of Argonne Premium Coals Doped with Nitroxide Spin Probes," *Fuel* **69**, 564 (1990).

2. R. Spears, J. Goslar and L. D. Kispert, "EPR Spin Probe Studies of Porosity in Solvent Swelled Coal," *ACS Adv. in Chem. Series: Magnetic Resonance of Solid Carbonaceous Fuel*, Edt. R. Botto and Y. Sanada, in press 1991.

3. D. R. Spears, L. D. Kispert and L. Piekara-Sady, "Low Temperature Swelling of Argonne Premium Coal Samples: Effect on Pore Structure" *Am. Chem. Soc. Div. Fuel Chem. Preprints*, **36**, 29 (1991); 201st ACS National Meeting, Atlanta, April 14, 1991.

TITLE: Advanced NMR Approaches in the Characterization of Coal DATE: 4/3/91

P.I.: Gary E. Maciel

STUDENT(s) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Haiou Vicky Pan (Ph.D.) and Yahong Sun (Ph.D.)

INSTITUTION/ORGANIZATION: Department of Chemistry, Colorado State University, Fort Collins, CO 80523, tel.: (303) 491-6480

GRANT NO.: DE-FG22-90PC90290

PERIOD OF PERFORMANCE: 1 August 1990 - 31 July 1993

I. ABSTRACT

OBJECTIVE:
To develop and apply advanced NMR techniques for the structural characterization of coals.

WORK DONE AND CONCLUSIONS:
Examined large-volume magic-angle spinning approaches for ^{13}C NMR analysis.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:
Substantially improved prospects for quantitation in ^{13}C magic-angle spinning analysis of coals.

PLANS FOR THE COMING YEAR:
a) Extend the large-volume ^{13}C SP-MAS approach to other premium coals.
b) Develop methodology for detailed functional group analysis through a combination of ^{1}H, ^{13}C and ^{1}H-^{13}C NMR approaches.

II. HIGHLIGHT ACCOMPLISHMENTS

The analytical characteristics of the three Argonne Premium coals 801, 601 and 501 have been examined by magic-angle spinning (MAS) ^{13}C NMR, using large samples (2.5 cm^3). This study was based on experiments with ^{13}C magnetization generated by both cross polarization (CP) and by 90° single-pulse (SP) approaches. Various ^{13}C-based relaxation measurements were made. Using the Delrin ^{13}C signal of the Delrin/zirconia spinner as a built-in intensity reference, spin counting was carried out. It was determined that the single-pulse magic-angle spinning (SP-MAS) ^{13}C approach accounts for about 80%, and that the customary cross-polarization magic-angle spinning (CP-MAS) technique accounts for only about 50% of the carbon known to be in each sample; however, a CP-MAS approach that incorporates a better $T^{H}_{1\rho}$ determination accounts for more than 80% of the carbons.

Dipolar-dephasing ^{13}C NMR studies provide a measure of the contributions of proton-bearing and non-proton-bearing carbons in the three coals and the fraction of aromatic or aliphatic carbons that are proton-bearing. The attractiveness and utility of large-volume ^{13}C MAS approaches in the analysis of coal are demonstrated. Although useful results can be obtained via ^{13}C CP-MAS experiments (if one carries out the proper characterization of CP dynamics), the SP-MAS approach with large samples is more straightforward.

III. ARTICLES AND PRESENTATIONS

Paper:
"Recent Advances in Coal Characterization by ^{13}C and ^{1}H NMR," G.E. Maciel, C.E. Bronnimann, A. Jurkiewicz, R.A. Wind and V.H. Pan, *Fuel*, in press.

Presentation:
"Recent Advances in Coal Characterization by ^{13}C and ^{1}H NMR," International Symposium on Coal Structure, Cambridge University, 9/5-7/1991.

TITLE: The Effect of Selective Solvent Absorption on Coal Conversion

DATE: 20 Mar 1991

P.I.(s): John W. Larsen

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Jewel Amui, Ph.D.
Lazarin Lazarov, Visiting Scientist

INSTITUTION/ORGANIZATION: Department of Chemistry, Lehigh University, Bethlehem, PA 18015 (215) 758-3489

GRANT NO.: DE-PS22-90PC90304

PERIOD OF PERFORMANCE: September 1, 1990 through August 31, 1993

I. ABSTRACT

OBJECTIVE: This project has two objectives:

1. To determine the composition of the recycle solvent actually present within the coal during the early stages of direct liquefaction.

2. To determine the effect of the presence or absence of hydrogen donors within the coal during the early stages of coal conversion.

WORK DONE AND CONCLUSIONS: Our experimental work to date has been directed solely at the first of the objectives listed above. An apparatus has been designed and constructed which allows the exposure of coals to Wilsonville recycle oil at temperatures between 120 and 180°C at various solvent: coal ratios. Both Illinois No. 6 coal and Wyodak sub-bituminous coal have been so exposed. The coals do absorb solvent and swell. The amount of solvent absorbed increases with the exposure temperature. The proton NMR of the whole recycle oil and of the non-absorbed part of the recycle oil have been compared (Illinois No. 6 coal). The spectra are identical, in spite of the fact that the coal has absorbed between 15 and 23% of the recycle oil, depending on conditions. The molecular weight distributions of the recycle oil before and after a portion has been removed by absorption, are identical. Our tentative conclusion is that, for this relatively non-polar recycle oil, no selective absorption by Illinois No. 6 coal is occurring.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: An enormous amount of work has gone into rationalizing the behavior of coals during direct liquefaction reactions, yet no one has determined the exact composition of the reacting system. It consists not only of coal but also of that portion of the recycle oil which has dissolved in and swollen the coal. Coals are known to be highly selective absorbants and may extract a particular fraction from the recycle oil. In order to understand the chemistry which is occurring, the reacting system must be carefully defined. We tentatively conclude that for non-polar recycle oils having a low heteroatom contents. Illinois No. 6 coal is a non-selective absorbent.

PLANS FOR THE COMING YEAR: We plan to extend this work to a broader range of coals and to study recycle oils containing more heteroatoms, if such samples can be obtained. We are also comparing the conversion of coals in 2-*t*-butyltetralin, which does not diffuse into coals, with conversions in tetralin.

II. HIGHLIGHT ACCOMPLISHMENTS

The demonstration that Illinois No. 6 coal is a non-selective absorbent for Wilsonville recycle oil.

III. ARTICLES AND PRESENTATIONS

None.

COAL SURFACE SCIENCE

Date: April 5, 1991

TITLE: ROLES OF ADDITIVES AND SURFACE CONTROL IN SLURRY ATOMIZATION

PI: Professor Shirley C. Tsai

STUDENTS AND THE DEGREES FOR WHICH THEY ARE REGISTERED:

Senior students working for B.S. in Chemical Engineering:
Nuragung Widjaja and John Estes
Graduate students working for M.S. in Engineering:
Brian Viers, Dale Botts, and Khashayar Ghazimorad

INSTITUTION/ORGANIZATION:

Department of Chemical Engineering
California State University at Long Beach
Long Beach, CA 90840
Tel. No.: (213)985-7534 (O) or (714)854-0917 (H)

GRANT NO.: DE-FG22-88PC88912

PERIOD OF PERFORMANCE: September 15, 1988 - September 15, 1991

I. ABSTRACT

OBJECTIVES:
1. To promote further understanding of the mechanisms and the roles of additives in airblast atomization of coal water slurry (CWS).
2. To investigate the impacts of coal particle surface properties and interparticle forces on CWS rheology.

WORK DONE AND CONCLUSIONS:

In the past year, this project has focused on the effects of anionic dispersant (A23M, an ammonium salt of naphthalene sulfonic acid formaldehyde polymer, from Henkel) on the rheology and atomization of micronized (4 μm to 20 μm) coal water slurries (CWSs). The effect of nonionic surfactant (Tergitol NP-40, nonylphenol polyethylene glycol ether from Union Carbide) on CWS rheology was also examined. It was found that the micronized CWS is pseudoplastic (shear thinning) at a low additive concentration of either anionic dispersant or nonionic surfactant because coal particles aggregate under the influence of interparticle van der Waals attraction. The micronized CWS becomes Newtonian because the interparticle van der Waals attraction is counterbalanced by the interparticle electrostatic repulsion as more anionic dispersant molecules are adsorbed onto the coal particle surface. The CWS turns shear thickening at a higher surfactant concentration as the nonionic surfactant molecules adsorbed on different particles cross link with each other.

The relative viscosity of a pseudoplastic coal slurry, at a constant volume fraction, can be approximated as a function of the particle Peclet number, which equals the time required for a particle to diffuse a distance comparable to its radius multiplied by the shear

rate. It is independent of particle density, but increases substantially as the viscosity of the suspending liquid decreases. The relative viscosity (η_r) of a Newtonian CWS (anionic dispersant concentration equal to and greater than 0.74 wt% A23M polymer) is considerably higher than that predicted by the Krieger/Dougherty (K/D) rigid sphere model using an intrinsic viscosity $[\eta]$ of 2.67 and the maximum packing fraction φ_M obtained from sedimentation:

$$\eta_r = (1 - \varphi/\varphi_M)^{-[\eta]\varphi_M}$$

Micronized CWSs with flow behavior indices ranging from 0.7 (pseudoplastic) to 1.0 (Newtonian) and anionic dispersant concentrations ranging from 0.32 wt% to 1.35 wt% polymer (on a coal basis) have been atomized using twin-fluid atomizers of various designs. The atomized drop mass median diameters (MMDs) are found to fit, with correlation coefficients of 0.95 to 0.97, the wave mechanism-based models established for primary atomization of both viscous liquids and coal slurries containing glycerol or other alcohols:

$$MMD/D = (1+\dot{M}_S/\dot{M}_A)\{x2 \cdot We^{-x1} + x3 \cdot Z^{x1}\} \qquad (1)$$
$$MMD/D = (1+\dot{M}_S/\dot{M}_A)\{x2 \cdot We^{-x1} + x3 \cdot Z^{2 \cdot x1}\} \qquad (2)$$

where D is the diameter of the distributor for slurry passage, the Weber number (We) equals $\rho_A V_A^2 D/\sigma_L$, representing the ratio of aerodynamic force to surface tension, and the Ohnesorge number (Z) equals $\eta_S/(\rho_S \sigma_L D)^{1/2}$ based on the upstream high shear slurry viscosity prior to its interaction with the atomizing air. The linear dependency on $1+\dot{M}_S/\dot{M}_A$ is based on the momentum balance and energy consideration. The exponents and the coefficients of these models, as determined by the generalized inverse method, are given in Table I. It should be noted that the +/- deviations of the exponents and the coefficients in this Table are calculated from the 95% confidence intervals of the correlation coefficients. Much smaller drop MMDs (as small as 40μm) than what these models predict have been obtained for CWS with 0.55 volume fraction of 18μm coal at air-to-slurry mass ratios of 0.175 - 0.30 (equivalent to $1+\dot{M}_S/\dot{M}_A$ of 4.0 to 6.7), and may be attributed to secondary atomization (breakup of primary drops). In fact, the atomized CWS drop MMDs ranging from 40 to 60μm at $1+\dot{M}_S/\dot{M}_A$ ranging from 3.0 to 7 are comparable to those of atomized glycerol-water liquid mixture of 3.8 P.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Coal water slurry (CWS) is potentially the most economical usage of coal. It must be broken into fine drops in order to be effectively burned. Understanding the effects of slurry rheology and atomizer design on drop formation and breakup is imperative to development of a physical model for CWS atomization. This model should depict the mechanisms of CWS atomization and serves as a guideline for the design and scale-up of CWS atomizers. Understanding the impacts of coal particle surface properties and interparticle forces on CWS rheology should improve slurry preparation and coal utilization.

PLANS FOR THE COMING YEAR:

The studies on rheology and airblast atomization mechanisms will continue, emphasizing the effects of particle size and nozzle geometry (twin-fluid atomizers for boiler use vs for diesel engine use). Characterization of coal particle surface, modified by additives, will also be carried out in the coming year. Specifically, the zeta potential will be measured as a function of pH value and additive concentration. The corresponding particle surface charge will be calculated using the Electrical Double Layer Theory.

TABLE I

Semi-empirical Model for Airblast Atomization of Micronized Coal Water Slurries#

$$\mathrm{MMD}/\mathrm{D} = (1+\dot{M}_S/\dot{M}_A)\{x2\cdot \mathrm{We}^{-x1} + x3\cdot Z^{x1}\}\cdot 10^{-2} \tag{1}$$

$$\mathrm{MMD}/\mathrm{D} = (1+\dot{M}_S/\dot{M}_A)\{x2\cdot \mathrm{We}^{-x1} + x3\cdot Z^{2\cdot x1}\}\cdot 10^{-2} \tag{2}$$

	x1	x2	x3	c.o.c.*	95% confid. Interval	Equation
(a)	0.39±0.02	13.5±0.9	1.90±0.06	0.96	0.90-0.98	(1)
(b)	0.36±0.01	12.0±0.4	0.23±0.02	0.97	0.94-0.99	(1)
(a)	0.30±0.02	11.5±0.9	1.26±0.02	0.95	0.87-0.98	(2)
(b)	0.37±0.01	13.3±0.6	0.17±0.02	0.97	0.94-0.99	(2)

The units of MMD and D are μm and cm, respectively

* Coefficient of correlation

(a) 19 data of atomization at air pressures below a threshold value

(b) 33 data of atomization at air pressures above a threshold value

II. HIGHLIGHT OF ACCOMPLISHMENTS

1. Micronized CWSs with flow behavior indices ranging from 0.7 (pseudoplastic) to 1.0 (Newtonian) have been prepared using anionic dispersant at concentrations ranging from 0.32 wt% to 1.35 wt% polymer (on a coal basis). The effect of particle size at similar size distributions on the relative viscosity of a pseudoplastic CWS can be approximated by particle Peclet number.

2. The atomized CWS drop MMDs resulting from primary atomization follow the wave mechanism-based models. Nevertheless, much smaller drops (MMD of 40 to 60 μm or SMD of 30 to 55 μm) than what these models predict have been obtained for CWS with 0.55 volume fraction of 18 m coal at air-to-slurry mass ratios of 0.175 - 0.30 and may be attributed to secondary atomization (breakup of primary drops).

III. ARTICLES AND PRESENTATIONS

1. S.C. Tsai, "Staged Froth Flotation of Fine Coal," ACS Industrial and Engineering Chemistry Research, 27, 1699-1674, (1988)

2. S.C. Tsai, B. Viers, and D. Botts, "Effects of Pseudoplastic Behavior on Airblast Atomization of Viscous Liquids", Proceedings of 3rd International Symposium on Liquid-Solid Flows, ASME, FED-75, 225-231, (1988)

3. Q.Y. Song and S.C. Tsai, "Flotation of Ilmenite Using Benzyl Arsonic Acid and Acidified Sodium Silicate," Int. J. of Mineral Processing, 26, 111-121, (1989)

4. S.C. Tsai, B. Viers, and D. Botts, "Airblast Atomization of Viscous Newtonian Liquids", presented at the 3rd Annual Conference on Liquid Atomization and Spray Systems, ILASS-Americas, May 16-17, (1989)

5. S.C. Tsai, B. Viers, and D. Botts, "Effects of Liquid Viscosity on Rheology of Suspensions," presented at the 20th Annual Meeting of the Fine Particle Society, and published in Pariculate Science and Technology, 7, 87-95, 1989.

6. S.C. Tsai and B. Viers, "Airblast Atomization of Viscous Liquids," Fuel, 69, 1412-1418, 1990.

7. S.C. Tsai, K. Ghazimorad, and B. Viers, "Correlation between the Hamaker Constant and the Folw Behavior Index of a Concentrated Suspension," J. of Rheology, 34, 1327-1332, 1990.

8. S.C. Tsai, K. Ghazimorad, J. Peters, and B. Viers, "Roles of Interparticular Forces in the Rheology of Concentrated Slurries," presented at the 21st Annual Meeting of the Fine Particle Society in conjunction with the 1990 AIChE Summer National Meeting, San Diego, CA, August 21-25, 1990.

9. Q.Y. Song and S.C. Tsai, "Selective Flocculation and Magnetic Seeding Flocculation of Weakly Magnetic Iron Minerals," to appear in Int. J. of Mineral Processing, 1991.

10. S.C. Tsai and B. Viers, "Airblast Atomization of Viscous Newtonian Liquids Using Twin-fluid Jet Atomizer," to appear in J. of Fluid Eng., 1991.

11. S.C. Tsai, K. Ghazimorad, and B. Viers, "Airblast Atomization of Micronized Coal Water Slurries Using Twin-fluid Jet Atomizer," to appear in Fuel, 1991.

12. S.C. Tsai, K. Ghazimorad, B. Viers, and N. Widjaja, "Rheology and Atomization of Micronized Coal Water Slurries," to appear in the Proc. of ASME 4th International Symposium on Solid Liquid Flow, 1991.

TITLE: A New Approach in Ultrapurification of Coal by Selective Flocculation

PI: Brij M. Moudgil

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED: S. Behl (8/89 -) Ph.D., E. Skompski, B.S.

INSTITUTION/ORGANIZATION: University of Florida
Department of Materials Science and Engineering
Gainesville, Florida 32611
(904) 392-9118

GRANT NO.: DE FG22-88PC88917

PERIOD OF PERFORMANCE: 9/1/88 to 8/31/91

I. ABSTRACT

OBJECTIVE: The general objective of the present study was to separate fine coal from ash forming minerals and pyrites using selective flocculation technology. Specifically, a mathematical model based on the "active" sites concept was to be developed so that experimental conditions to achieve the desired separations for a given coal sample could be predicted.

WORK DONE AND CONCLUSIONS: Samples of Pittsburgh coal, coal refuse and coal pyrite were used for single component flocculation tests. It was revealed that separation of coal from coal refuse/coal pyrite may be possible with highly cationic (Superfloc 362) and a nonionic polyacrylamide (Superfloc 16). However, selectivity indicated by single component tests was not realized in mixed mineral flocculation tests.

Mathematical Model of Selective Flocculation: The model is based on the concept that active sites on a surface strongly influence polymer adsorption on various substrates. The present mathematical model, unlike past studies, takes into account the entire floc growth process including corrections for changes in floc density and mobility. It is, however, assumed that the rate of polymer adsorption is much higher than kinetics of flocculation and that only binary collisions occur between particles/flocs in the system. The two parameters, active sites ratio (Φ_R) and fractional surface coverage (Θ), govern the selectivity of flocculation (in terms of Selectivity Index, S.I.). Experimentally determined values of Φ_R (ratio of active sites on coal pyrite to active sites on coal) of 2 and Θ of 0.5 were used in the above model to predict the optimum value of Selectivity Index. This was calculated to be less than 10, and was verified experimentally. The predicted low value of the Selectivity Index was primarily attributed to the presence of mineral matter which probably resulted in non-selective polymer adsorption. Attempts to remove mineral fines from coal and coal pyrite samples by washing were not successful.

SIGNIFICANCE OF FOSSIL ENERGY PROGRAM: Selective flocculation technology has the potential of cleaning fine coal - a major objective of the fossil energy program. The overall goal of the present study was to develop the scientific base for selection of polymers, to achieve the desired selectivity.

PLANS FOR THE COMING YEAR: The specific objective of the proposed research has been achieved, therefore, no further research is planned under this project.

II. HIGHLIGHT ACCOMPLISHMENTS

A major accomplishment of the research conducted is that a mathematical and computational model capable of predicting the optimum selectivity achievable with a given polymer has been developed and successfully verified experimentally.

III. ARTICLES AND PRESENTATION

ARTICLES:

1. Moudgil, B. M., "Controlled Adsorption of Polymers and Surfactants in Particulate Separation Processes," *Progr. Colloid Polym. Sci.* 82, pp. 3-9, 1990.

2. Moudgil, B.M., Behl, S., "Removal of Particulate Impurities from Ceramic Powders by Selective Flocculation," in *Proceedings* of the Second World Congress, Particle Technology, Kyoto, Japan, 1990.

3. Moudgil, B.M. and Behl, S., "A Model of the Selective Flocculation Process," Accepted for Publication in *J. Colloid Interface Sci.*, 1990.

4. Moudgil, B.M., Behl, S., "Ultrapurification of Fine Powder By Floc Flotation," Submitted for Publication in Proceedings of the 8th International Symposium on Surfactants in Solution, Gainesville, Florida, 1990.

5. Moudgil, B.M., Behl, S., and Pradip, "Scientific Design of A Selective Flocculation Process," Submitted for Publication in *Minerals and Metallurgical Processing Journal.* Society of Mining, Metallurgy, and Exploration, Littleton, Colorado, 1991.

PRESENTATIONS:

1. Moudgil, B.M., "Particulate Separation by Selective Flocculation," DuPont Co., Wilmington, DE, April, 1989.

2. Moudgil, B.M., Behl, S., "Ultrapurification of Fine Powders by Floc Flotation," 8th International Symposium on Surfactants in Solution, Gainesville, FL, June 1990.

3. Moudgil, B.M., Behl, S. "Removal of Particulate Contaminants from Fine Powders by Selective Flocculation," 2nd World Congress, Particle Technology, Kyoto, Japan, September, 1990.

4. Moudgil, B.M., "Factors Affecting Selective Flocculation of Coal and coal Pyrite," Engineering Foundation Conference, Palm Coast, FL, December, 1990.

5. Moudgil, B.M., Behl, S., Pradip "Scientific Design of A Selective Flocculation Process," SME-AIME Annual Meeting, Denver, CO, February, 1991.

6. Moudgil, B.M., "Removal of Trace Particulate Impurities by Selective Flocculation," EPA-Water and Hazardous Waste Division, Cincinnati, OH, May, 1991.

April 8, 1991

TITLE: Enhancement of Surface Properties for Coal Beneficiation

PIs: S. Chander and F. F. Aplan

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
J. Pang (PhD); D. Xu (M.S.)

INSTITUTION/ORGANIZATION: The Pennsylvania State University
Mineral Processing Section
115 Mineral Sciences Building
University Park, PA 16802
(814) 863-0373/865-9834

GRANT NO.: DE-FG22-88PC88934

PERIOD OF PERFORMANCE: 9/1/88 - 8/31/91

I. ABSTRACT

OBJECTIVE:

The need to clean coal for its effective utilization in steam generation is well recognized. To use the coal as a source of energy in an environmentally safe manner, pre-combustion desulfurization is considered to be a very cost-effective method. The main objective of this research project is to study ways to modify surface properties of coal, pyrite and ash-forming mineral matter for beneficiation of fine coal. Since the differences in surface properties of coal and mineral matter are utilized in several oil based preparation technologies, such as: froth flotation, emulsion flotation, spherical agglomeration and liquid-liquid separation, another objective is to delineate the role of oil.

The following studies are being carried out to achieve the objectives stated in the previous paragraph:

- Investigation of the natural hydrophobicity of coal and pyrite
- Development and evaluation of enhanced coal hydrophobicity
- Development and evaluation of reagents which modulate the hydrophobicity of pyrite
- Development and evaluation of emulsion processes and their underlying principles.

WORK DONE AND CONCLUSIONS:

To investigate the role of various reagents on hydrophobicity of pyrite, contact angle and flotation measurements were made in the presence of ethenediaminetetracetic acid (EDTA). A non-zero contact angle was obtained only in a limited potential range. This potential range was a function of reagent concentration. UV-VIS spectroscopy showed that iron-EDTA complexes are formed. On the basis of these studies and thermodynamic analysis, it was shown that removal of iron oxides exposes the underlying metal-deficient hydrophobic layer making pyrite floatable. These results show that iron compounds, possibly iron hydroxides are responsible for hydrophilic character of pyrite. The conditions which favor formation of metal-deficient sulfide and removal of iron oxide promote collectorless flotation of pyrite.

The flotation of several samples of coal-source pyrite was studied using xanthates containing 2, 5, 8 and 12 carbon atoms in the hydrocarbon group. In no case was it possible to float ~100% coal source pyrite with ethyl xanthate even at concentrations as high as 10^{-2} mole/liter. Although the flotation improved with increase in the number of carbon atoms, the dodecyl xanthate acted differently than did the amyl or octyl xanthate. This is being studied.

As a part of our program to quantify the role of oil in selective coalescence processes a novel technique was developed to measure the contact angle of particles at fluid-fluid interfaces. In this technique, the contact angle is estimated from partitioning of particles at the fluid-fluid interface. The method has been validated using several coals and other materials. The results of these measurements are being combined with the emulsification characteristics of oil in the presence of coals of different rank.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

The extended use of coal as a major source of energy requires that the coal be effectively desulfurized in order to reduce the acid rain problem. Pyrite creates environmental and operation problems whenever coal is utilized either through direct combustion or after conversation into more desirable combustion products such as gas or oil. This project is concerned with the pre-combustion removal of the undersirable constituents through controlled surface modifications and judicious use of oil to enhance recovery and improve rejection of pyrite and ash forming minerals.

PLANS FOR THE COMING YEAR:

This project will be completed by 8/31/91.

II. HIGHLIGHT ACCOMPLISHMENTS

1. The major oxidation products on pyrite were found to be gypsum and a wide variety of iron sulfate minerals. There is a wide variation in the oxidizability of pyrite depending on both the nature of the pyrite and the conditions under which it is oxidized.
2. Coal source pyrites cannot be floated with ethyl xanthate. An increase in the hydrocarbon chain length to 5 (amyl) and 8 (octyl), improve flotation, but an increase to 12 (dodecyl) often does not.
3. Dispersants and xanthated polysaccharides are pyrite depressants.
4. Anodic oxidation of pyrite gives rise to an iron-deficient sulfur layer which is ordinarily covered by a layer of oxides, hydroxide, sulfate of iron. Conditions which favor removal of the iron-oxide layer gives rise to collectorless flotation. If pyrite is to be rejected during flotation one must avoid such conditions.
5. A new technique was developed to measure contact angle at fluid-fluid interfaces.
6. Partitioning of coal, pyrite and ash-forming mineral at oil-water interfaces depends on both chemical and physical variables.

III. ARTICLES AND PRESENTATIONS

T. Onlin and F. F. Aplan, "Surface Properties of Coal as Influenced by Collectors," Proc. Annual Tech. Conf. on Filtration and Separation, pp. 37-44, 1989.

J. Pang, A. Briceno, and S. Chander, "A Study of Pyrite/Solution Interface by Impedance Spectroscopy," submitted for publication in J. Electrochemical Soc., 1989.

T. Onlin and F. F. Aplan, "Use of Amines and Other Nitrogenous Compounds as Collectors for the Flotation of Coals of Various Ranks," Presented at the AIME Annual Meeting, Las Vegas, NV, Mar. 2, 1989.

T. C. Hsu and S. Chander, "Effect of Salts on Partitioning of Coal and Ash Minerals at Hydrocarbon Oil/Water Interface," paper presented at Annual SME Meeting, Salt Lake City, UT, February 26-March 1, 1990.

C. E. Raleigh, Jr. and F. F. Aplan, "The Effect of Feed Particle Size and Reagents on Coal-Mineral Matter Selectivity During the Flotation of Bituminous Coals," AIME/SME Preprint 90-118, Annual Meeting, Salt Lake City, UT, Mar. 1, 1990. Accepted for publication in Minerals and Metallurgical Processing.

S. Chander, "Electrochemistry of Sulfide Flotation Growth Characteristics of Surface Coatings and Their Properties," Proceedings of the 2nd Workshop on Flotation of Sulfide Minerals, Lulea, Sweden, June 18-19, 1990, pp. 117-137.

S. Chander, J. Pang, and R. Zhou, "Effect of Anodic Oxidation on Collectorless Flotation of Pyrite," paper presented at the Annual SME Meeting, Denver, CO., February 25-28, 1991.

M. C. Esposito and F. F. Aplan, "Use of Ordinary and Xanthated Polysaccharides as Pyrite Depressants During Coal Flotation," paper presented at the AIME Annual Meeting, Denver, CO., February 25-28, 1991.

Y. H. Chen and F. F. Aplan, "Comparative Flotation of Coal-Source and Ore-Source Pyrite," paper presented at the AIME Annual Meeting, Denver, CO., February 25-28, 1991.

Date: April 8, 1991

TITLE: Pelletization of Fine Coals

PI: K. V. S. Sastry

STUDENT AND THE DEGREE: Mitchell Yee, Master of Science

INSTITUTION/ORGANIZATION:
University of California
Department of Material Science
and Mineral Engineering
University of California
Berkeley, California 94720
Phone 415-642-3808

GRANT NO.: DE-FG22-89PC89766

PERIOD OF PERFORMANCE: September 1, 1989 to August 31, 1992

I. ABSTRACT

OBJECTIVE: The primary goal of this project is to provide the coal industry with a formal understanding and basis for selection, design and operation of coal pelletizing systems. Four specific research topics are chosen towards this end. These include - development of a unified agglomeration index for correlating growth and strength characteristics of coal fines, identification and development of methods for coal pellet characterization, surface (physical and chemical) principles of coal pelletization, and the role of binders and basis for binder selection.

WORK DONE AND CONCLUSIONS: During the last one year, our research was concerned primarily with

- investigations on the method of production of coal fines, the batch pelletization behavior of the base coals to establish the moisture requirements for pelletization, the extent of oxidation of coals, and the type and amount of additives, and
- mathematical modeling investigations to aid in the fundamental understanding of the coal pelletization process, and
- exploratory studies on the methods for coal pellet characterization.

A major observation from our experimental study is that the reproducibility of batch pelletization results is very poor and extreme precautions are needed to generate experimental data that can be meaningfully interpreted. We have also discovered that pelletization behavior of coal fines is highly sensitive to even minor variations in the coal characteristics especially changes (such as oxidation) taking place during storage. One conclusion we were able to draw from our experiments is that oxidation of coal fines influences very strongly the moisture requirements for pelletization. We found that the coal surface becomes increasingly hydrophilic with oxidation and this results in substantially higher moisture requirement. Another conclusion from the experimental program is that the addition of surfactants during froth flotation can change the pelletization behavior considerably. For example, dodecane collector when added in minor quantities increases the rate of pelletization but when added in higher amounts reduces the rate. This is expected to result from a balance between the moisture available for pelletization and the strength of agglomerates.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Environmental problems associated with acid rain are attributed to sulfur emissions from coal-fired utility boilers. Sulfur contents of 2 to 6 percent in coals from Eastern and Midwestern states are considered to be responsible for the bulk of the US sulfur emissions. A significant portion of total sulfur can be removed prior to combustion through such low-cost generic coal cleaning techniques as advanced froth flotation and oil agglomeration. DOE recognized a need to develop a fundamental understanding of the coal surface properties as well as techniques to optimize the engineering process of these technologies. Accordingly, in 1987, a DOE/PETC Clean Coal Research Initiative has been designed to make these technologies viable candidates for private sector investment. This initiative resulted in the award of four contracts involving the fundamental (at the University of California and University of Pittsburgh) and engineering studies (by the Kaiser Engineers and Southern Services) of the flotation and oil agglomeration technologies. In addition to the environmental concerns, demands for low-ash, low-sulfur coals and economic constraints for high productivity are requiring the coal industry to use such modern mining methods as longwall mining. Also, better utilization of coals is attempted through synthetic fuel production.

All these technologies are faced with one common problem -- fine coals. Dealing effectively with these fine coals during handling, storage, transportation, and/or processing continues to be a challenge facing the industry. Agglomeration, the unit operation of producing larger bodies from fine powders, alleviates many of the problems associated with fine particulates. This project is directed to delineating the fundamental principles of the agglomeration of fine coals by pelletization and providing a formal basis for process engineering practice.

PLANS FOR THE COMING YEAR: Our plans for the next year include

- continuation of our studies to formalize methods for coal pellet characterization,
- preliminary studies on the role of binders,
- establishment of the role of binders and a basis for binder selection, and
- development of a unified agglomeration index for correlating growth and strength characteristics of coal fines.

II. HIGHLIGHT ACCOMPLISHMENTS

Pelletization of coal fines can be primarily characterized by the amount of moisture required for pelletization which is determined by the coal properties. Kinetics of coal pelletization is discovered to be highly sensitive to minor variations in the coal properties during storage (oxidation) and during cleaning steps (flotation). Our current efforts are being directed to understanding the reasons for this sensitivity and to find practical engineering solutions.

III. ARTICLES AND PRESENTATIONS

A paper entitled "An Experimental Investigation of Pelletization of Coal Fines" was presented at the 1991 Annual Meeting of the Society for Mining, Metallurgy, and Exploration (SME) that was held in February 1991 in Denver, Colorado. A paper is currently under preparation and will be submitted for publication in *Coal Preparation* within next few months. Also a paper entitled "Influence of Coal Characteristics and Reagent Addition on Pelletization of Coal Fines" has been proposed and accepted for presentation at the 1992 Annual Meeting of the Society for Mining, Metallurgy, and Exploration (SME) that is to be held in February 1992 in Phoenix, AZ.

TITLE: Control of Pyrite Surface Chemistry in Physical Coal Cleaning

P.I.'s: Dr. Gerald H. Luttrell and Dr. Roe-Hoan Yoon

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Joseph Zachwieja, Ph.D.
Dong-Ping Tao, Ph.D.
Margaret Lagno, M.S.

INSTITUTION: Virginia Polytechnic Institute and State University
Department of Mining and Minerals Engineering
146 Holden Hall
Blacksburg, VA 24061-0258 (703) 231-4508

GRANT NO.: DE-FG22-89PC89789

PERIOD OF PERFORMANCE: 9-1-89 to 8-31-92

I. ABSTRACT

OBJECTIVE:

The primary objective of this research is to obtain fundamental knowledge concerning the surface properties of coal pyrite as they relate to advanced physical coal cleaning (APCC) processes. This objective will be met by (1) investigating the mechanisms responsible for the inefficient rejection of coal pyrite and (2) developing schemes for improving the rejection of coal pyrite based on information gathered from part (1).

WORK DONE AND CONCLUSIONS:

Studies conducted during the first year of this project indicate that the flotation recovery of coal pyrite may be attributed to (1) the presence of hydrophobic inclusions of carboneous material or (2) the formation of hydrophobic oxidation products, such as metal polysulfides, on the pyrite surfaces. In light of these findings, two different approaches were examined during the past year for improving pyrite rejection. The first approach involved the testing of organic depressants which are capable of selectively depressing pyrite particles containing carboneous material. The second approach focused on the development of reagents which create a reducing environment, thereby preventing the formation of hydrophobic oxidation products on the pyrite surfaces.

Orfom-D8, a commercially available sulfide mineral depressant from Phillips Chemicals, and MAC, a proprietary reagent from the American Cyanamid Company, were examined as possible depressants for coal pyrite. In addition, a novel reagent, named NVT, was synthesized in our laboratory and evaluated along with the sulfur-based surfactants listed above. Results obtained from microflotation and bench-scale flotation tests showed that NVT possessed better selectivity than Orfom D8 or MAC for the rejection of coal pyrite in

acidic and neutral pH solutions, while the selectivity of Orfom-D8 and MAC was found to be superior to NVT in alkaline solutions.

The control of the pulp oxidation-reduction potential was also examined as a possible means of improving pyrite rejection. Several potential modifiers were examined including sodium sulfide, hydrazine and pyrogallic acid. In many cases, this approach was found to be more effective than the addition of organic depressants for preventing the recovery of coal pyrite in microflotation and bench-scale tests. Another benefit of utilizing these potential-controlling reagents is that they have no detrimental effects on the floatability of the coal itself. Surface analysis of flotation products suggests that the mechanism of depression by these reagents can be attributed to (1) the lowering of the pulp potential which inhibits the formation of hydrophobic oxidation products and (2) the formation of hydrophilic iron-oxide complexes on the pyrite surfaces.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

In light of the DOE objective to include sulfur reduction in coal beneficiation, the findings to date indicate that improvements in the rejection of pyritic sulfur by APCC processes can be realized through a better understanding of the nature of coal pyrite surface chemistry and methods for its control.

PLANS FOR THE COMING YEAR:

The following work effort is planned for the upcoming year:

- Detailed investigations related to the use of potential control for the depression of pyrite during coal flotation.

- Evaluation of promising depressants using microbubble column flotation.

- Completion of surface characterization studies of pyrite samples from several sources using various spectroscopic and electrochemical methods.

II. HIGHLIGHT ACCOMPLISHMENTS

Accomplishments of the research conducted to date are as follows:

- The hydrophobicity of coal pyrite is induced by superficial oxidation and/or the presence of carbonaceous material. The iron polysulfides formed during the superficial oxidation appear to be responsible for the induced hydrophobicity.

- Reducing the pulp potential is an effective means of preventing coal pyrite from acquiring hydrophobicity without deleterious effects on coal flotation. The mechanism of depression may be due to (1) the reduction of the pulp potential and (2) the formation of hydrophilic iron-oxide surface complexes.

- A novel organic depressant has been synthesized which contains no sulfur group in its structure. This depressant exhibits a stronger affinity toward coal pyrite at relatively low concentrations and neutral pH than several commercially available sulfur-based pyrite depressants.

III. ARTICLES AND PRESENTATIONS

"Coal Desulfurization by a Novel Pyrite Depressant in Froth Flotation," by M. S. Celik, M. L. Stallard and R. H. Yoon, in Proceedings of the 3rd International Mineral Processing Symposium, (G. Önal, Editor), Istanbul, Turkey, September 11-13, 1990, pp. 256-266.

"On the Hydrophobicity of Coal Pyrite," by R. H. Yoon, M. L. Lagno, G. L. Luttrell and J. A. Mielczarski, in 4th International Conference on Processing and Utilization of High Sulfur Coals (P. Dugan, Quigley, Editors), Idaho Falls, Idaho, August 26-30, 1991.

"Control of Surface Chemistry for Coal Pyrite Depression," by J. B. Zachwieja, in Proceedings of the Advanced Coal Cleaning Technologies Symposium/Workshop, Blacksburg, Virginia, October 2-3, 1990.

"Removal of Organic Sulfur by Photochemical Treatment," by Mike Stallard, in Proceedings of the Advanced Coal Cleaning Technologies Symposium/Workshop, Blacksburg, Virginia, October 2-3, 1990.

"Studies on the Hydrophobicity of Coal and Mineral Pyrite," by R. H. Yoon, M. L. Lagno, G. L. Luttrell and J. A. Mielczarski, Coal Preparation; in preparation.

DATE: March 20, 1991

TITLE: A New Model of Coal-Water Interactions and Relevance for Dewatering

P.I.: Prof. Eric M. Suuberg

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Ivan Milosavljevic, Ph.D. and one more student to be determined

INSTITUTION / ORGANIZATION :
Brown University, Division of Engineering
Providence, RI 02912
(401) 863-1420

GRANT NO.: DE-FG22-90PC90308

PERIOD OF PERFORMANCE:
August 10, 1990- August 9, 1993

I. ABSTRACT

OBJECTIVES: 1) To develop a quantitative theory of moisture retention in coal, based upon solvent swelling theory and 2) to use this understanding to design new coal dewatering strategies.

WORK DONE AND CONCLUSIONS: A comprehensive review of solvent swelling theories, of relevance to moisture retention in coals, has been prepared. This review has made the case that water behaves as a moderately good swelling solvent in low rank coals. It is not as strong a swelling agent as nitrogen bases, but is better than alcohols. The process of swelling can in no way be described by classical Flory-Rehner theory, or any minor variants of it. A new theory must be developed that addresses explicitly specific interactions in the coal-solvent system.

The measurements necessary for testing the theory of interaction of strong swelling agents with coal have begun. The strategy is to perform separate measurements of heats of mixing of solvents with coals and of elastic response of coals, so as to decompose the contributions to the free energy change upon swelling into its constituent parts. This will permit determining how the final thermodynamic equilibrium is established and thus what the moisture retentive capacity of coal is. A sensitive flow microcalorimeter has been acquired for this purpose, and is being modified to allow further work of this kind.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM: The recently released National Energy Strategy has highlighted the important role that coal must continue to play in the Nation's energy policy. The role of coal in electricity generation was particularly stressed, and the challenges presented by the recently enacted clean air legislation were noted. Low rank coals from the midwestern U.S. can be a major source of fuel in meeting the needs and constraints that have been defined. The low rank coals are, however, very "wet" as mined (30-40% by weight water) and there are severe technological problems associated with conventional minemouth drying (e.g. moisture regain upon storage or shipment, formation of fines, promoting tendency towards spontaneous combustion). There are strong economic incentives for finding alternative permanent drying procedures that will alleviate these problems. This program directly addresses these needs.

PLANS FOR THE UPCOMING YEAR: The plan for the next year is to continue to focus mainly on establishing the mechanisms by which moisture is held in the coal, and to determine the extent to which this behavior is comparable to swelling in all other strong solvents. The actual dewatering experiments will not begin until late in the second year of the project.

II. HIGHLIGHT ACCOMPLISHMENTS

The principal accomplishment at this early stage of the project has been the completion of the review of swelling mechanisms of coals in the presence of specifically interacting solvents. We feel that a new, fundamentally sound understanding of these swelling phenomena has been developed, one that challenges a significant number of earlier theories of moisture retention in coals as well as theories of organic solvent swelling of coals.

III. ARTICLES AND PRESENTATIONS

Suuberg, E.M. and Otake, Y. "The Physical Structure of the Coal Macromolecular Network: Characterization by Solvent Swelling", submitted for publication review, December, 1990.

Suuberg, E.M., Otake, Y., and Deevi, S.C. **ACS Div. Fuel Chem. Prepr.**, 36(1), 258 (1991).

Also presentation of a paper is planned for the 1991 Int. Conf. on Coal Science, and aspects of this work were presented at the Conf. on Coal Structure and Reactivity, Cambridge Univ. , September, 1990.

TITLE: **OXIDATION OF COAL AND COAL PYRITE;** April 5, 1991
MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS

P.I.: FIONA M. DOYLE

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
MIGUEL N. HERRERA, Ph.D.

INSTITUTION: UNIVERSITY OF CALIFORNIA AT BERKELEY
Dept. of Materials Science and Mineral Engineering
Hearst Mining Building, Berkeley, CA 94720.
(415) 642 2846

GRANT NO.: DE-FG22-90PC90287

PERIOD OF PERFORMANCE: September 1, 1990 - August 31, 1993.

I. OXIDATION OF COAL AND COAL PYRITE: MECHANISMS AND INFLUENCE ON SURFACE CHARACTERISTICS

OBJECTIVE:

The objective of this research is to develop a mechanistic understanding of the oxidation of coal and coal pyrite, and to correlate the intrinsic physical and chemical properties of these minerals, along with changes resulting from oxidation, with those surface properties that influence the behavior in physical coal cleaning processes. The results will provide fundamental insight into oxidation, in terms of the bulk and surface chemistry, the microstructure, and the semiconductor properties of the pyrite.

WORK DONE AND CONCLUSIONS:

Preliminary work has been done on Illinois No. 6 coal, to learn standard preparation methods and analytical techniques (crushing, grinding, sizing, storage, proximate, ultimate and sulfur analysis), to ensure that our studies are directly comparable with others. The coal has been characterized by fourier transform infrared spectroscopy, using a reflectance cell, BET analysis and electrochemical methods, to master these techniques. Dry thermal oxidation tests, and wet oxidation with hydrogen peroxide and aqueous ferric chloride have been done.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

There is increasing public pressure to reduce the national dependence on imported oil, without compromising the quality of our environment. In the short term, this can only be achieved by improving our supply of clean-burning domestic coal. In order to utilize high sulfur coals, we must improve our ability to design and implement effective coal-cleaning processes, without using extensive empirical testing. Oxidation adversely affects cleaning, particularly desulfurization, but is poorly understood. This work directly addresses this deficiency.

PLANS FOR THE COMING YEAR:

In the coming year, work will focus on bituminous coals from the Upper Freeport seam, PA, the Illinois No. 6 seam, IL, and the Pittsburgh No. 8 seam, PA, which have high pyritic sulfur contents. We will refer extensively to the literature on these coals, for information to supplement and complement our own work. These coals will be characterized extensively, by proximate, ultimate and sulfur analysis, optical and electron microscopy. The pore size distribution, surface area, electrokinetic behavior, wettability, and concentration of surface functional groups will be determined. Samples will be oxidized at different temperatures, oxygen and water partial pressures, and by different aqueous oxidants potentials, then thoroughly characterized again. The oxidation of pyrite will be studied electrochemically. Flotation tests will be made to relate the bulk and surface properties of raw and oxidized coal and pyrite with their flotation behavior. We intend to develop mathematical models to describe the oxidation of coal and pyrite, to use in interpreting future experimental results for other coals.

II. HIGHLIGHT ACCOMPLISHMENTS

During the first two quarters of the grant, our efforts have focussed on acquiring the background, and learning the skills needed to ensure that our oxidation studies are as relevant as possible to the technical community, and to minimize overlap with previous work.

III. ARTICLES AND PRESENTATIONS

Abbas H. Mirza, Miguel N. Herrera, and Fiona M. Doyle, "Characterization of pyrite-bearing materials by chemical oxidation", to be presented in Cleaner Environment '92, SME Annual Meeting, February 24-27, 1992.

Miguel N. Herrera, Abbas H. Mirza, and Fiona M. Doyle, "Electrochemical oxidation of n- and p- type pyrite", to be presented at Electrochemistry in Mineral and Metal Processing III, 181st Electrochemical Society Meeting, May 17-22, 1992.

PYRITE SURFACE CHARACTERIZATION AND CONTROL FOR ADVANCED FINE COAL DESULFURIZATION TECHNOLOGIES

APRIL 1, 1991

P.I.: XIANG-HUAI WANG
CO-PIs: JOSEPH W. LEONARD and B.K. PAREKH
GRADUATE STUDENTS: A.M. RAICHUR (M.S) and C.L. JIANG (M.S)
INSTITUTION: Department of Mining Engineering and
Center for Applied Energy Research,
University of Kentucky,
Lexington, Kentucky 40506
Phone: (606)257-8026 and (606)257-0205

GRANT NO: DE-FG22-90PC90295
PERIOD OF PERFORMANCE: Sept. 1, 1990 -- August 31, 1993

ABSTRACT

OBJECTIVE: The objective of this project is to conduct extensive studies on the surface reactivity of pyrite by using electrochemical, surface spectroscopic analysis, potentiometric and calorimetric titration, and surface hydrophobicity characterization techniques and to correlate the alteration of the coal-pyrite surface with the efficiency of pyrite rejection by flotation and oil agglomeration. The products as well as the their structures, the mechanisms and the kinetics of the oxidation of coal-pyrite surfaces and interactions with various chemical reagents will be systematically studied and compared with that of mineral-pyrite and synthetic pure pyrite to determine the correlation between the surface properties and the bulk physical and chemical properties and impurities.

WORK PERFORMED AND CONCLUSIONS: Sample acquisition and preparation (Task I) was accomplished during the first five months of this project. Four high quality coal-pyrite samples from the Illinois No.6, Kentucky No.9, Pittsburgh No.8 and upper Freeport coal seams, and several high purity mineral pyrite samples were obtained. Synthetic pyrite single crystals (5 mm in size) and microcrystalline pyrite particles (averaging 6 μm in size) were also obtained with the purity of the samples being 99.9%.

Surface hydrophobicities of coal- and mineral-pyrite have been studied by contact angle titration and film flotation methods. The results indicated that the

surfaces of coal-pyrites are much more hydrophobic than the surfaces of mineral-pyrite and approach the hydrophobicity of coal surfaces. The Kentucky No.9 coal-pyrite (88% purity) has an average critical surface tension of wetting (γ_c) of 40 to 45 dyne/cm. The Illinois No.6 coal-pyrite shows a contact of above 60 degrees in solution below pH=11, while the cubic ore-pyrite single crystal surfaces studied has a contact angle of 30 to 40 degrees.

The oxidation and reduction behavior of the coal-pyrite, ore-pyrite and synthetic pyrite single crystals have been studied using electrochemical methods: including cyclic voltammetry, rotating-disc electrode technique, open-circuit potential measurements and steady-state polarization measurements. The results indicated that surfaces of the pyrite electrodes, when ground in distilled water, were covered by a layer of oxidation products whose chemical nature has not yet been fully characterized. That the reduction behavior of the surface oxidation products is independent of the rotation suggests that the products are insoluble species. The anodic oxidation of pyrite in acidic pH solutions (pH=0.5 to 4) shows a Tafel slope ($\partial E/\partial \log I$) close to 90 mV. The Tafel slope is independent of rotation, the solution pH, the presence of Fe^{3+}, and most importantly the sources of the pyrite samples. Two most probable oxidation routines have been sought to rationalize the experimental results. The open-circuit potentials of the pyrite electrodes are strongly dependent on the solution's chemical and hydrodynamic conditions, but again are nearly independent of the sources of the pyrite samples.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Production of ultraclean coal and mitigation of the acid rain problem are the major mission of DOE's fossil energy programs. This project is directed toward understanding the causes of the difficulties of pyritic sulfur removal from coal by using advanced cleaning technologies such as flotation and oil-agglomeration, and toward improving the efficiency and the range of applicability of these advanced processes in eliminating pyrite and ash-forming minerals from coal. The project's success will also contribute to improvement of other surface-based coal beneficiation processes as well as the basic understanding of the surface chemical structure of coal-pyrite and its relation to bulk properties.

PLANS FOR THE COMING YEAR: We will continue working on the surface hydrophobicity characterization of different pyrite samples. The surface hydrophobicity of synthetic pyrite will be studied using the microcalorimetric method. Electrochemical studies will be extended to coal-pyrites from other sources. ESCA and SEM techniques will be intensively used to identify the exact chemical nature and structure of the surface species of different pyrites. Comprehensive bulk physical, chemical and mineralogical characterization of the samples, including impurities, semiconducting type, porosity, crystallinity, specific gravity and surface area, will be one of the major tasks for the coming year.

TITLE: A Rheometer for Measuring the Material Moduli
for Granular Solids

DATE: 4/19/91

P.I. (s): K.R. Rajagopal

STUDENT(s) AND THE DEGREE FOR WHICH THEY ARE REGISTERED: G. Gupta, Ph.D.

INSTITUTION/ORGANIZATION: (Include address and telephone number) University of Pittsburgh, Pittsburgh, PA 15261, (412) 624-9799

GRANT NO.: DE-FG22-90PC90306

PERIOD OF PERFORMANCE: (From inception to completion of grant) 8/7/90 - 8/7/93

I. ABSTRACT

OBJECTIVE: We have proposed to build an orthogonal rheometer which consists of two disks rotating with the same angular speed about distinct axes. By measuring the forces and the torque acting on the top and bottom disks and correlating them with the theoretical expressions for the tractions and moment we can characterize the properties of the material that is placed between the disks. The above described technique draws upon a method devised for measuring the properties of viscoelastic solids and fluids (cf. Maxwell and Chartoff [1]).

The rheometer consists of a motor A rotates the lower disk. There is a torque sensor connected to the motor A through a flexible coupling and another flexible coupling connects the torque sensor with the lower disk A. There is a bearing in between the torque sensor and the lower disk A. This is required in order to eliminate any bending moment due to the shear force generated at the surface of the lower disk A, so that the torque sensor only measures the pure torque. The upper portion of the instrument consists of the upper disk B rotated by the motor B at the same speed as the lower disk. Both the motor A and B are of the same specifications. There are load cells connected to the upper shaft. Load cell A and B are required to measure the forces generated in the two planes XZ and YZ, while the load cell C measures the normal force generated due to the shearing. These load cells also act as bearings. Thus we can measure all components of the forces and the torque and then correlating these with the theoretical expressions, we can determine the material moduli.

The main component consists of two disks which are rotating at the same speed but about different axes. In order to make the instrument versatile we are deigning the instrument such that we can control the distance between the axes of rotation. We are providing for horizontal movement of the platform on which the lower part of the system supporting the lower disk is to be mounted. This platform is going to also have the capability to move vertically.

WORK DONE AND CONCLUSIONS: The various parts, instrumentation and motors which are required for the device or in the process of either being fabricated at the university workshop are under order. Once the components are in, they will be assembled and the device constructed.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM: The device when built will be able to characterize the material properties of granular materials like coal and also coal slurries. Understanding the properties of such materials will go a long way in the design of bins, hoppers, silos, hydrocyclones and combustors, and in improving their reliability and performance.

PLANS FOR THE COMING YEAR: We plan to assemble the device and if possible try to run some experiments on measuring the property of granular solids.

REFERENCE:

[1] B. Maxwell and R.P. Chartoff, Trans. Soc. Rheol., 9, 41, (1965).

TITLE: HYDROCARBON-OIL ENCAPSULATED BUBBLE FLOTATION OF FINE COAL
DATE: April 9, 1991

P.I. (s): Felicia F. Peng and Eung Ha Cho

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Steven L. Li and David X. Zhang. Both are for M.S. degrees.

INSTITUTION/ORGANIZATION: Mineral Processing Engineering Department
College of Mineral and Energy Resources, West virginia University
Morgantown, West Virginia 26506-6070, (304) 293-7684

GRANT NO.: DE-FG22-90PPC90314

PERIOD OF PERFORMANCE: October 1, 1990 to September 30, 1992

I. ABSTRACT

OBJECTIVE: The overall objective of the project is to obtain the flotation rate data using two type of bench scale flotation experiments to evaluate the effectiveness of oil-encapsulated bubble flotation for six ranks of coal. The six ranks of coal are Upper Freeport seam, Lower Kittaning seam, Pittsburgh seam, Wyodak seam, lignite and anthracite. The flotation cells are a stirred tank cell and a column flotation cell. When a mixture of air and gasified collector, such as kerosene, is dispersed into flotation cell, the oil-coated air bubble are created. This new collector dispersion technique applied in coal fine flotation will be compared with the flotation results obtained from using i) direct collector addition, ii) ultra-sonically collector emulsifying and iii) atomizing collector addition techniques. The rate data and the surface characteristics of coal particles and oil-coated air bubbles will be correlated to achieve an understanding of the mechanisms of oil-coated bubble flotation on various ranks of coal for industrial applications.

WORK DONE AND CONCLUSIONS: This paper summarized the technical progress during the period of October 1, 1990 to March 31, 1991 for hydrocarbon-oil encapsulated bubble flotation of fine coal, DE-FG22-90PC90314, sponsored by the U. S. Department of Energy, Pittsburgh Energy Technology Center (DOE/PETC). This period of work emphasized on establishing the testing methods and procedures for characterization of coal particle surfaces and oil-coated bubbles, as well as measurement of flotation responses for six ranks of coal, by using four different collector dispersion techniques. Upper Freeport seam coal was used in development of flotation procedures, and the hydrophobicity of coal particles determination. Similar procedure and instruments will be extended to study other five coals for comparison purposes.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The hydrocarbon-oil encapsulated bubble flotation of fine coal proposed here is a pre-combustion coal up-grade technique to remove ash and sulfur by improving reagents/collectors dispersion and the bubble-coal particle surface attachment time for fast flotation rate and recovery. This refined flotation

process cleans coarse and fine coal effectively for the production of coal-water slurry or coal fuel for industrial boilers, utility plants or gas turbine engine combustion.

PLANS FOR THE COMING YEAR: 1) The work is in progressing to determine the oil-coated air bubble and reagentless air bubble distributions, by using the photographic pictures and Electron Scanning Microscope with Image Processing Analyzer (ESM/IPA). The oil droplet size distributions prepared from using three different reagent dispersion techniques will be determined by freezing the samples with liquid nitrogen. The freezed samples will be analyzed by ESM/IPA. 2) Air bubble-coal particle contact time will also be determined by using Electronic Induction Timer and high speed camera. 3) Advancing contact angle measurement and surface functional groups will be performed using goniometer and FTIR. Currently, the 3-inch diameter lab size column flotation cell unit is in the processing of assemble and preparing for preliminary tests. The flotation tests using ultra-sonically collector emulsification and collector atomizing methods are also in progressing. These flotation responses will be compared with the results obtained from conventional direct collector addition method. 4) The flotation test methods, coal particle surface characterization methods and air bubble characterization methods established and described will be used to studied and compared with other five different ranks of coal.

II. HIGHLIGHT ACCOMPLISHMENTS

The pulverized Upper Freeport coal samples were sieve to three size fractions, -30 mesh, -200 mesh and -400 mesh (US sieve). 1) The fine coal samples were subjected to several analyses: a) coal samples were characterized including heating value, proximate and ultimate analyses. b) Mineral matter and pyrite liberation distributions, as well as particle size distribution for each size fractions were analyzed using Scanning Electric Microscope with Image Processing Analyzer. c) Zeta potentials and pH values were measured for coal sample using a Zeta-meter and pH meter. d) Washability analyses of coal samples were conducted at three size fractions and at five specific gravity levels. 2) Development of Standard Flotation Tests: An automatic flotation machine was built for the stirring tank cell unit. Stainless steel tubing with heating tape were used to set up a lab size furnace for gasifying the collector, which is then connected to the air dispersion hood in the cell. The operation conditions and experimental procedures for standard oil-coated air bubble flotation tests were developed. A Hallimont cell was used for reagentless froth flotation tests. The data were used as one of the indicators of hydrophobicity of coal surfaces. 3) Collector Dispersion and Addition Studies: Modification of air bubble surface was studied by mixing the gasified kerosene in air stream to form oil-coated air bubbles. The particle size effect on the oil-coated air bubble flotation were analyzed. The flotation responses showed that the significantly improvement in the flotation rate and recovery were observed, particularly for coarser particle size ranges.

III. ARTICLES AND PRESENTATIONS

1. Peng, F. F. and Li, H. R., 1991, "Oil-Coated Air Bubble Flotation to Improve Coal Flotation Rate and Recovery," Preprint, Annual Meeting SME/AIME, Denver, CO., February 25-28 (Submitted to Minerals and Metallurgical Processing).

REACTION CHEMISTRY

Date: 4/04/91

TITLE: Effects of Light Metal Compounds on Coal and Carbon Gasification

PI: M.J.D. Low

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

none

INSTITUTION: NEW YORK UNIVERSITY
Department of Chemistry
4 Washington Place
New York, NY 10003
(212)-998-8470

GRANT NO.: DE-FG22-87PC79920.M003

PERIOD OF PERFORMANCE: 9/15/87-9/14/91

I. ABSTRACT

OBJECTIVE: To obtain direct information by infrared spectroscopy about the functional groups present when coals are pyrolyzed and oxidized, and specifically how light metal compounds affect these processes.

WORK DONE AND CONCLUSIONS: The pyrolyses of model materials (cellulose, lignin and sucrose) and of three different coals, the oxidations of the pyrolyzates, and the effects of sodium and potassium salts on these processes, have been studied in detail. Potassium has a profound effect on the conversion mechanisms.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Coal conversion processes are affected by the presence of light metals. The present work helps to explain how and why this occurs.

PLANS FOR THE COMING YEAR: This project will end during the coming September. The remaining time will be spent on data analysis.

II. HIGHLIGHT ACCOMPLISHMENTS

Infrared Fourier transform photothermal beam spectroscopy has been successfully applied to the study of coals. The series of spectra of sodium- or potassium-impregnated coals provide detailed information about functional groups which are present, formed, and/or altered during coal pyrolysis and oxidation.

III. ARTICLES AND PRESENTATIONS

Presentations: none

Articles Published:

1. N. Wang and M.J.D. Low, Mater. Chem. Phys. 26, 67 (1990).
2. N. Wang and M.J.D. Low, Mater. Chem. Phys. 26,465 (1990).
3. M.J.D. Low and N. Wang, Spectrosc. Lett. 23, 983 (1990).

Articles Submitted:

4. N. Wang and M.J.D. Low, Mater. Chem. Phys., in press.

Articles in Preparation:

A Topical Report dealing with the use of diffuse reflection spectroscopy for the examination of coals is in preparation, to be followed by submission of the paper to *Applied Spectroscopy*.

Three Topical Reports dealing with the effects of sodium and potassium salts on the charring and oxidation of cellulose are in preparation, to be followed by submission of manuscripts to *Carbon* for publication.

Three Topical Reports dealing with the effects of sodium and potassium salts on the charring and oxidation of coals are in preparation, to be followed by submission of manuscripts to *Carbon* and to *Fuel* for publication.

TITLE: Bioprocessing of Lignite Coals Using Reductive Microorganisms

P.I.: Donald L. Crawford

STUDENTS:
1) Mark A. Roberts, Ph.D.
2) Eric Nielsen, M.S.

INSTITUTION/ORGANIZATION: University of Idaho, Department of Bacteriology and Biochemistry

GRANT NO: DE-FG22-88PC88919

PERIOD OF PERFORMANCE: September 1, 1988 to August 31, 1991

I. ABSTRACT

OBJECTIVE: Characterize selected aerobic bacterial strains for their abilities to depolymerize lignite coal polymers, and identify the extracellular enzymes responsible for coal depolymerization. Characterize selected strictly anaerobic bacteria, previously shown to reductively transform coal substructure model compounds, for their abilities to similarly transform polymeric coal. Isolate additional strains of anaerobic bacteria using coal substructure model compounds and coal as enrichment substrates.

WORK DONE AND CONCLUSIONS: A number of aerobic bacteria, anaerobic bacteria, and anaerobic bacterial consortia capable of transforming lignite coals were isolated and characterized. The anaerobes carry out numerous reductive transformations of coal substructure model compounds. Transformations include decarboxylations, demethylations, dehydroxylations, and reduction of carbonyl groups and carbon-carbon double bonds. A number of aerobic, lignite coal-depolymerizing bacteria have been isolated. These strains depolymerize coal without significantly oxidizing it. Three selected strains have been shown to produce extracellular coal depolymerizing enzyme activities. Crude enzyme preparations from culture supernatants of these strains will substantially reduce the average molecular weight of a water soluble lignite coal polymer over incubation periods of 2-4 hours at 30-35°C. Recent research shows that the enzymes involved may include extracellular peroxidases, esterases, and/or etherases.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: There is good potential for using these microorganisms or their enzymes for the depolymerization and liquefaction or gasification of low rank coals. These biotransformations are also of potential value because of the high specificity of their chemistry, lower costs in terms of energy input, and because

they are non oxidative and therefore do not reduce the fuel value of the coal being biotransformed.

PLANS FOR THE COMING YEAR: Selected of the coal substructure model transforming anaerobic bacteria will be characterized for their abilities to similarly transform macromolecular coal. Several new assays will be developed to more accurately quantify reductive biotransformations of coal. The extracellular enzymes catalyzing coal depolymerization will be isolated, identified, and characterized for their biochemical mechanisms of action of the coal macromolecule.

II. HIGHLIGHT ACCOMPLISHMENTS

We are the first to report the production by bacteria of extracellular enzymes that catalyze the depolymerization of a macromolecular coal polymer. We have evidence that indicates that three different types of enzymes, including peroxidases, esterases, and etherases, may be involved in the depolymerization process. We have also isolated a number of strictly anaerobic bacteria which catalyze potentially useful reductive transformations of coal substructure model compounds. Methods are being developed to monitor and quantify these reductive biotransformations using lignite when coals as substrates.

III. ARTICLES AND PRESENTATIONS

Articles

1)Gupta,R.K.,L.A.Deobald,and,D.L.Crawford.1990. Depolymerization and chemical modification of lignite coal by *Pseudomonas cepacia*. Appl.Biochem.Biotechnol.**24/25:** 899-911.

2) Gupta,R.K. and D.L.Crawford.1990.Influence of cultural parameters on the depolymerization of a soluble lignite coal polymer by *Pseudomonas cepacia* Res. Cons. Recyc. In Press.

3) Crawford,D.L., R.K.Gupta, L.A.Deobald, and D.J. Roberts.1990. Biotransformations of coal and coal substructure model compounds by bacteria under aerobic and anaerobic conditions. Proc. First Int'l. Symp. on the Biological Processing of Coal. Orlando, FL. Electric Power Res. Inst. Palo Alto, CA pp. 4-27 to 4-32.

4) Crawford, D.L. and R.K. Gupta. 1990. Characterization of extracellular bacterial enzymes which depolymerize a soluble lignite coal polymer. Fuels (In press).

5) Roberts, M.A. and D.L. Crawford. 1991. Extracellular enzymes produced by coal-depolymerizing bacteria. Proc. Second Int'l. Symp. on the Biological Processing of Coal. (Submitted, May 1991).

Presentations

1) Gupta, R.K. and D.L. Crawford. 1989. Influence of cultural parameters on the depolymerization of a soluble lignite coal polymer by *Pseudomonas cepacia* DLC-07. Presented, Symp. on Biological Processing of Fossil Fuels. Sponsored by DOE Office of Fossil Energy Res.,Idaho DOE Operations Office, and the Idaho National Engineering Laboratory. Aug.8-10. Tyson's Corner, VA.

2) Deobald,L.A. and D.L.Crawford.1989.Isolation of microorganisms able to reductively transform aromatic compounds and their relevance to coal liquefaction. Presented, Inst.Gas Technol. 2nd Symp. on Gas, Oil, and Coal Biotechnol.Dec.11-13.New Orleans, LA.

3) Crawford,D.L.,R.K. Gupta,L.A. Deobald, and D.J.Roberts. 1990. Biotransformations of coal and coal substructure model compounds by bacteria under aerobic and anaerobic conditions. Presented, 1st Int'l. Symp. on the Biological Processing of Coal. Sponsored by U.S. DOE (PETC) and the Electric Power Research Institute. May 1-3. Orlando, FL.

4) Crawford, D.L. and R.K Gupta. 1990. Characterization of extracellular bacterial enzymes which depolymerize a lignite coal polymer. Presented, Amer. Chem. Soc. Symp. on Biotechnology for the Production of Clean Fuels. Fuel Chemistry Division. August 26-31. Washington, D.C.

5) Roberts, M.A. and D.L. Crawford. 1991. Extracellular enzymes produced by coal depolymerizing bacteria under induced and uninduced growth conditions. To be Presented. Second Ann. Symp. on the Biological Processing of Coal, May 1-3, San Diego, CA.

TITLE: Electrochemistry of Thiobacillus ferrooxidans Reactions with Pyrite

DATE: April 1, 1991

PI's (Authors): Batric Pesic (P.I.)
David J. Oliver (Co P.I.)

STUDENTS: Inbeum Kim (Ph.D. student)
Gopal Chandra De (Ph.D. student)

INSTITUTION: Department of Mining and Metallurgical Engineering, College of Mines, University of Idaho, Moscow, Idaho 83843 (208) 885-6569

GRANT NUMBER: DE-FG22-88PC88920

PERIOD PERFORMANCE: August 1989-September 1990

I ABSTRACT

OBJECTIVE: To perform fundamental study toward understanding of interaction mechanisms of T. ferrooxidans with pyrite. Further understanding of involved mechanisms will help develop more efficient processes for biodesulfurization of coal.

WORK DONE AND CONCLUSIONS:

A detailed cyclic voltametry study was performed on mineral pyrite. The following parameters were studied: effect of turbulence, scanning rates, and effect of nutrient addition. Two types of pyrite electrodes were used, which were characterized according to their use. One pyrite electrode was continuously present during fermentation and the other electrode was used as a control electrode.

The key feature of the research was the study of pyrite interaction with T. ferrooxidans during their most active stage, i.e. growth. This kind of work was never performed before. Very important results were obtained. According to the obtained results, pyrite surface becomes quickly covered with T. ferrooxidans (within 2 days) which completely isolates the pyrite surface from the solution. The obtained cyclic voltametric data were also correlated with the SEM study.

The reaction product which was responsible for pyrite passivation was characterized chemically and by X-ray diffraction. The chemical analysis showed its chemical composition very close to jarosite.

The X-ray diffraction analysis also demonstrated the formation of jarosite. The reaction product formed on the pyrite surface was identical to the product formed in solution.

Considerable research effort was made on how to avoid the formation of jarosite. Addition of complexing agents, vitamins, and lithium salts (lithium does not form jarosite) were not successful in preventing its formation.

Other experiments were directed toward the study on how to increase the bacteria population. It was found that the excess of food did not have any beneficial effects on the increase of population density. Contrary to that the "clean" environment had the most important effect.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: This study is very important because:

1. It will provide more understanding on how biodesulfurization of inorganic sulfur with *T. ferrooxidans* work.
2. The research will further reveal the most important biodesulfurization process parameters.
3. Without understanding the mechanisms of *T. ferrooxidans* reactions with pyrite it is not possible to perform any modeling toward the reactor design.

PLANS FOR THE COMING YEAR: In the past, most of the work was done with the mineral pyrite because it was easier to acquire it in the pure form and the shape convenient to make the adequate electrodes. In the future, coal pyrite will be used too. However, coal pyrite electrode will be used in those cases which are identified as the most important from the study with the mineral pyrite electrode.

The next year (work in progress) other electrochemical techniques (chronopotentiometry, chronoamperometry, etc.) will be studied.

The research will be targeted to provide the answer if the attachment of bacteria cells to the pyrite surface is useful or detrimental to pyrite dissolution. This is the major question opened by this research. The answer to this question is of utmost importance from the engineering point of view, and in the author's opinion no reactor design can be performed, or process developed, until the full answer is obtained. If it was proven that bacteria coverage of pyrite surface was detrimental to pyrite dissolution then methods of keeping the bacteria off the surface would have to be developed. In the other case, that bacteria attachment was useful, then the methods of more efficient attachment would have to be devised. This research raised this important question, and hopefully it will also be able to provide the answer.

More work will be done to examine if an appropriate additive can be found which prevents the formation of jarosite.

Corrosion techniques will also be used to quantify the reactions of pyrite with T. ferrooxidans.

II. HIGHLIGHT ACCOMPLISHMENTS

- The present research has produced further information on the interfacial phenomena between pyrite and T. ferrooxidans.

- During bacteria growth, a product is formed which is freely suspended in solution, and which is also attached to the pyrite surface. Product layer is jarosite. There is no difference in composition between the product layer and product suspended in solution.

- Probably the most important contribution of this research project is the identification that bacteria cells serve as the nucleation cites for formation of jarosite. Because bacteria have a natural tendency to attach to the solid surface, and because they also form jarosite, the product layer attached to pyrite surface will be formed which will contain jarosite.

- According to obtained results, T. ferrooxidans attachment on the pyrite surface has a detrimental effect on pyrite dissolution. This conclusion was reached on the basis of zero cyclic voltametric currents after two days of fermentation when the complete surface was covered with bacteria. Accordingly, the pyrite surface became isolated from the solution. However, what remains unanswered, is the role of bacteria, with respect to pyrite dissolution, in the layer itself.

III) ARTICLES AND PRESENTATIONS

Batric Pesic and Inbeum Kim, (1990) "Electrochemistry of T. ferrooxidans Interactions with Pyrite", EPD Congress '90, The Minerals, Metals and Materials Society, 1990, Edited by D.R. Gaskell, pp. 133-160.

Batric Pesic and Inbeum Kim, (1990) "Electrochemistry of T. ferrooxidans Interactions with Pyrite", Presented at the TMS/AIME Annual Meeting, Anaheim, CA, February 19-22, 1990.

Batric Pesic and Inbeum Kim, (1991), "Electrochemistry of T. ferrooxidans Interactions with Pyrite", Engineering Foundation Conference, Minerals Bioprocessing, June 16-21, Santa Barbara, California.

March 26, 1991

TITLE: Genetics of Coal Bioliquefaction by Neurospora crassa

PIs: Dr. N.C. Mishra, Department of Biological Sciences

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED: Alex Almasan (Ph.D.), and Brian Odom (Ph.D.).

GRANT NO.: DE-FG22-88PC88936

INSTITUTION/ORGANIZATION: Department of Biological Sciences
University of South Carolina
Columbia, South Carolina 29208
(803) 777-5938

PERIOD OF PERFORMANCE: August 9, 1988-August 8, 1991

I. ABSTRACT

OBJECTIVE:

The main objectives of this proposal include: (1) Isolation faction; (2) Identification of coal derived products obtained after biosolubiliation in vitro. (3) Selection of Neurospora strain capable of efficient coal liquefaction and biochemical characterization of mutants.

WORK DONE AND CONCLUSIONS:

A 84 kd protein with Coal Solubilization Activity (CSA) has been identified from the wildtype strain of Neurospora crassa, a filamentous fungus. This protein has been now very well characterized with respect to pH of Coal Solubiliation Activity, molecular weight, amino acid composition and heat stability. The protein has been found to be altered in a Neurospora mutant (ty-1) which is unable to solubilize coal. The mutant protein is altered with respect to its reduced stability, glycosylation pattern and isoelectric point (PI). These findings conclusively establish that Coal Solubilization is genetically controlled and that the above 84 kd Neurospora protein is involved in the Solubiliation of Coal. Further study is aimed at determining the mechanism of the action of this 84 kd Neurospora protein.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Results of this research porject will provide the biochemical and molecular genetic basis for the bioliquefaction of coal. Neurospora, a genetically characterized fungus, will be further manipulated to yield a strain capable of

maximal coal liquefaction leading to the development of a bioreactor useful for generation of utilizable clean energy from coal.

PLANS FOR THE COMING YEAR:

The mechanism of the action of this 84 kdalton protein in Coal Solubilization will be determined by further characterization of the wild type and mutnat protein. The chemical nature of the Coal Solubilized products will be determined by NMR Spectroscopy and other analytical methods such studies can alone establish whether this protein cause Coal Solubilization by the mechanism of Chelation or by its calalytic (enzymatic) activity.

II. HIGHLIGHT ACCOMPLISHMENTS

A. Identification and purification to near homogeneity of Neurospora enzyme capable of coal liquefaction have been accomplished. This 84 kdalton protein has been shown to be altered in terms of the biochemical properties in a mutant deficient in Coal Solubilization *in vivo*.

B. Development of an electrophoretic system capable of separation of insoluble prodects (ash) from heteroatomic compounds present in coal liquefied by Neurospora enzyme has been achieved.

C. Neurospora mutants defective in coal bioliquefaction, useful for further genetic analysis have been obtained.

D. A Neurospora plasmid (pstpb) capable of self replication has been isolated and fully characterized at the molecular level. This is the first report of the occurrence of such plasmid in filamentous fungi.

III. ARTICLES AND PRESENTATIONS

1. Odom, C.B., M. Cooley and N.C. Mishra, Conservation and Recycling (Submitted), 1990.
2. Odom, C.B. Dissertation, The University of South Carolina. 1990.
3. Almasan, A. and Mishra, N.C. 18, 5871-5877.
4. Almasan, A. and Mishra, N.C., Proc. Natl. Acad. Sci. U.S.A. (submitted), 1990.
5. Odom, C.B. and Mishra, N.C. Resources, Conservation and Recycling (in press), 1990.
6. Mishra, N.C., Adv. in Genetics, (in press), 29, 1991.
7. Mishra, N.C., Cooley, M. and C.B. Odom. (San Diego, CA) Submitted, 1991.

TITLE: Bimetallic Promotion of Cooperative Hydrogen Transfer and Heteroatom Removal in Coal Liquefaction March 27, 1991

P.I.(s): John J. Eisch, Distinguished Professor of Chemistry

STUDENT(s) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Mona Singh, Ph.D. candidate;
Xin Ma, Ph.D. candidate

INSTITUTION/ORGANIZATION:
State University of New York at Binghamton,
P.O. Box 6000,
Binghamton, New York 13902-6000
(607-777-4261)

GRANT NO.: DE-FG22-88PC88930

PERIOD OF PERFORMANCE: September 1, 1988 - December 31, 1991

I. ABSTRACT

OBJECTIVE: The ultimate objective of this research is to uncover new catalytic processes for the liquefaction of coal and for upgrading coal-derived fuels by removing undesirable organosulfur, organonitrogen and organooxygen constituents. Basic to both the liquefaction of coal and the purification of coal liquids is the transfer of hydrogen from such sources as dihydrogen, metal hydrides or partially reduced aromatic hydrocarbons to the extensive aromatic rings in coal itself or to aromatic sulfides, amines or ethers. Accordingly, this study is exploring how such crucial hydrogen-transfer processes might be catalyzed by soluble, low-valent transition metal complexes and/or Lewis acids under moderate conditions of temperature and pressure. By learning the mechanism whereby H_2, metal hydrides or partially hydrogenated aromatics do transfer hydrogen to model aromatic compounds, with the aid of homogeneous, bimetallic catalysts, we hope to identify new methods for producing superior fuels from coal.

WORK DONE AND CONCLUSIONS: In individual studies the catalytic potential of various Lewis acids in effecting hydrogen transfer from hydrogen donors to aromatic hydrocarbons, sulfides, ethers and amines has been evaluated. In parallel studies the corresponding catalytic potential of soluble nickel(0) complexes for such hydrogen transfers has also been evaluated. Now in our present work we are concentrating on the possible synergistic action of combinations of Lewis acids with nickel(0) complexes in hydrogen transfer that can lead to reduction of carbon-carbon unsaturation and the rupture of carbon-heteroatom bonds. At this point we have concluded that there is a synergistic action of these catalyst combinations and that desulfurization, deoxygenation and possibly denitrogenation can be promoted by these bimetallic catalysts.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Through our studies of bimetallic catalysis of hydrogen transfer, we hope to gain insight into the molecular basis for the transfer of hydrogen and the rupture of carbon-heteroatom bonds. We are convinced

that such insights will prove most valuable in the rational design of novel, modified heterogeneous catalysts for the important process of coal hydrogenation and the upgrading of coal liquids.

PLANS FOR THE COMING YEAR: Our studies are now concentrating on the synergistic action of catalyst combinations of organoaluminum Lewis acids and olefin complexes of nickel(0) in promoting hydrogen transfer. In addition, we are probing the mechanisms whereby such nickel(0) complexes themselves can cleave C-O, C-S, C-X and C-N bonds. Knowledge of these transformations is crucial in understanding how heteroatom removal from coal is facilitated.

II. HIGHLIGHT ACCOMPLISHMENTS

The following are the new insights that we have gained from this research: 1) nickel(0) complexes can promote the shuttling of hydrogen between aromatic and hydroaromatic systems; 2) organoaluminum Lewis acids can promote the transfer of hydrogen to aromatic sulfides with concomitant desulfurization; 3) combinations of nickel(0) complexes and organoaluminum Lewis acids show a synergistic action in promoting such hydrogen transfers; 4) nickel(0) complexes have been shown to rupture a variety of covalent bonds such as C-H, C-S, C-O, C-N and C-X bonds by the process of oxidative addition; and 5) such results have given us an insight into the mode of action of heterogeneous hydrogen-transfer catalysts such as nickel adsorbed onto alumina supports.

III. ARTICLES AND PRESENTATIONS

1. J.J. Eisch, S.R. Sexsmith and M. Singh, Energy & Fuels, 3, 761 (1989).
2. J.J. Eisch, S.R. Sexsmith and K.C. Fichter, Journal of Organometallic Chemistry, 382, 273-293 (1990).
3. J.J. Eisch and S.R. Sexsmith, Research on Chemical Intermediates, 13, 149-192 (1990).
4. Symposial lecture, "Interaction of Unsaturated Organic Compounds with Nickel(0) Complexes", ACS Northeast Regional Meeting, June 18-21, 1989, Albany, New York.
5. Symposial lecture, "Stoichiometric and Catalytic Reactions of Nickel(0) Complexes in Organic Synthesis", German Democratic Republic-Poland Colloquium on Organometallic Chemistry, April 24-29, 1989, Holzhau, German Democratic Republic.
6. Lecture, "Nickel(0) Komplexe in Reaktionsmechanismen und Synthesen", Max Planck Institute for Coal Research, March 6, 1990, Mülheim (Ruhr), West Germany.
7. Lecture, "Bimetallic Promotion of Cooperative Hydrogen Transfer and Heteroatom Removal in Coal Liquefaction, University Coal Research, Contractors Review Meeting", Pittsburgh, Pennsylvania, July 17, 1990.

DATE: April 9, 1991

TITLE: Fundamental Studies in Production of C_2-C_4 Hydrocarbons From Coal

P.I.(s) Wendell H. Wiser and Alex G. Oblad

STUDENT AND THE DEGREE FOR WHICH REGISTERED:
Kui Liu, working toward a Ph. D. Degree
K. S. Yang, Post-Doctoral Fellow

INSTITUTION/ORGANIZATION: Department of Fuels Engineering
University of Utah
Salt Lake City, Utah 84112
(801) 581-8602

GRANT NO. DE-FG22-88PC88940

PERIOD OF PERFORMANCE: September 1, 1988 - August 31, 1992

I. ABSTRACT

OBJECTIVE: The project objectives are to demonstrate, in a specially-designed, continuous-flow reactor system, direct conversion of coal to C_2, C_3 and C_4 hydrocarbons; to examine the kinetics of the conversion process; and to gain understanding of the reaction pathways. A computer program will be developed to define the maximum yields of C_2, C_3, and C_4 hydrocarbons (individually) thermodynamically possible as a function of temperature, pressure, and percent steam in the steam-hydrogen feed to the reactor. The process will then be optimized for production of each of the hydrocarbons C_2, C_3 and C_4, and for production of olefins among these hydrocarbons.

WORK DONE AND CONCLUSIONS: A single-stage, continuous reactor system has been constructed, and has undergone several modifications, as dictated by the desire to obtain the most valid kinetic data. The present configuration utilizes a semi-continuous system, the coal and catalyst being batch, while hydrogen is fed continuously, and liquid and gaseous products are removed continuously. The kinetics are evaluated by measuring the rate of formation of products. A gas-sampling manifold, utilizing a series of electrically-operated valves, is under construction and nearly ready for use. This sampling system is constructed to permit computer operation of sampling and on-line GC analysis.

In consideration of certain problems in conversion of a strongly-caking coal, a two-stage, continuous reactor system has been designed and is under construction. It is desirable to compare the product yields, operational reliability, and other factors associated with direct conversion of coal, including both caking and non-caking coals, to C_2, C_3 and C_4 hydrocarbons.

PLANS FOR THE COMING YEAR: A single-stage, semi-continuous reactor has been constructed and is now being operated. We are now constructing

a two-stage, continuous system, in order to compare the two systems for technical reliability and product yields. During the coming year both reactor systems will be operated, one by the graduate student, the other by a technician under the guidance of the Post-Doctoral Fellow, to satisfy the factors identified above in the Objective.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Today there exists in the United States concern about the high level of petroleum imports (greater than 50% of demand, and growing), prompting a search for alternate sources of transportation fuels. Inasmuch as coal represents about 96% of known U. S. fossil fuel reserves recoverable by currest technology, production of transportation fuels from coal is very desirable. It is observed that a fuel like LPG (consisting of C_3 and C_4 hydrocarbons) is clean burning and exhibits a high octane number. If these hydrocarbons can be produced directly from coal in a technologically sound manner, with acceptable economics, the benefits will be great.

II. HIGHLIGHT ACCOMPLISHMENTS

This researcher, experienced in kinetic studies involving coal, has observed a rather large amount of experimental data in the literature concerned with coal conversion, which yielded erroneous kinetic interpretations because of insufficient care in the experimental procedure. It is believed we have now refined the equipment and procedure for our kinetic studies such that valid kinetic data will be obtained. These data are to be used in the design of a prototype reactor in connection with another DOE-sponsored Grant.

III. ARTICLES AND PRESENTATIONS

Sufficient data have not as yet been produced from this research program for publication or for presentation.

Date: April 5, 1991

TITLE: Applications of Micellar Enzymology to Clean Coal Technology

PI: Carol T. Walsh, Ph.D.

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Majid Yazdani, M.A. in Medical Sciences (awarded January 1991)
John Pezzullo, M.A. in Medical Sciences

INSTITUTION/ORGANIZATION:
Boston University School of Medicine
80 East Concord Street, L-603, Boston, MA 02118
Tel: 617-638-4326

GRANT NO: DE-FG22-89PC89772

PERIOD OF PERFORMANCE: October 1, 1989-September 30, 1992

I. ABSTRACT

OBJECTIVE:

The principle objective of this project is to investigate the technology of reverse micelle enzyme biochemistry in the desulfurization of model coal compounds and coal samples. The goal is to develop micellar systems that enhance enzyme-mediated oxidation of organic sulfur and its removal from organic substrates with minimum cleavage of carbon-carbon bonds. Model compounds in this study include dibenzothiophene (DBT) and ethylphenylsulfide (EPS). The primary emphasis is the investigation of isolated enzymes in micellar systems including horseradish peroxidase (HRP), chloroperoxidase, and laccase; microbial extracts are under study as well.

WORK DONE AND CONCLUSIONS:

We have examined the activity of enzymes in a reverse micelle system which has been shown to enhance catalytic activity of a number of enzymes. This system is especially effective in producing reverse micelles of relatively uniform size, which incorporate hydrophilic enzymes. The components include the surfactant AOT, an organic phase of isooctane, and an aqueous phase of 10:1 to 25:1 H_20:AOT depending on the molecular size of the enzyme. The oxidative activity of enzymes in this reverse micelle system has been demonstrated with conventional substrates, and the systems then tested for their effect on model coal compounds.

HRP in reverse micelles catalyzed H_20_2-dependent coupling of 4-aminoantipyrine and phenol in a concentration-dependent manner. This micellar enzyme system was tested for its effects on DBT and its oxidation products, DBT sulfoxide and DBT sulfone. Incubations were carried out for 24 hr with HRP Type I or Type VI, a more purified form of the enzyme. Samples were analyzed by reverse

phase HPLC, modified to minimize interference of AOT with assay of model compounds. No significant differences were observed between control and enzyme-containing incubates in the concentrations of the heterocyclic sulfur-containing starting materials, and there was no evidence of enzyme-mediated production of metabolites.

Laccase from Polyporus versicolor in the reverse micelle solution oxidized pyrocatechol to *o*-quinone at a rate which was dependent on enyzme and substrate concentrations. Studies of this enzyme system were similar in design and analysis to those conducted with HRP. Alterations in DBT, DBT sulfoxide or DBT sulfone in the laccase-containing reverse micelle solution were not detected after 24-hr incubations.

An intracellular fraction from the microbe, GB-1, previously shown to oxidize DBT, was incorporated into reverse micelles and incubated for 7 days with DBT. DBT concentrations did not decrease relative to controls, and no consistent evidence of the formation of sulfur oxidation products was observed.

Methodology for quantitation of ethylphenylsulfide (EPS), ethylphenylsulfoxide and ethylphenylsulfone in aqueous and reverse micelle solutions has been developed and validated. Compounds are recovered from aqueous or reverse micelle solutions by elution from C-18 or 20H (diol) Bond Elut columns respectively and then quantitated by normal phase HPLC.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

This project is based on the premise that new methods must be developed to rapidly and efficiently convert existing reserves of high sulfur coals, a significant source of environmental pollution, to low sulfur forms. The studies are designed to address methods for precombustion coal remediation by implementing recent advances in enzyme biochemistry. Use of hydrophilic, oxidative enzymes stabilized within a micellar environment may enhance catalytic activity towards sulfur contained in hydrophobic organic components of the coal structure.

PLANS FOR THE COMING YEAR:

Having developed quantitative techniques for EPS and its sulfur oxidation products, we intend to compare the effect on EPS of enzymes from microbial and plant sources in aqueous and reverse micelle solutions. Initial work is being carried out with chloroperoxidase. We will also be screening enzymes for sulfur-oxidizing activity in reverse micelle solutions produced with other types of surfactant agents.

II. HIGHLIGHT ACCOMPLISHMENTS

Analytical methodology for quantitation of DBT, EPS and their sulfur oxidation products in reverse micelle solutions have been developed. The oxidative activity of HRP and laccase in the reverse micelle system has been demonstrated using conventional substrates. Tests of these enzymes in reverse micelles, as well as a microbial extract, have not indicated efficacy in oxidation of sulfur in DBT under conditions of study.

III. ARTICLES AND PRESENTATIONS

None to date.

TITLE: **MECHANISM OF HYDRODENITROGENATION** DATE: April 10, 1991

P.I.: Raul Miranda
STUDENTS: Jorge Marzari, PhD student
Sakamuri Rajagopal, Post-Doctoral student
INSTITUTION:
Department of Chemical Engineering
University of Louisville
Louisville, Kentucky 40292, (502)588-0191

GRANT NO. DE-FG22-89PC89771
PERIOD OF PERFORMANCE: 9/1/89 - 8/31/91

I. ABSTRACT

OBJECTIVE

The general objective of this project is to clarify the extent of participation of support acidity and catalyst acidity in general in the mechanistic steps leading to denitrogenation of hetero-aromatics. In particular, it is of interest to prove or disprove a bifunctional mechanism in which the acidic functionality catalyzes a Hofmann-like elimination step; to investigate which secondary reactions are catalyzed by acidity; and to qualify and quantify the effect of acidity on surface structure of Mo species.

The particular objectives during this past year were (a) to continue with the characterization of the acidic catalysts developed in this project: molybdena supported on silica-aluminas of varying composition, and (b) to investigate the role of acidic sites by means of the pyridine HDN reaction.

WORK DONE AND CONCLUSIONS

Well characterized silica-aluminas of composition varying from 0-100% silica, and of uniform characteristics, such as same precursor, same method of preparation, etc., are not available in the market. Thus, initially the work was focused on preparing and characterizing a series of silica-aluminas of smoothly varying acidity. The silica-aluminas were then used directly as catalysts in the denitrogenation reactions of piperidine, in order to directly assess the catalytic function of Bronsted and Lewis acid sites.

Various methods were tested to prepare silica-aluminas of widely varying composition, with high yield, good flowing characteristics (large grain size) and smoothly varying acidity. The method selected was then used to prepare large batches of silica, silica-alumina of 10, 25, 50, 75, and 90% silica, and gamma-alumina. The characterization of the support material included BET surface area; total acidity by ammonia chemisorption; acidity strength distribution by temperature programmed desorption of ammonia, pyridine, n-butyl- and n-pentylamine; and type of acidity by diffuse reflectance infrared spectra of adsorbed pyridine. The total acidity, as measured by ammonia chemisorption at 120°C, is a smooth function of composition of the silica-alumina, increasing with alumina content, with a maximum between 75 and 90% alumina. Lewis acidity smoothly increases with alumina content from silica to alumina. Bronsted acidity (by IR of pyridine at 120°C), on the contrary, is present only in the silica-aluminas and increases uniformly with silica content.

The denitrogenation of piperidine catalyzed by acidic catalysts was carried out in a flow reactor at various temperatures between 320 and 380°C, using hydrogen as a carrier gas. The numerous products were classified into (a) hydrocarbons (formed by denitrogenation), (b) pyridine (dehydrogenation-cracking) and (c) others (disproportionation-condensation). It was observed that the total activity is a direct function of the total acidity (Bronsted and Lewis) of the catalysts. The denitrogenation activity, on the other hand, is only a function of Bronsted acidity. Lewis acidity does not catalyze the denitrogenation of piperidine. Thus strong evidence is being provided in favor of a Hofmann-like elimination mechanism for the denitrogenation of piperidine over purely acidic catalysts.

During the third, fourth and fifth quarters, molybdena was supported over the series of supports, and was reduced with hydrogen. The oxidic and reduced catalysts were characterized by BET, total acidity, type of acidity, acidity strength distribution, reducibility, and x-ray diffractometry, in order to assess the changes introduced by the supported molybdena. It was found that the percent increase in acidity is greatest for the silica-rich supports, although the new acid sites were mostly weak. The reducibility and XRD results indicated the appearance of more than one molybdenum phase, whose abundance varied depending on the support composition. The conclusions were that alumina-rich supports (<50% silica) disperse molybdena finely, producing an x-ray amorphous phase that is reducible at 350-400°C, and a strongly interacting phase that is reducible at >550°C. Pure silica support, however, produced only a clustered molybdena phase that is reducible at 550-600°C. The silica-rich supports (>50% silica) gave rise to an additional phase of $Al_2(MoO_4)_3$, which disappeared upon reduction at 500°C. This new phase was formed by calcination at low temperature, and only appeared on silica-aluminas.

During the sixth and seventh quarter, pyridine HDN was carried out in a differential reactor at atmospheric pressure, on the reduced molybdena catalysts. Oxygen chemisorption was used to titrate the density of coordinated unsaturated sites (cus) of Mo on the various catalysts. The results indicated that the main parameter affecting the overall activity of the catalysts is the degree of reduction of Mo (or density of cus), thus the silica-supported catalysts were the most active ones. This is a consequence of the high activity for hydrogenation needed for the partial saturation of the hetero-aromatic before ring opening. Acidity of the catalysts affected the selectivity for HDN and for other reactions. These aspects will be fully discussed during the oral presentation.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM

Liquid hydrocarbons for energy production will be progressively derived from coal, shale oils and tar sands. A common denominator to these feedstocks is the high content of S-, N-and O-heterocyclic aromatics, which have to be decomposed if environmental and technical concerns are to be satisfied. A major process for the removal of S and N as hydrogen sulfide and ammonia is catalytic hydroprocessing, whose catalyst has been optimized for petroleum and light feedstocks. Need for catalyst development is apparent in the case of coal liquid and heavier crude hydrotreatment. The work in this project has as a main objective to understand the role of catalyst structural features in the hydrodenitrogenation mechanism. Such understanding will lead to better design of hydrodenitrogenation catalysts. The preliminary results obtained so far are already providing evidence of how support acidity may impact the hydrodenitrogenation selectivity of catalysts.

PLANS FOR THE COMING YEAR

The only remaining part of the funded project is the isotopic labeling of Bronsted sites and tracing of such in products of HDN. This work is being done at the moment.

II. HIGHLIGHT OF ACCOMPLISHMENTS

(a) Developed a complete series of silica-aluminas of varying composition and acidity characteristics.
(b) Developed a method to analyze (on-line) all of the products of piperidine denitrogenation reaction (see ref. 1 below).
(c) Showed the role of each type of acidity in the mechanism of piperidine denitrogenation and overall reaction (see ref. 2 below).

III. ARTICLES AND PRESENTATIONS

(1) S. Rajagopal, T. Grimm, D.J. Collins and R. Miranda, Anal. Chem. Lett., 23(4), 649-57 (1990)
(2) S. Rajagopal and R. Miranda; three articles submitted to Applied Catal. and J. Catal.
(3) Poster and paper presentations at AIChE Meeting (Chicago) and at the North American Catalysis Society Meeting (Lexington).

3/31/91

TITLE: Fundamental Studies of Catalytic Processing of Synthetic Liquids

P.I.: Prof. Philip R. Watson

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Glenn R. Tinseth (Ph.D), Chang-Seop Ri (Ph.D)

INSTITUTION/ORGANIZATION:
Dept. of Chemistry, Oregon State University, Corvallis, OR 97331; (503)-737-2081

GRANT NO.: DE-FG22-89PC89783

PERIOD OF PERFORMANCE: 9/89 - 8/92

I. ABSTRACT

OBJECTIVE:

This project investigates, using surface science techniques, the reactions of simple furans and phenols, acting as models for the O-heterocycles found in coal liquids, at designed surface sites on sulfided Mo and W surfaces. The objectives of the study are to elucidate the changes in the mode of adsorption, reactions and poisoning behavior, with particular attention to dehydrodeoxygenation (HDO), of normal and sterically-hindered heterocycles at various well-defined catalytic centers designed to have different chemical characteristics.

WORK DONE AND CONCLUSIONS:

We have discovered how to realiably obtain and have characterized the adsorption/reaction sites on sulfided Mo(100) and (110) surfaces using Auger electron spectroscopy (AES) and low energy-electron diffraction (LEED). Above a S/Mo ratio of about 0.6 ML, furan does not adsorb on these surfaces. As the sulfur coverage is lowered increasing amounts of furan can be adsorbed, but temperature-programmed reaction spectroscopy (TPRS) reveals that decomposition occurs. The major products of adsorption are molecular CO and strongly chemisorbed hydrocarbon fragments that dehydrogenate over a range of temperatures. Performing the adsorption or thermal reaction in 10^{-6} torr of hydrogen does not change the mode of reaction significantly.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Liquids derived from coal contain relatively high amounts of oxygenated organic compounds, mainly in the form of phenols and furans that are deleterious to the stability and quality of these liquids as fuels. HDO using Mo/W sulfide catalysts is a promising method to accomplish this removal, but our understanding of the reactions occurring on the catalyst surface during HDO is very limited. Rather than attempting to examine the complexities of real liquids and catalysts we have adopted an approach here using model systems amenable to surface-sensitive techniques that enable us to probe in detail the fundamental processes occurring during HDO at the surfaces of well-defined model catalysts. The results of this work may lead to the development of more efficient, selective and stable catalysts.

PLANS FOR THE COMING YEAR:

To better elucidate the reaction pathways of adsorbed furan we will investigate deuterated and hindered 2-Me and 2,5-diMe furans. Further, we intend to perform collaborative experiments under much higher pressures of hydrogen to better mimic real HDO conditions. To compare different reactant types we will extend this series of experiments to simple phenols

II. HIGHLIGHT ACCOMPLISHMENTS

1. We have established conditions for the reliable preparation of various sulfided Mo(100) and (110) surfaces.
2. The processes of adsorption and reaction of furan on these surfaces is well understood:
    - adsorption of furan is suppressed for S/Mo > 0.5-0.6 ML
    - in the absence of large quantities of hydrogen, CO extraction and decomposition to hydrocarbon fragments occurs
3. Experiments are in progress to establish the role of steric interference and the reaction pathways at higher hydrogen pressures.

III. ARTICLES AND PRESENTATIONS

Articles:

"Observation of direct CO extraction from furan on sulfided Mo surfaces", P.R. Watson and G.R. Tinseth, submitted to J. Am. Chem. Soc.

"The adsorption and reaction of furans on sulfided surfaces of molybdenum", P.R. Watson and G.R. Tinseth, submitted to J. Phys. Chem.

Presentations:

"Surface chemistry studies of furan hydrodeoxygenation", P.R. Watson and G.R. Tinseth, Annual Meeting of Oregon Academy of Sciences, March 16th, 1991

"Surface chemistry studies of furan hydrodeoxygenation", P.R. Watson and G.R. Tinseth, American Chemical Society Regional Meeting, June 12th, 1991

"Reactions of furan on sulfided Mo surfaces", P.R. Watson and G.R. Tinseth, American Vacuum Society Annual Meeting, Oct. 1991

Date: April 8, 1991

TITLE: Preconversion Catalytic Deoxygenation of Phenolic Functional Groups

PI: Professor Clifford P. Kubiak

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
David Dockter, Ph. D.
Rebecca Lentz, Ph. D.
Anne Meyers, Ph. D.

INSTITUTION/ORGANIZATION:
Purdue University
Department of Chemistry
West Lafayette, Indiana 47907
(317)494-5323

GRANT NO.: DE-FG22-89PC89770

PERIOD OF PERFORMANCE: 9/1/89 - 8/31/92

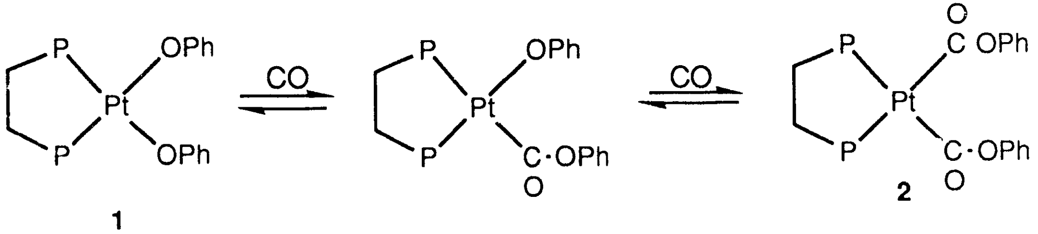
I. ABSTRACT

OBJECTIVE: To prepare new catalysts for the deoxygenation of phenolic functional groups using carbon monoxide as the oxygen atom acceptor.

WORK DONE AND CONCLUSIONS:

The deoxygenation of phenols is a conceptually simple, but unusually difficult chemical transformation of importance in coal liquefaction. Present catalysts for removal of phenolic oxygen atoms are based on hydrodeoxygenation (HDO) methods. Typical HDO catalysts require high temperatures and H_2 pressures and lack selectivity. We are studying the deoxygenation of phenols via the unprecedented use of the CO/CO_2 couple.

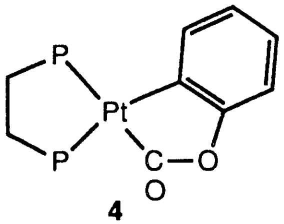
Insertions of CO into the metal-oxygen bonds of several late transition metal alkoxide and aryloxide complexes have been reported. We have found that the complex $Pt(dppe)(OPh)_2$, **1**, (dppe = bis(diphenylphosphino)ethane) **1** incorporates CO into both Pt-OPh bonds to give $Pt(dppe)(COPh)_2$, **2**.



1

2

Complex **2** effects deoxygenation of one phenoxide ligand under CO to give CO_2, phenylbenzoate, and $Pt(dppe)(CO)_2$, **3**. The identification of phenyl benzoate and CO_2 as the predominant organic products demonstrates that one of the two phenoxy groups of complex **1** was deoxygenated. In a competing pathway, **2** undergoes elimination of PhOH to yield $Pt(dppe)(COOC_6H_4)$, **4**. The competing pathways may be controlled by CO pressure. An X-ray structure determination of **4** was undertaken. Complex **4** crystallizes in space group $P2_1/n$ with **a** = 12.155(2) Å, **b** = 13.527(2) Å, **c** = 17.417(2) Å, ß = 99.50(1)°, V = 2824(1) Å^3, Z = 4. The structure has been refined to R = 0.033 and R_w = 0.038 for 343 variables and 2373 observations.



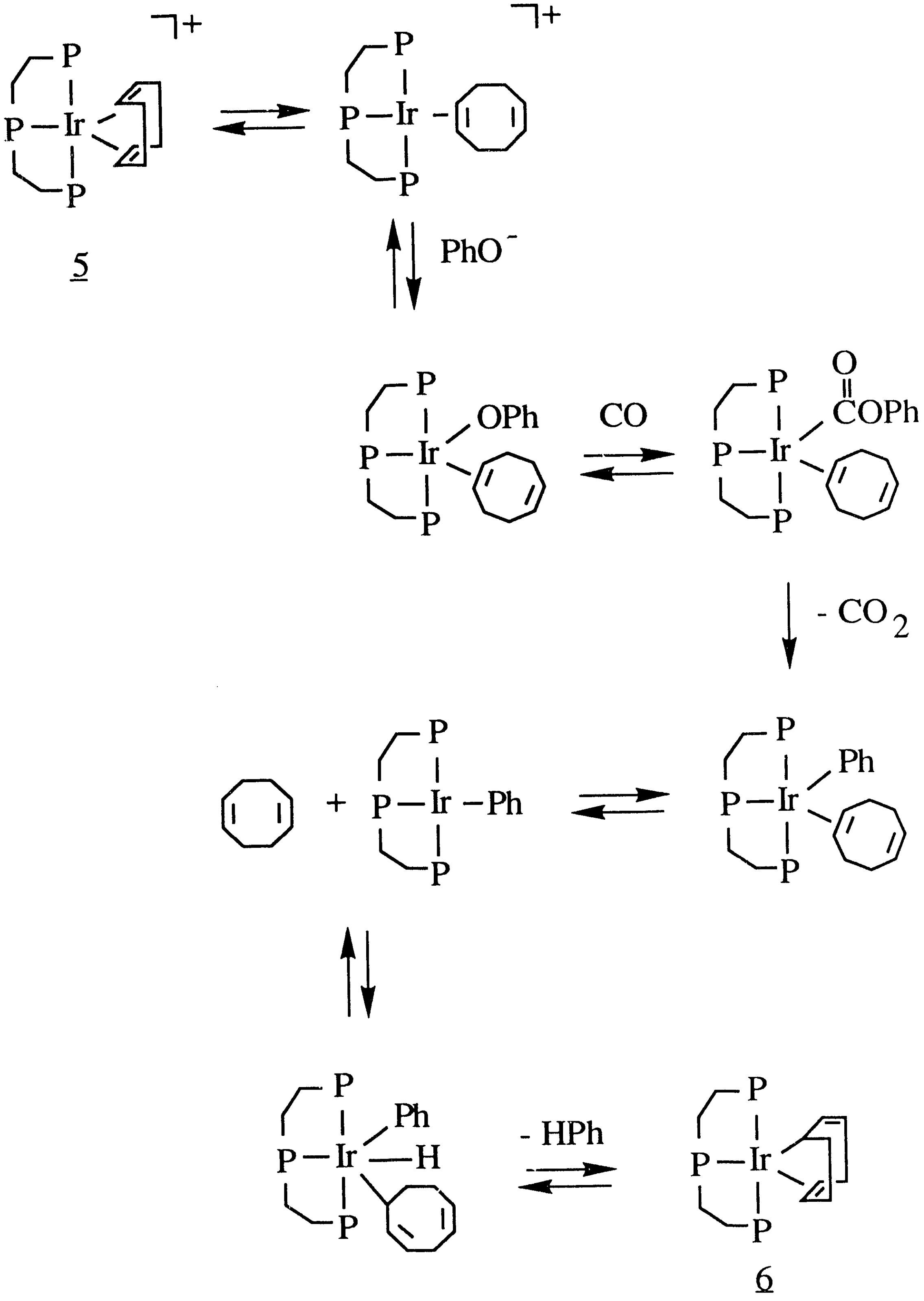
4

Complex **4** consists of a central platinum atom chelated by a dppe ligand and a bidentate ortho-$C_6H_4OC(O)$- ligand. Complex **4** is the first example of an *ortho*-metallolactone. Complex **4** is thermally stable, but photochemically reactive. Trapping studies indicate a *benzyne intermediate* is formed under phenoxide deoxygenation conditions. We recently reported our findings pertaining to the key intermediacy of benzyne intermediates formed via *ortho*-metallolactones such as **4**.

Over the past year we extended our studies to triphos (bis(2-diphenylphosphinoethyl) phenylphosphine) complexes of iridium, since our mechanistic studies suggested greater promise as catalysts for phenol deoxygenation.

The synthesis of Ir(triphos)Cl was attempted by reacting $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) with triphos. The resulting compound was found to be [Ir(triphos)(COD)]Cl, **5**. An X-ray structure determination of **5** was performed. The complex crystallizes in space group $P2_1/c$ with **a**= 15.165(2)Å; **b**= 10.791(2) Å; **c**= 23.488(2)Å; β=90.8395°; V=3843(2)Å^3; Z=4. The structure was refined to R=.029 and R_w=.038 for 428 variables and 5339 observations. This complex is thermodynamically quite stable and shows no reaction with 1 atm of H_2 at temperatures up to 40° C. The reaction of **5** with phenol under 1 atm of CO shows the persistent evolution of CO_2.

The prolonged reaction of **5** with PhOH and 1 atm of CO yielded crystals of Ir(triphos)(σ,η^2-COD), **6**. An X-ray structural determination of **6** indicated space group Cc with **a**=9.578(1)Å; **b**=39.313(5)Å; **c**=11.252(2)Å; β=112.60(9)°; V=3911.5Å^3; Z=4. The structure was refined to R=.027 and R_w=.034 for 425 variables and 2611 observations. HPLC studies suggest that arene products are being produced from phenol under the conditions which lead to complex **6**. A mechanism for our preliminary findings of phenol deoxygenation with the new iridium compounds is summarized below.


PhO⁻
CO
- CO$_2$
- HPh
5
6

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM:

The deoxygenation of phenolic functional groups is of key importance in coal liquefaction and heteroatom removal. The use of CO as the oxygen atom acceptor in phenol deoxygenation offers several advantages compared to present HDO technology: (i) CO is more easily obtained from coal than H_2. (ii) CO does not participate in undesirable side reactions such as ring hydrogenation which occurs under HDO conditions. (iii) Our preliminary studies with platinum compounds suggest that CO is capable of phenol deoxygenation at significantly less severe pressures and temperatures compared to HDO.

PLANS FOR THE COMING YEAR:

Our plans for the coming year involve "translating" deoxygenation activity of soluble molecular complexes of platinum, iridium, nickel, and cobalt to solid, supported heterogeneous catalysts by complexation with metal sulfide anions of the type MS_4^{2-} (M = Mo, W) and anchoring onto metal oxide and sulfide supports. This work is currently in progress and the mixed metal sulfide material $Na_2[Pt(MoS_4)_2]$ is being survyed for catalytic activity in the deoxygenation of phenolic redidues by CO. We are also examining the use of CO for the desulfurization of thiophenols by platinum and iridium catalysts.

II. HIGHLIGHT ACCOMPLISHMENTS

First demonstration of the deoxygenation of a coordinated phenoxide ligand by use of the CO/CO_2 couple.

Preparation of potential catalysts for the deoxygenation of phenolic redidues by CO.

III. ARTICLES AND PRESENTATIONS

A. ARTICLES

1. Ni, J.; Fanwick, P. E.; Kubiak, C. P., J. Amer. Chem. Soc., 112, in press, (1991).
2. Ni, J.; Kubiak, C. P., Advances in Chemistry Series, Moser, W. R., Slocum, D. W. (eds.), American Chemical Society, Washington, D. C., accepted for publication.
3. Meyers, A.; Fanwick, P. E.; Kubiak, C. P, Organometallics, 10, submitted.

B. PRESENTATIONS

1. "Deoxygenation of Phenols Mediated by a Platinum Complex", Ni*, J. and Kubiak, C. P., Paper INOR-345 presented at the 198th National American Chemical Society Meeting, Miami, FL, September 14, 1989.
2. "Catalytic Deoxygenation of Phenols by CO", Kubiak, C.P., invited symposium address: "New Science in Homogeneous Transition Metal Catalyzed Reactions", presented at 199th National American Chemical Society Meeting, Boston, MA, April 25, 1990.
3. "The Activation of Carbon-Oxygen Bonds: The Deoxygenation of Phenols by Oxygen Atom Transfer To CO", an invited presentation at the Gordon Research Conference on Organometallic Chemistry, Newport, RI, June 25-29, 1990.

DATE: April 1991

TITLE: REACTIVITY OF YOUNG CHARS VIA ENERGETIC DISTRIBUTION MEASUREMENTS

P.I.: J.M. Calo

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

W.G. Rachel, Ph.D. Candidate; B. Snyder, Sc.B. Student

INSTITUTION/ORGANIZATION: Brown University
Chemical Engineering Program
Division of Engineering, Box D
Providence, Rhode Island 02912
(401) 863-1421

GRANT NO.: DE-FG22-90PC90307

PERIOD OF PERFORMANCE: September 15, 1990 to September 15, 1993

I. ABSTRACT

OBJECTIVE:

The objective of this project is to apply recently developed techniques to the prediction/correlation of the reactivity of "young" chars, as produced from "mild gasification" processes, for example.

The principal thrust of the project is concerned with the quantitative *mapping* of the reactivity behavior of coal chars, as revealed by the energetic heterogeneity of carbon-oxygen surface complexes, with char preparation conditions; i.e., heating rate and ultimate temperature. The energetic distributions of oxygen surface complexes produced by carbon dioxide, steam, and oxygen will be determined from thermal desorption spectra obtained by temperature programmed desorption/mass spectrometry (TPD./MS), using techniques that have been developed in our laboratory for these purposes.

WORK DONE AND CONCLUSIONS:

- The apparatus has been moved to a new laboratory and has been rebuilt.
- A new mass spectrometer has been acquired and interfaced with the TPD reactor.
- The effect of CO_2 partial pressure on subsequent TPD spectra has been examined in a scoping study involving a Wyodak coal char and a resin char.
- The effects of the "inert," diluent gases, Ar, N_2, and He, on char reactivity have been examined in a scoping study.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

DOE is currently sponsoring various projects focused on the development and demonstration of commercial-scale "mild gasification" processes that will be economically viable in the near term. The solid char products from these processes are "young" and expected to be quite reactive. The capability to predict/correlate the reactivity of these chars with process conditions does not exist currently and would represent a signal advance in the development and operation of these processes. The current project is directed at developing such capabilities using new techniques focused on the measurement and interpretation of the energetic distributions of surface complexes produced during subsequent reactions of these chars with gaseous oxidants.

PLANS FOR THE COMING YEAR:

- Investigations on the effects of oxidant partial pressure on TPD spectra.
- Investigations on the effects of "inert," diluent gases on char reactivity and subsequent TPD spectra.
- The development of a steam addition capability for the TGA reactor system.

II. HIGHLIGHT ACCOMPLISHMENTS

- The TPD/MS apparatus has been rebuilt and improved.
- It has been found that one of the principal effects of reducing CO_2 partial pressure during gasification on TPD spectra, is a marked decrease in the *high temperature, stable oxygen complexes*. However, it is still not known whether these complexes are primary oxygen complexes and/or rechemisorbed CO produced during gasification.
- Investigations of char reactivity in mixtures of "inert," diluent gases, Ar, N_2, and He, with 21% oxygen have demonstrated that the heavier the "inert" species, the more rapid the gasification rate for the same char under the same conditions. The TPD spectra from these chars are being studied to reveal possible reasons for this behavior.

III. ARTICLES AND PRESENTATIONS

Calo, J.M., and P.J. Hall, *Applications of energetic distributions of oxygen surface complexes to carbon and char reactivity and characterization,* in Fundamental Issues in Control of Carbon Gasification Reactivity, J. Lahaye and P. Ehrburger, eds., NATO ASI Series, Series E, Vol. 192, Kluwer Academic Publishers, London, 1991, pp. 329-368.

Calo, J.M., *The nature of isothermal desorption of carbon-oxygen surface complexes following gasification,* in Fundamental Issues in Control of Carbon Gasification Reactivity, J. Lahaye and P. Ehrburger, eds., NATO ASI Series, Series E, Vol. 192, Kluwer Academic Publishers, London, 1991, pp. 369-376.

Calo, J.M. and P.J. Hall, "The prediction/correlation of char reactivity from distributions of desorption activation energies," to be presented at the Twentieth Biennial Conference on Carbon, UC Santa Barbara, June 1991.

TITLE: Microbial Mineralization of Coal-Derived
Hydrophobic Organic Contaminants:
The Role of Bio-Surfactant/Emulsifier
and Solubilization

DATE: April, 1991

P.I.: Richard G. Luthy

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

Zhongbao Liu, Ph.D., Civil Engineering
Matthew Blough, M.S., Civil Engineering

INSTITUTION/ORGANIZATION: Department of Civil Engineering
Carnegie Mellon University
Pittsburgh, PA 15213-3890
(412) 268-2941

GRANT NO.: DE-FG22-90PC90303

PERIOD OF PERFORMANCE: September 1990 - August 1993

I. ABSTRACT

OBJECTIVE:

This research addresses physico-chemical and biochemical solubilization and mineralization reactions for polycyclic aromatic hydrocarbon (PAH) compounds in coal tar. The emphasis of the investigation is on understanding the rate-controlling processes for microbial degradation of organic-phase PAH in the environment and in wastewater treatment processes through determination of the kinetics of solute solubilization and rates of mineralization. The project will evaluate abiotic and biotic solubilization phenomena, and explore possible synergistic interactions between PAH-degrading bacteria and bio-surfactant/emulsifier-producing organisms that have been shown to be potentially useful in coal biotechnology.

WORK DONE AND CONCLUSIONS:

PAH-degrading microorganisms and a bio-surfactant producing microorganism have been cultured. These organisms are being used in tests to assess the rates of mineralization of phenanthrene, a 3-ring PAH compound. PAH solubilization studies are in progress with coal tar-impregnated porous glass beads. This material will be evaluated as a substrate matrix for the microbial mineralization tests with coal tar.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

The results from the research will provide fundamental information on mechanisms governing microbial degradation of oil or tar phase contaminants in treatment systems for coal conversion process effluents, or in remediation systems for soils contaminated with coal tar materials. The research will provide insight into possible enhancement in the rate of degradation of organic-phase PAH compounds through microbially-produced emulsifying substances that may enhance the rate and extent of solubilization.

PLANS FOR THE COMING YEAR:

Comparative microbial mineralization tests will be performed to assess the rate of mineralization of naphthalene and phenanthrene by PAH-degrading organisms. These tests will be performed in the presence and absence of a bio-surfactant producing microorganism.

II. HIGHLIGHT ACCOMPLISHMENTS

PAH-degrading microorganisms have been cultured and prepared for use in mineralization tests. Bio-surfactant producing microorganisms have been procured and cultured. A protocol for assessing coal tar solubilization rates has been developed; this procedure is being evaluated.

III. ARTICLES AND PRESENTATIONS

Luthy, R.G., Research Journal Water Pollution Control Federation, 63(2):99(1991).

TITLE: Design of a High Activity and Selectivity Alcohol Catalyst
DATE: June 25-27, 1991

P.I.(s): Henry C. Foley, G. Alex Mills

STUDENTS: Eric E. Lowenthal, David Hilscher

INSTITUTION/ORGANIZATION: Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, DE 19716
(302) 451-6856
FAX (302) 451-2085

GRANT NO.: DE-90PC90291

PERIOD OF PERFORMANCE: 9/90 - 9/93

I. ABSTRACT

OBJECTIVE: The objective of this research is to design a new alumina-supported bimetallic catalyst, containing molybdena and a second reduced metal like rhodium, for the selective reduction of carbon monoxide to methanol and higher alcohols. It is paramount that a thorough understanding of the respective roles of rhodium and molybdenum be established in terms of the kinetics of reduction, as well as the chemical and physical states of the metals.

WORK DONE AND CONCLUSIONS: This program is a new one in the P.I.'s laboratory. Consequently the early work has focussed upon developing the experimental capability to carry out the experiments aimed at defining the structure and properties of the bimetallic catalysts. To date we have constructed and brought on-line a microflow reactor for low pressure reactor studies. This will be used, first, to examine the effect of alkali upon the rate of secondary dehydration of alcohols, especially methanol, to ethers. Next it will be utilized to examine the effects of Rh to Mo ratios on the rates of structure - sensitive and structure - insensitive reactions. Alcohol dehydration studies are currently underway in this reactor. Metal particle size effects are considered linked to the valency of the metals at the active site and hence to their chemistry. Hydrogen and carbon monoxide chemisorption are expected to be crucial measures of particle size and even valency. To this end we have designed a volumetric chemisorption unit that is based on the units currently in use in Professor Gary Haller's laboratories at Yale University. This unit is nearly constructed and will be used to examine total hydrogen chemisorption as a function of the rhodium to molybdenum ratio and the total metals content. We also expect to be able to compare the classically prepared catalysts with

molybdenum ratio and the total metals content. We also expect to be able to compare the classically prepared catalysts with the metal carbonyl preparation, to determine what effect, if any, these surface processes have upon the final morphology and chemistry of the catalysts.

Other work that has gone on in support of this project in our laboratory includes the redesign and upgrading of a high-pressure microflow reactor for carbon monoxide hydrogenation, the installation of a Schlenk line for the synthesis of catalysts using organometallic reagents, and the construction of C.I. microbalance that will be used to make total adsorption measurements, especially ammonia for total acidity of catalyst surfaces. The high pressure reactor was redesigned to give efficient in-line trapping of condensible alcohols and accurate on-line analyses of the product yields and feed conversions.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: This research is significant to the fossil energy program because the importance of oxygenates for fuel blends has increased recently with the recognition that these molecules will be needed in reformulated gasoline to maintain and to enhance the octane rating. Further incentive arises from the fact that fuel imports from abroad continue to rise, accounting for nearly 50% of U.S. consumption, despite this nation's abundant resources of coal. These increased incentives for oxygenate fuels has brought into focus the need for better process technology for their production. The goal of this research is to provide the basis for the development of significantly improved bimetallic catalysts comprised of molybdena on alumina and group VIII transition metal.

PLANS FOR THE COMING YEAR: During the upcoming year we expect to be able to examine the microstructural properties of the bimetallic catalysts using structure-sensitive and structure-insensitive reactions. In particular we hope to determine whether the molybdenum on alumina serves to "site-isolate" the rhodium at higher Mo/Rh ratios. The relationship between the acidity of the catalyst surface and the rate of secondary dehydration of primary product alcohols will be quantitatively determined. The use of other metals in place of rhodium will be considered, as well as the use of carbon dioxide along with or in place of carbon monoxide in the feed is also of interest to us.

II. ACCOMPLISHMENTS

The experimental facilities that are required to do this research have been designed and constructed during this first year. These include the installation of a Schlenk line for anaerobic catalyst synthesis, the redesign of the high pressure reactor, the design and construction of a low pressure reactor, and the design and construction of a volumetric chemisorption unit and a C.I. electrobalance. Work is underway to examine the secondary acid dehydration of primary product alcohols and to determine compositional effects on metals dispersion.

III. ARTICLES AND PRESENTATIONS

H.C. Foley, A.J. Hong, J.S. Brinen, L.F. Allard, and A.J. Garratt-Reed, " Bimetallic Catalysts Comprised of Dissimilar Metals for The Reduction of Carbon Monoxide with Hydrogen", Applied Catalysis,
61, 351 (1990).

N.A. Bhore, K.B. Bischoff, W.H. Manogue, and G.A. Mills, " Carbon Monoxide Hydrogenation over Rh-Molybdena-Alumina Catalysts: Selectivity Control Using Activation Energy Differences," in Novel materials in Heterogeneous Catalysis. T.K. Baker and L.L Murrelll, Eds., ACS Symposium Series, 437, 256 (1990).

X-D. Hu, H.C. Foley and A.B. Stilles, " Design of Alcohol Synthesis Catalysts Assisted by A Knowledge - Based Expert System," Industrial and Engineering Chemistry Research, accepted (1990).

G.A. Mills, " Improving Perspectives for Oxy-Fuel," Proceedings of the Seventh Annual Coal Conference, 605 (1990).

TITLE: Catalysis and Cocatalysis of Bond Cleavages in Coal and Coal Analogs. **DATE:** April 3, 1991

P. I: Bernard Miller

STUDENT AND THE DEGREE FOR WHICH HE IS REGISTERED: George Grosu, M.S. degree.

INSTITUTION/ORGANIZATION: Department of Chemistry, University of Massachusetts, Amherst, MA 01003. Phone: (413)-545-0805

GRANT NO: DE-FG22-90PC90298

PERIOD OF PERFORMANCE: August 1990 - July 1993.

I. ABSTRACT

OBJECTIVE: To elucidate mechanisms for transfer hydrogenolysis and catalysis of hydrogenolysis of aryl-heteroatom and aryl-carbon bonds, and to develop more effective, inexpensive catalysts for coal conversion.

WORK DONE AND CONCLUSIONS: In order to verify our previously published hypothesis that mixtures of phenols and aromatic polyethers catalyze cleavage of bonds between aromatic rings and oxygen or sulfur atoms by initial electron transfer from the polyethers to the substrates, thermolyses of tetralin solutions of 9-phenylthio-, 9-bromo-, and 9,10-dibromoanthracene were carried out in the absence and presence of phenols and of 1,4-dimethoxynaphthalene and 1,3,5-trimethoxybenzene.

It was established that the anthracene derivatives, either in the absence or presence of additives, decomposed in glass reaction tubes at temperatures above 250°C. Products of the reactions were identified by GC-MS as anthracene, 1-(1-1,2.3,4-tetrahydronaphthalenyl)naphthalene (both *R,S* and *meso* forms), 1-(2-1,2.3,4-tetrahydronaphthalenyl)naphthalene, 1-(2-naphthalenyl)naphthalene, and 9-(1-tetrahydronaphthalenyl)anthracene. Mechanisms for formation of these products have been proposed. The decomposition of 9-phenylthioanthracene was rapid and no evidence was observed for catalysis by phenols or aromatic ethers. However, the decompositions of bromoanthracenes were catalyzed by aromatic polyethers even in the absence of phenols, providing support for the electron transfer theory of catalysis.

Rates of transfer hydrogenolysis of 1-benzylnaphthalene at 600°C in stainless steel reactors were variable. However, evidence was obtained for some rate acceleration by mixtures of phenols and aromatic polyethers.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Our work has shown that thermolysis of anthracene derivatives under conditions for transfer hydrogenolysis results in appreciable addition of carbon radicals derived from the solvent to C-9 of anthracenes, rather than in simple hydrogenolysis. This observation suggests a mechanism for incorporation of solvent into coal structures during coal conversion, and a limitation to the effectiveness of transfer hydrogenolysis as a method for coal conversion. Confirmation of the electron-transfer mechanism for catalysis of the cleavage of aryl-heteroatom bonds should assist in development of more effective catalysts.

PLANS FOR THE COMING YEAR: We intend to investigate the efficacy of molecules containing both electron-donating and hydrogen bonding (chelating) groups as catalysts for transfer hydrogenolysis. Studies on the mechanisms of aryl-carbon hydrogenolysis and of the relationship between aryl-carbon bond cleavage and thermolyses of dihydroaromatic molecules have been initiated, and will be continued.

II. HIGHLIGHT ACCOMPLISHMENTS

Products from thermolysis of 9-substituted anthracenes in tetralin, including a product resulting from incorporation of solvent at C-9 positions of the anthracenes, have been identified. The first examples of catalysis of transfer hydrogenolysis of aryl-heteroatom bonds by aromatic polyethers in the absence of hydrogen bonding agents have been observed.

III. ARTICLES AND PRESENTATIONS

None.

TITLE: "Probe Molecule Studies: Active Species in Alcohol Synthesis" **DATE:** April 9, 1991

P.I.'s:
Donna G. Blackmond
Irving Wender

STUDENTS AND DEGREES FOR WHICH THEY ARE REGISTERED:
Jian Wang (Ph.D.)
Rachid Oukaci (Research Assistant Professor)

INSTITUTION/ORGANIZATION:
University of Pittsburgh
Department of Chemical Engineering
Pittsburgh, PA 15261
(412) 624-9646

GRANT NO: DE-FG22-90PC90305

PERIOD OF PERFORMANCE: 8/16/90 - 8/16/93

I. ABSTRACT

OBJECTIVE:

The objective of this work is to study the in-situ addition of probe molecules to CO hydrogenation reactions for the formation of alcohols. The incorporation of these probe molecules, which include nitromethane and substituted acetylenes, into the reaction network promises to provide important information about the mechanisms of alcohol formation.

WORK DONE AND CONCLUSIONS:

The first half year of the project has been devoted to building a high pressure reaction system with a liquid syringe pump for addition of the probe molecules. Analytical systems for identifying and quantifying products have also been set up and tested, including a GC-MS system with dual capillary and

packed columns for separation and analysis of hydrocarbon and oxygenate products. Experiments are currently being carried out with a Cu/ZnO catalyst under methanol-producing conditions.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Previous work using the addition of nitromethane to Ru catalysts led to a number of important conclusions about the mechanism for hydrocarbon formation from syngas. The current research promises to help provide the same sort of understanding of the processes which produce alcohols from CO/H_2. Since oxygenates are becoming increasingly important as fuels and fuel additives, this research is timely as well as fundamental.

PLANS FOR THE COMING YEAR:

During the coming year we plan to investigate CO hydrogenation reactions over Cu/ZnO under methanol-producing conditions as well as supported CO under conditions which produce higher alcohols. In both cases, the in-situ addition of probe molecules will be studied as a means of understanding chain initiation, chain growth, and chain termination under these different conditions.

II. HIGHLIGHT ACCOMPLISHMENTS

III. ARTICLES AND PRESENTATIONS

TITLE: Biotic and Abiotic Carbon To Sulfur Bond Cleavage DATE: 4/9/91

P.I.: John W. Frost, Associate Professor

STUDENTS: Kurt Stimpfl and Bernard Heymann, Ph.D. Candidates

INSTITUTION: Purdue University, West Lafayette, IN 47907

GRANT NO.: DE-FG22-90PC90294

PERIOD OF PERFORMANCE: 9/1/90 - 4/1/91

I. ABSTRACT

OBJECTIVE: Mechanisms exploited by microbes to cleave carbon to sulfur (C-S) bonds in organosulfur molecules are to be delineated. Chemical mimics of these biotic processes are then to be elaborated.

WORK DONE AND CONCLUSIONS: The ability of *Escherichia coli* to use organosulfonic acids as a sole source of sulfur during growth has been established. This degradative system possessed by *E. coli* will cleave virtually any organosulfonate C-S bond as long as there is one methylene adjacent to the sulfonic acid. Degradation results in products where the sulfonic acid is replaced by an alcohol. Based on deuterium labelling experiments, the mechanism responsible for this biotic C-S bond cleavage involves an intermediate α-hydroxyorganosulfonate. An alternate formulation involving direct insertion of oxygen between the carbon and sulfur atoms of the sulfonic acid is not consistent with the deuterium labelling experiments.

SIGNIFICANCE: Organic sulfur in coal presents an environmental problem due to the acidic oxides of sulfur formed during combustion. Elaboration of biotic carbon to sulfur bond cleavage exploited in nature may lead to a process for biotic removal of coal's organic sulfur. Alternatively, chemistry which is developed to mimic biotic C-S bond cleavage may provide an abiotic process for removal of organic sulfur from coal.

PLANS FOR THE COMING YEAR: Organosulfonate C-S bond cleavage might involve either oxygen insertion into the carbon to hydrogen bond adjacent to the sulfonic acid or hydrolysis of an intermediate sulfene. Differentiation between these two mechanisms will rely on whether ^{18}O is incorporated into the alcohol degradation product when the biodegradation proceeds in ^{18}O-labelled water.

II. ACCOMPLISHMENTS

The mercaptans present in coal can be divided into three structural types: (a) mercaptans where the thiol sulfur is attached to long chain aliphatic functionality; (b) mercaptans where the thiol sulfur is attached directly to an aromatic ring; (c) mercaptans which have at least one methylene group separating the thiol sulfur from aromatic rings. Since attachment of oxygen to sulfur is known to weaken the carbon to sulfur bond, biodegradation of organosulfonic acids was examined first.

Escherichia coli was discovered to be capable of using n-hexanesulfonic acid, 3-phenylpropanesulfonic acid, 2-phenylethanesulfonic acid, and phenylmethanesulfonic acid as a sole source of sulfur during growth. In order to verify that the observed growth was not simply due to sulfate contamination, a search was initiated for the organic products of the degradation. An isolation procedure was developed whereby the centrifuged growth medium was extracted with chloroform. Organics in the extract were separated and characterized by gas chromatography interfaced with a mass spectrometer. Further characterization was afforded by ^1H and ^{13}C NMR evaluation of the extracts. *E. coli* use of n-hexanesulfonic acid, 3-phenylpropanesulfonic acid, 2-phenylethanesulfonic acid, and phenylmethanesulfonic acid as sole sources of sulfur was thus discovered to lead to the formation, respectively, of n-hexanol, 3-phenylpropanol, 2-phenylethanol, and phenylmethanol. No growth was observed when organosulfonates possessing an aromatic ring attached directly to the sulfonic acid were used as a sole source of sulfur during growth.

Two mechanisms might account for the biotic C-S bond cleavage:
Mechanism A. An oxygen might be inserted between the carbon and sulfur atoms via a Baeyer-Villiger process resulting in formation of an organosulfate. Sulfatase action on the organosulfate would result in formation of inorganic sulfate and an alcohol.
Mechanism B. An α-hydroxyorganosulfonic acid might be formed where the carbon immediately adjacent to the sulfonic acid is hydroxylated. This bisulfite adduct of an aldehyde would fragment to yield inorganic sulfite and an aldehyde. Subsequent reduction of the aldehyde by the *E. coli* would generate the observed alcohols.

Differentiation between the two mechanisms was accomplished by synthesis of 2-phenyl-1,1-dideuteroethanesulfonic acid. Operation of Mechanism A would lead to an alcohol where the carbon attached to the alcohol oxygen would retain both deuterium atoms. Mechanism B would predict formation of an alcohol where the carbon attached to the alcohol oxygen would retain only one deuterium atom. Growth of *E. coli* in medium where 2-phenyl-1,1-dideuteroethanesulfonic acid was the only source of sulfur led to the formation of monodeuterated 2-phenyl-1-deuteroethanesulfonic acid. Mechanism B can thus account for the degradation of organosulfonic acids by *E. coli.* Further corroboration followed from the discovery that 2-phenylacetaldehyde is efficiently converted to phenylethanol by *E. coli* cultured in medium where an organosulfonic acid is the sole source of sulfur.

III. ARTICLES

"Biotic Carbon to Sulfur Bond Cleavage: Oxygen Insertion or Sulfene Hydrolysis?"
Stimpfl, K.; Frost, J. W. *J. Am. Chem. Soc.* In preparation.

Date: April 19, 1991

TITLE: Comparative Study of the Reactions of Metal Oxides with SO_2 and H_2S

PRINCIPAL INVESTIGATOR: Stratis V. Sotirchos

STUDENTS: E. Efthimiadis, Ph.D.; S. V. Krishnan, Ph.D.; M. Tomadakis, Ph.D.

INSTITUTION/ORGANIZATION: University of Rochester
Dept. of Chemical Engineering
Rochester, NY 14627
Tel.: 716/275-4626

GRANT NO.: DE-FG22-90PC90301

PERIOD OF PERFORMANCE: 9/1/90 - 8/31/93

I. ABSTRACT

OBJECTIVE: The primary objective of this project is the investigation of the effects of pore structure on the capacity of porous metal oxides for removal of gaseous pollutants from flue gases of power plants (SO_2) and hot coal gas (primarily H_2S). Our experimental studies will include reactivity evolution studies and pore structure characterization using a variety of methods, and our work will focus on oxides that can react (sufficiently fast) both with SO_2 and H_2S. We intend to appropriately exploit the differences of the sulfidation and sulfation reactions (for instance, different molar volumes of solid products) to elucidate the dependence of the sorptive capacity of a porous sorbent on its physical microstructure.

WORK DONE AND CONCLUSIONS: Extensive studies of the reactions of several ZnO-based sorbents with H_2S and CaO-based sorbents with SO_2, derived from limestone precursors, were carried out by my research group in past studies. Therefore, in order to progress faster in the comparative study of the reactions of metal oxides with SO_2 and H_2S that is proposed to be carried out under this project, it was decided to use the above mentioned solids as model solids in our initial experiments. Reactivity evolution experiments (conversion vs. time) were carried out for three calcines derived from limestone precursors of high very high (> 95%) calcitic content. Various mathematical models for transport, reaction, and structure evolution during gas-solid reactions with solid product occurring in porous media were used to obtain a preliminary picture of the expected behavior of porous zinc oxide sorbents during reaction with SO_2 and of porous calcium oxide sorbents during reaction with H_2S. In addition to models developed in the past, we also used a mathematical model based on the use of partially ovrelapping grains to repesent the solid phase. Comparison of the model predictions with experimental data for the reactions of the same sorbents with H_2S and SO_2, respectively, obtained in past studies revealed that if the pore plugging assumption used in the development of single particle or single pellet models for gas-solid reactions with solid product is correct, the solid conversions reached during sulfation of these sorbents should be considerably lower than those reached during sulfidation. Finally, we analyzed the problem of diffusion coefficient measurement in porous solids using the diffusion-cell method and proved, in contrast to the conclusions of other studies, that moment analysis of transient response data should give the same diffusivity as steady-

state experiments in the absence of adsorption.
SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The results of this study will be directly applicable to the removal of gaseous pollutants from coal gas and flue gases of power plants, both during and after combustion. The fundamental results on transport and reaction in porous media that will be produced in this project will prove useful to any problem involving transport and reaction in porous media, such as the problems of coal combustion and gasification encountered in the area of fossil energy conversion and utilization.
PLANS FOR THE COMING YEAR: We plan to complete the study of the sulfidation behavior of calcium oxide sorbents derived from limestone precursors and the comparison of the theoretical and experimental results obtained from these studies with past results from the sulfation of the same solids. We will also carry out reactivity and pore structure evolution studies on the sulfation behavior of zinc oxide sorbents.

II. HIGHLIGHT ACCOMPLISHMENTS

Experiments have been carried out on the reactivity and pore structure evolution of CaO sorbents during reaction with H_2S.

Various mathematical models for gas-solid reactions with solid product were used to theoretically investigate the reactions of limestone calcines with H_2S and zinc oxide sorbents with SO_2 on the basis of past experimental results for the sulfation and sulfidation, respectively, reactions of these sorbents.

A detailed analysis of the problem of effective diffusivity measurement using the diffusion-cell method was carried out.

III. ARTICLES AND PRESENTATIONS

Efthimiadis, E.A., Sotirchos, S.V., Physicochemical Changes in Coal Gas Desulfurization Sorbents: Theory vs. Experiments, AIChE 1990 Annual Meeting, Chicago, IL, November 1990.

Krishnan, S.V., Sotirchos, S.V., Effective Diffusivity Evolution during Carbonation, Calcination, and Sulfation of Limestones, AIChE 1990 Annual Meeting, Chicago, IL, November 1990.

Sotirchos, S.V., Transient vs. Steady-State Measurement of Effective Diffusivities in Porous Solids Using the Diffusion-Cell Method, (to be presented at the AIChE 1991 Annual Meeting and submitted for publication).

Efthimiadis, E.A., Sotirchos, S.V., Effects of Pore Structure on the Performance of Coal Gas Desulfurization Sorbents, (to be presented at the AIChE 1991 National Summer Meeting).

Efthimiadis, E.A., Sotirchos, S.V., A Partially Overlapping Grain Model for Gas-Solid Reactions: Application to the ZnO-H_2S Reaction, (submitted for publication).

TITLE: **Advanced, Soluble Hydroliquefaction and Hydrotreating Catalysts** DATE: April 8. 1991

P. I.S: Richard M. Laine, Thomas Stoebe

STUDENT(s) AND THE DEGREES FOR WHICH THEY ARE REGISTERED:

Nicole Budrys, B. S. Chemistry
Martin L. Hoppe, Postdoctoral Student

INSTITUTION/ORGANIZATION:

Depts of Materials Science and Engineering, University of Washington, and University of Michigan

GRANT NO.: DE-FG22-90PC90313

PERIOD OF PERFORMANCE: August 7, 1990-August 7, 1993

I. ABSTRACT

OBJECTIVE: Previous work in this group has shown that, surface confined, organometallic catalysts are exceptionally effective for hydrogenation and HDN of coal model compounds such as quinoline.[1-3] Unfortunately, surface confined catalysts have not proven to be particularly effective when used with coal itself. The problem derives from the fact that: (1) liquefaction is a solid (catalyst)-liquid (coal polymer) reaction system where, (2) diffusion of coal bonds to the heterogeneous catalyst surface is mass transport limited and controls liquefaction rates. Furthermore, heterogeneous catalyst mediated liquefaction is surface area dependent, placing another constraint on reaction rates.

The purpose of the present program is to develop soluble analogs of surface confined catalysts that can be impregnated directly into the coal structure at low temperatures. This approach should avoid problems related to surface area dependence, a two phase (surface-liquid) reaction system and, mass transport limitations.

Heteropolyanions (HPAs) offer the opportunity to develop soluble forms of surface confined catalysts. HPAs, are inexpensive, well-characterized, water soluble metal oxide clusters, e.g. $[EM_{12}O_{40}]^{4-}$ where E = Si or P and M = Mo or W. They are easily modified to contain other transition metals such as Co, Ni or Ru and, can be made soluble in organic solvents. The protic forms exhibit extremely high acidities $pK_a \approx 0\text{-}2$. In addition, selectively modified HPAs can function as low temperature hydrogenation catalysts that exhibit microporosity. HPAs are multi-functional catalysts that could be used to promote both hydroliquefaction and hydrotreating. In theory, these functions could be employed sequen-

tially or simultaneously and could permit exceptional control of liquefaction reactions and reaction conditions. Thus, the current research program involves efforts to evaluate HPAs as soluble liquefaction and hydrotreating catalysts, with the goal of developing soluble analogs of surface confined catalysts.

The program consists of three major tasks: (1) Preparation of candidate HPA precatalysts; (2) HDN and HDO modeling studies and, (3) Direct liquefaction studies.

WORK DONE AND CONCLUSIONS: This program experienced a hiatus when R. M. Laine moved to the University of Michigan. Currently, a new laboratory has been established, a series of catalysts including: $H_4PMo_{12}O_{40}$, $H_4PW_{12}O_{40}$, $(NH_3)_6H_4Co_2Mo_{10}O_{38}$ purchased or synthesized. HDS and HDN screening studies with quinoline and benzothiophene have begun. The current results are insufficient to warrant detailed discussion. All complexes studied are soluble in CH_3CN, stable to 220°C in solution and unreactive. $(NH_3)_6H_4Co_2Mo_{10}O_{38}$ apparently catalyzes the hydrogenation of quinoline at 220°C in the presence of added H_2S. Catalysis occurs via formation of a heterogeneous catalyst. No conclusions can be drawn from these preliminary results.

1. "Ruthenium Promoted Hydrodenitrogenation Catalysts." A. S. Hirschon, R. B. Wilson Jr., and R. M. Laine, J. Appl. Cat. (1987) **34**, 311-316.
2. "Use of Promoters to Enhance Hydrodenitrogenation and Hydrodeoxygenation Catalysis", A. S. Hirschon, L. L. Ackerman, R. M. Laine, and R. B. Wilson, Jr. Proc. of the 1989 Internat. Conf. on Coal Science, Tokyo,. Vol. **II**, p. 923.
3. "Catalysts for the Hydrodenitrogenation of Organic Materials and Process for the Preparation of the Catalysts.", R. M. Laine, A. S. Hirschon, R. B. Wilson, U. S. Pat.No. 4,716,142 (1987).

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Insufficient results do not permit a creditable evaluation of efforts.

PLANS FOR THE COMING YEAR: We plan to continue the HDS and HDN survey studies to identify a set of superior HPA catalysts. We will then evaluate two or three HPA catalysts using standard solution kinetics studies[1] to develop an understanding of the kinetics and mechanisms of reaction. These studies will permit formulation of conditions for liquefaction studies.

II. HIGHLIGHTS

N/A

III. ARTICLES AND PRESENTATIONS

N/A

ADVANCED PROCESS CONCEPTS

TITLE: Steam Gasification of Carbon: Catalyst Properties DATE: March 20, 1991

P.I.s: John L. Falconer and Lee L. Lauderback

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Alex Rosen, MS

INSTITUTION/ORGANIZATION: University of Colorado
Department of Chemical Engineering
Boulder, CO 80309-0424
phone (303) 492-8005

GRANT NO.: DE-FG22-88PC88915

PERIOD OF PERFORMANCE: 9/15/88 - 9/14/91

I. ABSTRACT

OBJECTIVE: Determine the catalyst composition and concentration for metal oxide catalyzed gasification of carbon. This involves measuring the concentration of active catalytic sites at reaction conditions, the composition of the catalyst, and the site-specific rate constant. This information will provide insight into the reaction mechanism and how to maximize catalyst dispersion.

WORK DONE AND CONCLUSIONS: A paper entitled "AES and SIMS Analysis of Potassium/Graphite Surfaces" was submitted for publication and the paper is presently in press for volume 29 of Carbon.

Most of our experimental efforts during the last year have been devoted to transient studies of gasification. A series of experiments with various catalyst loadings and at various temperatures were carried out. They identified modifications that were required to obtain accurate and reproducible data. Major modifications were made to the transient reaction system as a result of these experiments. The delay times were decreased dramatically from 26 sec to 2.6 sec, after an extensive experimental study to identify limiting factors. These modifications have allowed the system to be put into full operation and another series of experiments were carried out on $K_2CO_3/^{13}C$ mixtures using CO_2 to gasify the mixture. Based on these experiments, modifications in the sample preparation were required, and with this new preparation procedure, reproducible results were obtained. An isoproponal/water solution was found to be effective for dissolving K_2CO_3 and wetting carbon.

These experiments were of two types.

1) A ^{13}C sample containing reduced catalyst was exposed at high temperature to a step increase in $^{12}CO_2$ flow and the ^{12}CO signal significantly overshot its steady state value. The formation of $^{13}CO_2$ was observed because the catalyst oxidation step is reversible at gasification conditions. This type experiment, when both ^{13}CO and $^{13}CO_2$ amounts are taken into account, allowing the concentration of oxidizable sites to be measured.

2) A ^{13}C sample containing a potassium oxide catalyst was run at steady-state in flowing $^{12}CO_2$. Low conversions of $^{12}CO_2$ were used. The $^{12}CO_2$ flow was then replaced by He using a switching valve, and the responses of the ^{12}CO , ^{13}CO, and $^{13}CO_2$ signals were followed as a function of time. This experiment provides information about reactive sites

Four methods of data analysis were evaluated and two were concluded to be unsatisfactory because of complications in the reactions mechanism. The other two have been applied to the most recent data. An analysis method was developed to take into CO_2 cracking, which interferes significantly with the CO signals at low conversions and isotope exchange. Whenever ^{13}CO is formed, the $^{13}CO_2$ is created and this exchange process is fast relative to gasification.

Experiments were carried out on samples containing 4%, 6%, and 10% K_2CO_3 on ^{13}C. Steady state reaction was run at four temperatures for each loading, but conversions were held below 10%. The data analysis is presently being carried out.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Insight into the mechanisms of catalytic gasification and measurements of catalytic site concentrations will help in improving process kinetics of coal gasification. Knowledge of the active site concentrations under various conditions is critical for understanding how catalysts affect reaction rates and may help to improve reaction rates by increasing site concentrations.

PLANS FOR THE COMING YEAR: The transient reaction data will be analyzed and additional transient experiments will be carried out to study the effect of type of carbon, burnoff amount, and type of catalyst on the active site concentration. Similar transient experiments will be carried out using H_2O as the reactant.

II. HIGHLIGHT ACCOMPLISHMENTS

One paper was published. An apparatus and sample preparation procedure was developed for obtaining excellent reproducibility and short delay times in transient isotope reaction experiments. The concentration of active sites was measured as a function of weight loading and temperature.

III. ARTICLES AND PRESENTATIONS

Chang, J.S., Lauderback, L.L., and Falconer, J.L., "AES and SIMS Analysis of Potassium/Graphite Surfaces," Carbon, 29, in press (1991).

"A SIMS Study of the Interaction of Potassium Carbonate with Carbon Black," presented at the 19th Biannual Conference on Carbon, Pennsylvania State University, State College, Pennsylvania, June 25-30, 1989.

"Steam Gasification of Carbon: Catalyst Properties" presented at the University Coal Research Contractors Review Meeting, July 1990.

"Steam Gasification of Carbon: Catalyst Properties" presented at DOE Review of Fossil Energy Advanced Research Projects, October 24, 1990.

Date: April 9, 1991

TITLE: ALKALI/TX_2 CATALYSTS FOR CO/H_2 CONVERSION TO C_1-C_4 ALCOHOLS

PIs: Kamil Klier and Richard G. Herman

STUDENTS: Michelle Richards, Ph.D.; Mark Kieke, M.S.; Andrew Brimer, B.S.

INSTITUTION: Lehigh University
Department of Chemistry and
Zettlemoyer Center for Surface Studies
Sinclair Laboratory, #7
Bethlehem, PA 18015
(215) 758-3577

GRANT NO.: DE-FG22-88PC88933

PERIOD OF PERFORMANCE: September 1, 1988 to August 31, 1991

I. ABSTRACT

OBJECTIVE: To investigate and develop novel sulfur-tolerant catalysts for the conversion of coal-derived synthesis gas into C_1-C_4 alcohols by a highly selective process. Therefore, the variations of catalyst activity and selectivity for the synthesis of alcohols from $H_2/CO \leq 1$ synthesis gas for a series of A/TX_2 compounds, where A is a surface alkali dopant, T is a transition metal, and X is S is being determined.

WORK DONE AND CONCLUSIONS: Catalysts prepared and tested during this project year for catalytic activity at 8.3 MPa and 548-628K included the sulfide catalysts based on MoS_2, RuS_2, and NbS_2, which were prepared using a variety of different techniques. Both alkali-doped and undoped catalysts were tested and characterized. The catalysts have been examined using XRD for bulk analysis and HR-ESCA for surface analysis. Examination of the valence band spectra, obtained at low binding energies where mixing of bonding orbitals occur, demonstrated that insight into the d orbital levels can be obtained. Surface doping of the MoS_2 catalyst with 2 mol% KOH or KOH/dibenzo-18-crown-6 complex led to the same catalytic activity and product selectivity from $H_2/CO = 1$ synthesis gas after 250, 275, 250°C testing at 8.4 MPa, which indicated that the same degree of surface dispersion was achieved. Single crystal diffraction studies of MoS_2 have been successfully carried out using both Mg K_α and Al K_α anodes to provide insight into the forward focusing of photoelectrons from the surface layer of atoms on these catalysts.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The benefit of this research rests in providing a scientific foundation and a database for catalytic processes leading to high octane oxygenated fuels such as ethanol/methanol/propanol mixtures, as well as to olefins obtained by further catalytic dehydration of the C_2-C_4 alcohols. Since the source of carbon can be coal-derived synthesis gas, this research makes a contribution to the technology for high quality clean transportation fuels and for basic chemicals from coal.

PLANS FOR THE COMING YEAR: This three-year research project will be finished later this year. Until then, studies with the alkali-doped and undoped RuS_2 and NbS_2 catalysts will be continued in terms of systematically carrying out the catalytic testing and characterization of these catalysts. The results will be compared with those previously obtained with MoS_2- and TaS_2-based catalysts. Characterization of the catalysts will include detailed surface analysis *via* high resolution ESCA and angularly resolved photoelectron spectroscopy of model single crystal catalysts.

II. HIGHLIGHT ACCOMPLISHMENTS

The preparation, catalytic testing, and characterization of MoS_2, RuS_2, and NbS_2 catalysts has been accomplished. Both stoichiometric and non-stoichiometric TX_2 compounds have been examined. Under the reaction conditions employed to-date, the Cs/MoS_2 catalyst exhibits the highest activities and selectivities toward the synthesis of oxygenates. The HR-ESCA surface analyses of the catalysts using the SCIENTA-300 ESCA has demonstrated that useful chemical information is provided, especially from the valence band spectral region. For example, the MoS_2 band structure is well-developed for particles as small as 6 nm, but distinct differences are noted when compared with the spectrum obtained from single crystal MoS_2, e.g. states appear in the dispersed sulfide above the top of the valence band of the single crystal MoS_2, and these might be reflected in catalytic behavior. The thermodynamic stabilities of the TS_2 catalysts against lost of sulfur in a reducing environment have been calculated, and it is shown that MoS_2 and NbS_2 should be stable without H_2S being present in the synthesis gas.

III. ARTICLES AND PRESENTATIONS

"Physical and Chemical Structure of Alkali/MoS_2 Alcohol Synthesis Catalysts," J. G. Santiesteban, R. G. Herman, and K. Klier, Poster Paper at the Spring Symposium of the Catalysis Society of Metropolitan New York, Bethlehem, PA, March 15, 1989 and at the First Pennsylvania Surface Science Workshop, University Park, PA, August 1-3, 1989.

"Chemical and Physical Structure of Alkali/MoS_2 Alcohol Synthesis Catalysts," J. G. Santiesteban, R. G. Herman, and K. Klier, 11th North American Meeting of the Catalysis Society, Dearborn, MI, May 7-11, 1989, Abstr. No. B15.

"Specific Oxygen Retention During Higher Alcohol Synthesis: The Role of the Catalyst on the Kinetics and Mechanism of Branched vs Linear Carbon Chain Growth," R. G. Herman, K. Klier, J. G. Nunan, K. J. Smith, J. G. Santiesteban, C.-W. Young, C. E. Bogdan, and G. A. Vedage, Spring Symp., Catal. Club of Philadelphia, Newtown Square, PA, May 16, 1989.

"Cs/MoS_2 Catalysts for Higher Alcohol Synthesis," J. G. Santiesteban, R. G. Herman, and K. Klier, Poster Paper at the Spring Symposium of the Catalysis Club of Philadelphia, Newtown Square, PA, May 16, 1989.

"Kinetic Modelling of Higher Alcohol Synthesis over Alkali-Promoted Cu/ZnO and MoS_2 Catalysts," K. J. Smith, R. G. Herman, and K. Klier, Poster Paper at the 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 17-22, 1989.

"Kinetic Modelling of Higher Alcohol Synthesis over Alkali-Promoted Cu/ZnO and MoS_2 Catalysts," K. J. Smith, R. G. Herman, and K. Klier, 11th International Symposium on Chemical Reaction Engineering, Toronto, Canada, July 8-11, 1990.

"Kinetic Modelling of Higher Alcohol Synthesis over Alkali-Promoted Cu/ZnO and MoS_2 Catalysts," K. J. Smith, R. G. Herman, and K. Klier, Chem. Eng. Sci., **45**, 2639 (1990).

"Structure and Surface Properties of Sulfides," K. Klier, M. Richards, and R. G. Herman, in "*Synthesis and Properties of New Catalysts: Utilization of Novel Materials, Components, and Synthetic Techniques*," ed. by E. W. Corcoran, Jr. and M. J. Ledoux, Mat. Res. Soc. (1990).

"Reaction Engineering of Alkali/MoS_2 Catalysts for Synthesis of Alcohol Fuels," R. G. Herman, J. G. Santiesteban, K. J. Smith and K. Klier, 25th Middle Atlantic Regional ACS Meeting, University of Delaware, Newark, DE, May 21-23, 1991; Abstract No. 92.

"Transition Metal Disulfides: The Relationship Between Their Catalytic and Physical Properties," M. Richards, R. G. Herman, and K. Klier, Poster Presentation at the Spring Symposium of the Catalysis Society of Metropolitan New York, Bethlehem, PA, March 13, 1991.

"Transition Metal Disulfides: The Relationship Between Their Catalytic and Physical Properties," M. Richards, R. G. Herman, and K. Klier, 25th Middle Atlantic Regional Meeting of the American Chemical Society, Newark, DE, May 21-23, 1991; Abstract No. 93.

Date: April 1, 1991.

TITLE: Inhibition of Retrogressive Reactions in Coal/Petroleum Co-Processing

PIs: Harold H. Schobert

STUDENT(s) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Jasna Tomic, Ph.D. in Fuel Science

INSTITUTION/ORGANIZATION:
Fuel Science Program
Department of Material Science and Engineering
The Pennsylvania State University
University Park, PA 16802 (814) 865-6511

GRANT NO.: DE-FG22-88PC88935

PERIOD OF PERFORMANCE: September 1, 1988 - August 31, 1991

I. ABSTRACT

OBJECTIVE: The objective of this project is to develop a fundamental understanding of the reactions occuring at the onset of coke formation during the co-processing of coals with petroleum residua. The knowledge of pathways to coke formation would allow the selection of appropriate coal/petroleum feedstock combinations and processing conditions to minimize or eliminate coke formation. Specific objectives include examination of chemical components on retardation of enhancement of coke formation.

WORK DONE AND CONCLUSIONS: Set of five coals have been reacted with a set of five model compounds representative of components of heavy petroleum fractions. The model compounds range from purely aliphatic, eicosane, through alkylated aromatics to purely aromatic, pyrene. The coals were also reacted with three petroleum resids. Mass transfer and mixing effects were evaluated comparing data from reactions conducted in vertical *vs.* horizontal agitated microautoclave reactors. Three reaction temperatures and two gas atmospheres were used in all of the reactions. The yield of tetrahydrofuran (THF) insolubles is the lowest in the presence of pyrene. The values obtained for reaction with coal/eicosane and coal/1-phenyldodecane are very close to each other, as well as are the ones for coal in reaction with 1,4-diisoprolylbenzene and durene. The yields for THF-insolubles in the reactions with the petroleum resids at 400° C are in the range of the values obtained with pyrene. At the lower reaction temperature (350° C) the petroleum resids did not act as "good" solvents in terms of enhancing coal conversion while the results from the reactions at 450° C indicated the presence of retrogressive reactions, the coal conversion having negative values. The effect of the reaction temperature is in addition related to the fluidity of the coal. The optimum temperatures for coal conversion seem to coincide with the maximum fluidity temperature of the coal.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Co-processing offers the potential of producing liquid fuels from coal by introducing coal into petroleum refining operations. For a co-processing technology only the addition of co-processing units to existing refinery operations would be necessary. In addition the co-processing technology would enable better use of the hydrocarbon resources. However, the occurrence of retrogressive reactions can diminish the attractiveness of co-processing. Retrogressive reactions produce undesired solids that can accumulate in the reactor, upset the flow patterns and, diminish the residence time. An understanding of the nature of the retrogressive reactions and of the

components of the coal of resids that enhance these reactions will allow for a better selection of co-processing feedstock that would minimize the coking process.

PLANS FOR THE COMING YEAR: Experimental work on this project should be completed in the early fall, 1991. The remaining work to be accomplished includes measurement of kinetics of coking reactions for selected coal/resid pairs at various times and temperatures, reactions of solvent fractions of resids with coals, and supplemental analytical work using ^{13}C NMR, GC/MS, and pyrolysis/GC/MS. A no-cost extension has been requested to accommodate writing the final project report and the Ph.D. thesis that will result from this project.

II. HIGHLIGHT ACCOMPLISHMENTS

The coal/model compound reactions showed that the reactivity of the vehicle is based on radical generation: eicosane-like, durene-like, and pyrene-like. The yield of THF-insoluble, therefore the degree of retrogressive reactions, is the lowest in the presence of pyrene which is known as a good hydrogen shuttler. Statistical analysis of the the model compound results indicate that the tendency of the model compound to crack is a major factor in the retrogressive reactions. The availability of reactive sites in the coal is very important under nitrogen atmosphere but not under hydrogen atmosphere. This suggests that hydrogen intervenes somehow either in the attack on the coal or in the free radical chemistry of the model compound fragments. The optimum reaction temperature in terms of coal conversion is related to the fluidity temperature of the coal. The coal conversion steadily increased with increasing temperature for the coals that do not have a defined fluidity temperature. If the reaction temperature is higher than the maximum fluidity temperature of the coal, a decrease in coal conversion is observed. The overall optimum temperature for a minimum degree of retrogressive reactions is close to 400° C. Higher temperatures enhance cracking reactions and formation of gaseous as well as solid products. Fourier transform (DRIFT) spectra on the solid residues also indicated structural difference as a result of the reaction temperature. The change was observed especially in the region of the aromatic C-H out-of-plane modes. A greater influence of the reaction temperature was observed when the temperature is increased from 400 ° C to 450° C than for the increase from 350° to 400° C. Again this indicates that the temperatures greater than 400° C are the crucial for retrogressive reactions.

III. ARTICLES AND PRESENTATIONS

Tomic, Jasna and Harold H. Schobert.,"Investigation of Chemical Components Responsible for Retrogressive Reactions in Coal/Petroleum Co-processing", presented at the Cooperative Program in Coal Research, University Park, PA, November 20 - 22, 1990.,

Tomic, Jasna and Harold H. Schobert., " Retrogressive Reactions in Coal/Petroleum Co-processing ", to be presented at the 201st ACS National Meeting, Atlanta, GA, April 14-19, 1991.

Burgess, C.E., Tomic, J. and, Schobert, H.H., " Solvent Effects in Low-Severity Liquefaction and Co-processing of a Subbituminous Coal ", to be presented at the 1991 International Conference on Coal Science, Newcastle upon Tyne, United Kingdom, September 16-20, 1991.

April 8, 1991

TITLE: NOVEL SUPPORTS FOR COAL LIQUEFACTION CATALYSTS

P.I.: Henry W. Haynes, Jr.

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

1. A. Papaioannou, M.S. Ch.E. (Awarded December, 1988)
2. T. Zhang, Ph.D. Candidate, Ch.E.
3. S.K. Brauer, B.S. Ch.E. (Awarded May, 1990)
4. P.D. Jacobs, Ph.D. Candidate, Ch.E.

INSTITUTION/ORGANIZATION: Department of Chemical Engineering
University of Wyoming
P. O. Box 3295, University Station
Laramie, WY 82071
(307) 766-4923

GRANT No.: DE-FG22-88PC88942

PERIOD OF PERFORMANCE: 9/1/88 - 12/31/91

I. ABSTRACT

OBJECTIVE:

The objectives of this research are first to construct a Catalytic Coal Liquefaction Microreactor (CCLM) and then to use this unit to screen catalysts prepared from novel and/or modified supports for coal liquefaction applications. Run lengths will be sufficient to give a measure of catalyst deactivation rate. Modified supports will include aluminas treated with alkali and alkaline earth metals and halogens. Novel supports will include carbons, single component oxides and composite oxides. Efforts will be made to correlate coking tendency with catalyst acidity measurements.

WORK DONE AND CONCLUSIONS:

Work during the past year has concentrated on the construction and shakedown operation of the CCLM. Experimental work thus far has been limited to hydrotreating studies on a raw creosote oil feedstock (Allied Signal 24CB) using a CoMo/Alumina catalyst (Amocat 1A). Several runs of 20 to 30 days duration have been completed. Modifications to the unit now make it possible to consistently achieve 100 ± 2% total material balances.

The heart of this unit is a novel ebullated bed microreactor which charges

only five grams of catalyst. At normal operating conditions, internal recycle ratios exceed 1000/1. Thus the reactor may be treated as perfectly mixed. Temperature control is excellent, and catalyst attrition has been insignificant (or nonexistent). Depending upon the particular reactions of interest and the operating conditions, only a minor correction may be required for thermal reactions.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Catalysts having improved activity and activity maintenance characteristics could result in substantial improvements in both the performance and economics of direct coal liquefaction processes. The development of a continuous coal liquefaction microreactor suitable for both catalyst screening and kinetics studies should prove to be a valuable tool for researchers in the field of catalytic coal liquefaction.

PLANS FOR THE COMING YEAR:

Modifications to the CCLM to allow the introduction of coal paste are now complete. A coal paste is prepared from finely ground Black Thunder coal, residuum material derived from this coal, and the raw creosote oil. At room temperature this material has the consistency of toothpaste. The plan is to feed the coal paste via a high pressure syringe pump. A separate "makeup" solvent stream (also raw creosote oil) is combined with the paste just prior to entering the reactor.

Initial tests are planned to define limits of operability, and to culminate in identifying a standard set of conditions for catalyst screening. The hydrogen deficient nature of the combined feedstock (coal + residuum + raw creosote oil) is intended to place a substantial demand on the catalyst so that differences between our various preparations will be magnified. Promising catalysts from our earlier work will be evaluated under actual coal liquefaction conditions.

II. HIGHLIGHT ACCOMPLISHMENTS

Shakedown operations of the CCLM during the past year have resulted in significant improvements to the unit. In addition, these runs have demonstrated that the novel ebullated bed microreactor provides an excellent means for evaluating hydrotreating kinetics. Heretofore this has not been possible in a unit of this size. A firm foundation has thus been laid for the next step of the program -- the introduction of coal into the unit.

III. ARTICLES AND PRESENTATIONS

1. Papaioannou, A. and H.W. Haynes, Jr., "Alkali and Alkaline Earth Promoted Catalyst for Coal Liquefaction Applications", 197th ACS Natl. Mtg., Dallas, April 9-14, 1989 [ACS, Div. Fuel Chem. Prepr. 34(2), 589 (1989)].

2. Papaioannou, A. and H.W. Haynes, Jr., "Alkali-Metal- and Alkaline-Earth-

Promoted Catalysts for Coal Liquefaction Applications", Energy & Fuels 4, 38 (1990). [Expanded version of above presentation.]

3. Zhang, T.; Borgialli, R.R. and H.W. Haynes, Jr., "Cold Model Studies of the "Haynes-Borgialli" Liquid Fluidized Bed Microreactor", 1990 Spr. Natl. Mtg. of A.I.Ch.E., Houston, pap. 64c, March 18-22, 1990.

4. Borgialli, R.R.; Zhang T.; Jacobs, P.D. and H.W. Haynes, Jr., "A Novel Ebullated Bed Microreactor for Testing Coal Liquefaction Catalysts", CONFAB '90, spon. by Western Research Institute, Laramie, WY, Aug. 7-10, 1990.

5. Borgialli, R.R.; Zhang, T. and H.W. Haynes, Jr., "A Novel Liquid Fluidized Bed Microreactor for Coal Liquefaction Studies. II. Reactor Performance", 1990 Ann. Mtg. of A.I.Ch.E., Chicago, pap. 126c, Nov. 11-16, 1990.

6. Haynes, H.W. Jr.; Borgialli, R.R. and T. Zhang, "A Novel Liquid Fluidized Bed Microreactor for Coal Liquefaction Studies. I. Cold Model Results", Energy & Fuels, 5, 63 (1991).

7. Jacobs, P.D.; Zhang, T.; Borgialli, R.R. and H.W. Haynes, Jr., "A New Ebullated Bed Microreactor for Coal Liquefaction Studies", to be presented at Pittsburgh Natl. Mtg. of A.I.Ch.E., August 18-21, 1991.

TITLE: Control of Catalytic Hydrotreating Selectivity with Ammonia **DATE:** March 27, 1991

PI: Charles N. Satterfield

STUDENT: Chung M. Lee, Ph.D. Candidate

INSTITUTION: Massachusetts Institute of Technology
Cambridge, MA 02139
(617)253-4584

GRANT NO.: DE-FG22-89PC89775

PERIOD OF PERFORMANCE: October 1, 1989 to September 30, 1992

I. ABSTRACT

OBJECTIVE: We have discovered that the presence of a low concentration of ammonia can substantially reduce the rate of hydrogen uptake of an aromatic compound on an industrial NiMo/Al_2O_3 catalyst while under similar conditions it has only a mild inhibiting effect on hydrodenitrogenation (of quinoline). This suggests a method under industrial reaction conditions of minimizing undesired aromatic hydrogenation during catalytic hydrodenitrogenation and hydrotreating. We plan to explore this effect in more detail by model compound studies, with attention to their relevance to hydrotreating coal liquids.

WORK DONE AND CONCLUSIONS: Studies have proceeded in two phases: First, we observe that coal liquids contain substantial amounts of a base fraction that seems to consist of hydroxy pyridines, hydroxy indoles and/or hydroxy anilines. No information has been published on the HDN-HDO hydrotreating reactions of a compound in which a hydroxyl (phenolic) group is attached to a heterocyclic N compound. We therefore first performed a limited hydrotreating study with 8-hydroxy quinoline (8 HQ) dissolved in tetralin utilizing a NiMo/Al_2O_3 catalyst in a packed bed reactor operating at 360°C and 385°C and 6.9 MPa.

We find that the HDN reaction of this compound proceeds by three routes to enter the quinoline reaction network. The activity and selectivity to form hydrocarbons are unchanged by the presence of the OH group on 8 HQ. The HDO reactions of 8-HQ to form N compounds are much faster than the HDN reactions of N compounds to form hydrocarbons, i.e., the rate limiting steps are HDN reactions rather than HDO reactions -- the hydroconversion of 8 HQ is governed by the N center rather than the OH center. This work has been published.

In the second, more recent phase, we have been studying the hydrotreatment of a mixture of quinoline and naphthalene. Quinoline was chosen as the model

heterocyclic compound because its reactions are well known and N-removal is particularly of concern in hydrotreatment. Naphthalene was selected as the model aromatic hydrocarbon. It is readily available, its hydrogenation products are only tetralin and cis/trans-decalin, simplifying analysis, and tetralin is an excellent hydrogen donor in coal liquefaction, whereas decalin, formed by further hydrogenation, is poor.

In brief, we find that added NH_3 has little effect on the hydrogenation rate of naphthalene, but a marked inhibiting effect on hydrogenation of tetralin. Thus selectivity is controlled in the direction of a partially hydrogenated aromatic product, which is desired for coal liquefaction. The improved selectivity can be interpreted in terms of competitive adsorption effects, and a kinetic model is being developed to summarize these results.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: During catalytic hydrotreatment of coal liquids, control of hydrogenation of multi-ring aromatics towards saturation of one ring only should provide a more effective hydrogen donor liquid.

PLANS FOR THE COMING YEAR: We plan to see if the effectiveness of NH_3 also occurs with a 3-ring aromatic, namely phenanthrene. This will be followed by hydrotreatment studies of a mixture of benzofuran or dibenzofuran with naphthalene.

II. HIGHLIGHT ACCOMPLISHMENTS

The hydrotreatment of 8-hydroxy quinoline proceeds in much the same way as quinoline. In hydrotreating a mixture of quinoline and naphthalene, the addition of NH_3 has little effect on hydrogenation of naphthalene to tetralin, but substantially inhibits the hydrogenation of tetralin to decalin. This improves the H-donor capability of the product liquid.

III. ARTICLES

C.M. Lee and C.N. Satterfield, "Hydrotreatment of 8-Hydroxyquinoline on a NiMo/Al_2O_3 Catalyst," Energy & Fuels, 5, 163 (1991).

TITLE: Enhanced Coal Hydrogasification via Oxidative Pretreatment DATE: 4/5/91

P.I.: Dennis J. Miller

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Martin E. Toomajian (Master of Science in Chemical Engineering)
Michael G. Lussier (Master of Science in Chemical Engineering)

INSTITUTION/ORGANIZATION:
Michigan State University
Department of Chemical Engineering
East Lansing, MI 48824
(517) 353-3928

GRANT NO.: DE-FG22-89PC89777

PERIOD OF PERFORMANCE: 9/1/89 - 8/31/91

I. ABSTRACT

OBJECTIVE: Enhancement of coal hydrogasification rate via oxidative treatments is investigated with the objective of developing optimal oxidation methods and conditions to maximize conversion rate. Emphasis is placed on characterizing surface oxygen groups, which are responsible for the active sites for gasification, and on fundamental aspects of the carbon-hydrogen reaction, including catalysis and rate inhibition.

WORK DONE AND CONCLUSIONS: Hydrogasification kinetic studies of coal char and Saran char are coupled with surface characterization to elucidate the effects of oxidation on gasification rate. Coal char and Saran char are prepared by pyrolysis of Illinois #6 coal (PSOC 1493) and Dow Saran powder at 900°C. Char oxidation is accomplished via partial combustion in air. Characterization methods including CO_2 adsorption (TSA), oxygen chemisorption at 300°C (ASA), X-ray photoelectron spectroscopy (XPS) (surface oxygen concentration), and pH measurements (nature of oxygen groups) are used to describe changes in the char surface resulting from oxidation and gasification.

Oxidation of as-prepared coal char and Saran char results in little hydrogasification rate enhancement, regardless of whether basic or acidic surface oxide groups are placed on the char surface. These results suggest that char surfaces are initially activated.

Heat treatment (outgassing) of chars at 1000 K *in vacuo*, which destroys active sites via annealing, results in an 8-10 fold decrease in hydrogasification rate and a similar decrease in ASA. Oxidation of outgassed chars results in a three-fold increase in hydrogasification rate which is reflected in a proportional increase in ASA.

Uncatalyzed char hydrogasification rate decreases sharply with conversion under all conditions. If gasification is interrupted and the char oxidized, the rate upon subsequent reexposure is observed to increase as much as three-fold. This enhancement is seen for repeated cycles of gasification and oxidation.

Results of ASA measurements and XPS analyses indicate that active sites for hydrogasification are formed by desorption of oxygen surface

groups during heatup to gasification conditions. These initially-formed active sites may propogate but eventually are consumed in pure hydrogen gasification, as no additional oxygen is present. Oxidation enhances rate by replacing oxygen surface groups which form additional active sites for hydrogasification.

It is well-known that hydrogen inhibition in steam and CO_2 gasification results from dissociative hydrogen adsorption on the carbon surface. This dissociatively-adsorbed hydrogen is very stable and accumulates on the carbon surface as carbon is converted. We believe that partial combustion removes some of the strongly-adsorbed hydrogen, thus liberating sites at which hydrogasification can occur and resulting in further rate enhancement.

The sharp decrease in uncatalyzed hydrogasification rate with conversion resulting from consumption of active sites and hydrogen inhibition is moderated or even reversed upon addition of a catalyst such as K_2CO_3. As a result, the overall time required for carbon conversion is much reduced in the presence of catalyst.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Hydrogen gasification is a direct, exothermic route to methane and is potentially important as the primary conversion route in processes such as the HYDROCARB process and in enhancing methane formation in steam gasification processes (such as the EXXON process). Because the reaction is intrinsically slower and thermodynamically less favorable than other gasification reactions, implementation of hydrogasification will only be feasible if simple, effective means of enhancing rate such as oxidation are developed.

PLANS FOR THE COMING YEAR: Studies for the remainder of the grant period will focus on three topics: 1) effects of oxidation on catalyzed hydrogasification of chars, 2) type and amount of oxygen groups on the carbon surface as determined by pH and ASA measurements and the effect of such groups on gasification rate, and 3) characterization of the effect of dissociative hydrogen chemisorption on hydrogasification rate.

II. HIGHLIGHT ACCOMPLISHMENTS

1. Three-fold hydrogasification rate enhancements were observed following oxidation of partially gasified coal and Saran char. Similar results were obtained for outgassed chars. Moderate rate enhancements (50-100%) were observed following oxidation of partially gasified chars impregnated with K_2CO_3 catalyst.

2. Results indicate that oxygen groups desorb during heatup to provide reactive sites at which hydrogasification occurs; ASA measurements indicate more active sites following oxidation of the char surfaces. Hydrogasification rate is correlated with ASA.

III. ARTICLES AND PRESENTATIONS

Toomajian, M.E., M.G. Lussier, and D.J. Miller, "Enhanced Coal Hydrogasification via Oxidative Pretreatment," ACS Div. Fuel Chem. Prepr. 36(1), 139 (1991).

Date: 8 April 1991

TITLE: Effects of Calcium Magnesium Acetate on the Combustion of Coal-Water Slurries

PI.: Yiannis A. Levendis
Co-PIs: M. Metghalchi and D. Wise.
STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED: Ajay Atal, Bill Murphy and Grace Zhu, all registered for Masters.
INSTITUTION/ORGANIZATION:
Northeastern University
Department of Mechanical Engineering
360 Huntington Avenue, Boston, MA. 02115.
Tel.# (617) 437-3806

GRAND NO.: DE-FG22-89PC89776
PERIOD OF PERFORMANCE: 1 September 1989 - 31 August 1992.

ABSTRACT

OBJECTIVES: The general objective of the project is to investigate the combustion behavior of single Coal-Water Fuel (CWF) drops burning at high temperature environments. Combustion rates of both uncatalyzed as well as catalyzed CWS drops with Calcium Magnesium Acetate (CMA) catalyst will be obtained. Emphasis will also be given in assessing the effects of CMA on the sulfur capture during combustion.

WORK DONE AND CONCLUSIONS: An experimental facility for high temperature combustion studies of liquid drops or solid fuel particles has been constructed and tested. The setup consists of a laminar flow, drop tube furnace capable of achieving maximum wall temperatures of 2000 K, a three-color, near infrared optical pyrometer with associated calibration devices and a particle sampling probe. Furthermore, various droplet injector configurations were developed, and both a suction thermometer and a hot wire velocimeter were designed and constructed. Numerical techniques have been used to model the furnace environment, and optimize drop injection parameters and gas flow rates. Gas velocity and temperature profiles as well as particle water-evaporation times are also computed. Combustion data on CWF drops, obtained so far, clearly indicates heatup, devolatilization and char combustion periods.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM This is a fundamental study dealing with the combustion characteristics of coal-water fuels (CWF) that are being considered as alternative fuels for oil-fired powerplants, diesel engines and turbines. This study aims at investigating the importance of various physical and chemical parameters of CWF drops on the the combustion rates. Such parameters include the drop size, the

solids loading, the coal type and the coal grind, the dispersion agent, the porosity of the dry agglomerate (before and after swelling) and the surface temperature. Furthermore, various combustion related effects and periods as well as total burnout times will be observed and quantified. Finally, a water soluble form of calcium, namely calcium magnesium acetate (CMA), will be mixed with the CWF, and its performance as a combustion catalyst and an SO_2 sorbent will be explored. Such fundamental knowledge, in conjunction with more applied pilot-plant studies, will aid (i) in the energy conservation program by enabling substitution of oil with CWF with the minimum amount of derating, and (ii) in the abatement of acid rain by providing means of capturing the coal-sulfur in the fly ash.

PLANS FOR THE COMING YEAR: Tasks are as follows: (i) Generate smaller CWF drops (<100μm). (ii) Measure CWF-particle surface temperatures and burntimes under various conditions and explore the accuracy of the particle temperature-time data. (iii) perform combustion experiments with CWF drops of various sizes, and various coal grinds and types, both with catalyzed and uncatalyzed drops, (iv) monitor events related to water evaporation, heatup, devolatilization, ignition and combustion, (v) derive combustion rates by adapting pertinent combustion models. (vi) assess the sulfur capture capabilities by burning streams of drops/particles and monitoring the SO_2 emissions.

HIGHLIGHT ACCOMPLISHMENTS

An experimental facility has been constructed and tested to perform combustion experiments involving single as well as multiple CWS drops. A high temperature drop-tube furnace has been assembled and interfaced with various designs of droplet injectors and sampling probes. A three-color, electronic pyrometer has been designed, constructed and coupled with the furnace to monitor combustion related events. The pyrometer has been interfaced with a fast speed data acquisition system driven by a microcomputer. Calibration of this device is being carried out using a standard tungsten lamp as well as observing the melting temperature of metals.

Energy balance requirements and derivation of reaction rates require precise knowledge of the gas phase environment in the furnace. Thus, the gaseous environment in the furnace has been studied both experimentally with a specially designed suction thermometer and velocimeter as well as with numerical modelling for temperature and velocity profiles. Thus the local combustion environment of burning drops has been explored. Results indicate that both velocity and temperature profiles are influenced by the injector air flow whose momentum can take up to several injector diameters to dissipate. Thus, the injector flow rate should be kept at a minimum (0.1 lpm for the present furnace geometry) and residence time should be varied by altering the main gas flow. At all cases this information about the state of the local gas will be coupled with information about combustion events, that occur at any axial (and radial) position in the furnace, to assess the drop and/or particle combustion histories in detail. Numerical simulations were also executed to study the evaporation and heatup of CWF of different sizes as well as their trajectories and residence times in the furnace.

A micronized and beneficiated coal water slurry (from *Otisca*) containing 40% solids (bituminous coal) of mean particle size of 4-5 μm, is being used for experiments but homemade slurries of bigger size coal are being prepared. To prevent sedimentation an apparatus was constructed to continuously tumble bottles of slurry, at slow speed, using a small motor.

Devolatilization and char combustion behavior of CWF agglomerates is being studied analyzing temperature-profiles obtained by the pyrometer. Furthermore the structure and the swelling behavior of particles is studied using SEM. A dry particle fluidization system has been assembled for introduction of clouds of CWF particles in the furnace.

ARTICLES AND PRESENTATIONS

1. "Combustion Behavior of Single Coal-Water Slurry Droplets. Part I: Experimental Techniques", Levendis, Y.L., Metghalchi, M., and Wise, D., presented at the 15th Coal and Slurry Conference, Clearwater, Florida, April 23-26, 1990.
2. "Characterization of the Environment in a Laminar Flow Furnace with Applications to the Combustion of Coal and Coal-Water Slurries", Cumper, J.G., Levendis, Y.A., and Metghalchi, M., *HTD-Vol. 148.* Also presented at the *Symposium on Heat and Mass Transfer in Fire and Combustion Systems*, 1990 ASME Winter Annual Meeting, Nov. 25-30, Dallas, Texas.
3. "Studies on the Combustion Behavior of Single Coal-Water Slurry Droplets.", Levendis, Y.L., to be presented at the 16th Coal and Slurry Conference, Clearwater, Florida, April 22-25, 1991.
4. "Development of Multi-Color Pyrometers for Studying the Transient Response of Burning Carbonaceous Particles" Levendis, Y.A. and Estrada K.R. In preparation.

TITLE: A NOVEL PROCESS FOR METHANOL SYNTHESIS April 9, 1991

P.I.(s): John W. Tierney and Irving Wender

STUDENT(s) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
V. Palekar, PhD in Chemical Engineering

INSTITUTION/ORGANIZATION: Chemical and Petroleum Engr. Dept.
University of Pittsburgh,
Pittsburgh, PA 15261.
(412)-624-9630

GRANT NO: DE-FG22-89PC89786

PERIOD OF PERFORMANCE: Sept. 1, 1989 to Feb. 28, 1993.

I. ABSTRACT

A novel slurry phase synthesis of methanol under mild conditions of 110-150°C and 40-65 atm is being investigated. The synthesis involves the carbonylation of a molecule of methanol to methyl formate predominantly in the liquid phase followed by the heterogeneous hydrogenolysis of methyl formate to two molecules of methanol; the net result is the reaction of H_2 with CO to give methanol. A number of catalyst systems have been found to be active; a mixed catalyst comprised of KOMe/Cu-chromite was the most active. The system tolerates small amounts of CO_2 and H_2O and can give up to 90% conversion with 95% selectivity to methanol. The nature of the catalyst and the reactions involved, possible effects of alkali loading, interaction between catalysts and different species will be discussed.

OBJECTIVE: To investigate experimentally a novel method for synthesizing methanol from synthesis gas in the slurry phase. Specific objectives are to determine the nature of the active catalyst and the effect of deactivating agents, to determine rate-limiting steps for proper scale-up, to investigate alternate catalysts and to develop mathematical models for prediction of reaction rates.

WORK DONE AND CONCLUSIONS: Previous work in our laboratory has demonstrated the feasibility of methanol synthesis from CO and H_2 in a slurry reactor using a mixed catalyst comprised of KOMe/Cu-chromite. At the temperature and pressure used, the product MeOH is a liquid.

Work done in the past year for the current grant includes:

(i) assembling of a new experimental setup with improved instrumentation and on-line sampling.

(ii) activity studies using a number of alternate catalysts. Various alkali or alkaline earth salts in conjunction with Cu-chromite as well as Cu-chromite promoted with alkali or alkaline earths have been identified as catalysts for methanol synthesis. A mixed catalyst comprised of KOMe/Cu-chromite was found to be the most active catalyst. A regeneration cycle in the presence of Cu-chromite for generation of methoxide ions in solution is proposed.

(iii) comparison of K-methoxide/Cu-chromite with KOMe/Cu-ZnO at 150°C and 63 atm. The latter catalyst is essentially inactive under these conditions.

(iv) study of the interaction between the two catalysts. An optimum loading of KOMe at constant Cu-chromite loading was identified. A non-equilibrium film model was proposed to explain the higher activity in comparison to that predicted from the individual reactions.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: An improved synthesis of methanol would directly benefit the fossil energy program because of its proposed use in transportation fuels. Methanol comprises on third of MTBE - the most rapidly growing octane enhancer in the world. It can also be used neat or as an additive to gasoline. It is an important precursor to formaldehyde, acetic acid and other two-carbon oxygenated products.

PLANS FOR THE COMING YEAR: The effect of possible deactivating agents such as CO_2 and H_2O will be investigated in greater detail. Alternate catalysts as well as Cu-chromite with different surface areas will be prepared and tested for their activity. Spectroscopic studies to understand the nature of the catalyst will be initiated. Kinetic and process modelling will be continued.

II. HIGHLIGHT ACCOMPLISHMENTS

(i) Methanol synthesis rates up to 21 gmoles/h/kg cat. were obtained at mild conditions with the KOMe/Cu-chromite system.

(ii) A number of alkali or alkaline salts in conjunction with Cu-chromite as well as promoted Cu-chromite were identified as catalysts.

(iii) A synergism was identified between the KOMe and Cu-chromite catalyst.

(iv) The system was shown to be tolerant to up to 1% CO_2 in the gas and up to 1% H_2O in the reaction medium.

(v) Two patents covering this novel methanol synthesis have been applied for.

III. ARTICLES AND PRESENTATIONS

Liu, Z., J. W. Tierney, Y. T. Shah and I. Wender, Fuel Processing Technology, 23, p. 149-167 (1989).

Liu, Z., J. W. Tierney, Y. T. Shah and I. Wender, Fuel Processing Technology, 18, p. 185-199 (1988).

Palekar, V., J. W. Tierney and I. Wender, "The Synthesis of Methanol by a Novel Method", presented at the AIChE Fall National Meeting, Chicago, November (1990).

Palekar, V., J. W. Tierney and I, Wender, "The Synthesis of Methanol in a Methanol-Rich Phase", presented at the AIChE Summer National Meeting, CA, August (1990).

Date: April 9, 1990

TITLE: Novel reactor Configuration for Syngas Conversion to Alcohols

PIs: Aydin Akgerman and Rayford G. Anthony

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

G. Pass, M.S. (completed)
H. AlAdwani, M.S.
J. Wang, Ph.D.
H. A. Gadalla, Ph.D.

INSTITUTION/ORGANIZATION: Texas A&M Research Foundation
Box 3578
College Station, TX 77843
Tel. (409)-845-8600

GRANT NO.: DE-FG22-89PC89787

PERIOD OF PERFORMANCE: 9/1/89 - 8/31/92

I. ABSTRACT

OBJECTIVE: The objective of this research is to develop a new, efficient reactor configuration and process for the synthesis of methanol and higher alcohols from coal gasification products. Preliminary work has shown that a trickle bed reactor with a mineral oil flowing co-currently with the gas feed down the reactor over a fixed bed of catalyst is more efficient than existing gas phase and slurry reactors. We will determine the effects of temperature, space velocity, synthesis gas/mineral oil feed ratio, and $H_2/CO/CO_2$ ratio on conversion and product distribution in a small laboratory trickle bed reactor; determine the intrinsic kinetics of the reaction in a slurry reactor; optimize and design a pilot size trickle bed unit; simulate the performance of this unit; and compare the performance in terms of yield and selectivity to slurry reactors.

WORK DONE AND CONCLUSIONS: In accordance with the Tasks of the project and the Task Schedule, we have completed procurement of necessary parts for automation of the existing equipment. We have standardized the GC analysis for all phases. We have determined the reaction kinetics in a CSTR slurry system. We have developed a model for the trickle bed reactor and designed a dynamic tracer response system for determination of the relevant hydrodynamic parameters together with the algorithms for parameter estimation. At present we are working on reaction kinetics, numerical techniques for solution of design equations, and construction of a new trickle bed unit.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The U. S. Department of Energy has been supporting research on technology to convert coal derived gases to liquid fuels. Gasification of coal produces a synthesis gas with a low H_2/CO ratio which can be used in the synthesis of methanol and higher alcohols for use as a fuel or as a blending agent with gasoline.

Methanol synthesis in the slurry phase is one of the projects that has been supported by DOE. However, we propose the novel concept of employing trickle bed reactors for methanol and higher alcohol synthesis from coal gasification products. Furthermore, the same reactor configuration may also be feasible for Fischer-Tropsch synthesis, which is another program supported by DOE. Technology for design, construction and operation of trickle bed reactors is available and these reactors are cheaper to operate than bubble columns.

PLANS FOR THE COMING YEAR: We anticipate to complete numerical simulation of the design equations and the parameter estimation routines based on these equations by the end of the year. We will be continuing our studies on determination of the kinetics. The construction of the trickle bed unit is almost completed and the test runs will start by summer. We expect to complete our trickle bed studies by Spring of 1992. The trickle bed data will be combined with the parameter estimation algorithm based on the design equations to yield the design parameters at reaction conditions. Finally, the design of a pilot size unit will be constructed by Summer 1992.

II. HIGHLIGHT ACCOMPLISHMENTS

We have developed a model for the trickle bed reactor that takes into account gas and liquid phase hydrodynamics, mass transfer between the two phase together with vapor liquid equilibrium at the interface, mass transfer into catalyst particle, effective diffusion rates, partial wetting of the catalyst particle, wetted and dry regions in the bed, and the reaction kinetics.

We started determining the reaction kinetics in a slurry reactor that operates in the perfectly mixed mode with well defined hydrodynamics. Various kinetic model equations in the literature are simulated at typical operating conditions to determine how well they agree with each other and we run experiments at points of maximum discrepancy between the various models. This approach reduces the total number of experiments significantly.

III. ARTICLES AND PRESENTATIONS

Pass, G., Holzhauser, C., Akgerman, A., and Anthony, R. G., "Methanol Synthesis in a Trickle Bed Reactor", *AIChE Journal*,

DATE: April 9, 1991

TITLE: Novel Process for Depolymerization of Coal to C_2-C_4 Hydrocarbons

P.I.(s): Wendell H. Wiser and Alex G. Oblad

STUDENT AND THE DEGREE FOR WHICH REGISTERED:
Annapragada Rao, working toward a Ph. D. Degree

INSTITUTION/ORGANIZATION: Department of Fuels Engineering
University of Utah
Salt Lake City, Utah 84112
(801) 581-8602

GRANT NO.: DE-FG22-89PC89788

PERIOD OF PERFORMANCE: September 1, 1989 - August 31, 1992

I. ABSTRACT

OBJECTIVE: The overall project objective is to design, construct and operate a continuous-flow reactor system for direct catalytic depolymerization of coal to produce C_2-C_4 hydrocarbons, which reactor may serve as a prototype for scale-up. To aid in achieving that overall objective, a companion research project is to provide kinetic data to assist in the design. Any products removed in the liquid state from the reactor system of the companion project will be characterized, including evaluation of any hydrogen-donor capability. A special reactor has been designed and constructed, incorporating quartz glass windows for visual observation, in which the operation of a catalyst bed fluidized by super-critical, coal-derived fluids will be examined. The capability of a coal-derived, hydrogen-donor fluid, in the super-critical state, to control agglomeration of a strongly caking coal, in the catalyst bed, will be evaluated. Finally, a continuous reactor system intended to serve as a prototype for scale-up will be designed, constructed and operated.

WORK DONE AND CONCLUSIONS: A special reactor, equipped with quartz glass windows for visual observation of high-pressure fluidization and agglomeration control by super-critical fluids, has been constructed. The reactor will accomodate temperatures up to 550 °C at pressures up to 3000 psi. The reactor system also includes a fiber-optic system for viewing the processes within the reactor from a position behind a barricade. This reactor is now being tested. A minor modification in the design of the seals for the windows is now being implemented.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Today there exists in the United States concern about the high level of petroleum imports (greater than 50% of demand, and growing), prompting a search for alternate sources of transportation fuels. Inasmuch as coal represents about 96% of known U. S. fossil fuel reserves recoverable by current technology, production of transportation fuels from coal is very desirable. It

is observed that a fuel like LPG (consisting of C_3 and C_4 hydrocarbons) is clean burning and exhibits a high octane number. If these hydrocarbons can be produced directly from coal in a technologically sound manner, with acceptable economics, the benefits will be great.

PLANS FOR THE COMING YEAR: The special reactor with the quartz glass windows will be operated to obtain the required data concerning use of a supercritical fluid for agglomeration control of a caking coal and for high-pressure fluidization of a catalyst bed. The continuous phase in the bed during depolymerization of a caking coal will consist of hydrogen gas and steam fed to the reactor, as well as liquids and hydrocarbon gases formed during the reactions. It is important to know how the mix as it will exist will perform in fluidizing a catalyst bed, and to compare it with fluidization by a true gas phase. As these data are produced and evaluated, and as kinetic data from the companion project are obtained, the work on the design and construction of the prototype reactor system will commence.

II. HIGHLIGHT ACCOMPLISHMENTS

The experiments conducted to date indicate that, with the minor modifications to the seals for the quartz glass windows, the special reactor system will permit visual observation, as well as other measurements, of the success, or lack thereof, of high pressure fluidization of a catalyst bed by a super-critical fluid, as well as control of particle agglomeration of a caking coal by a hydrogen donor in the super-critical state. Sealing glass windows against internal pressures of 2000 psi or greater, at temperatures up to 550 °C, without cracking the glass windows, is viewed as a significant accomplishment. We believe the visual observations of the operations identified above will be helpful.

III. ARTICLES AND PRESENTATIONS

Sufficient data have not as yet been produced from this research program for publication or for presentation.

TITLE: **Mild Coal Pretreatment to Improve Liquefaction Reactivity** DATE: April 4, 1991

PI Ronald L. Miller

INSTITUTION: Dept. of Chemical Engineering and Petroleum Refining
Colorado School of Mines
Golden, Colorado 80401
(303) 273-3892

GRANT NO.: DE-FG22-90PC90289

PERIOD OF PERFORMANCE: 9/1/90 - 8/31/93

I. ABSTRACT

OBJECTIVE:

This project continues our research program at CSM to develop an advanced low severity coal liquefaction scheme using mild chemical pretreatment of the coal to enhance coal dissolution reactivity. The process consists of three main steps: 1) mild pretreatment of the feed coal at ambient temperature and pressure using methanol or other common organic solvent with a trace amount of hydrochloric acid (or other common acid) to enhance dissolution reactivity and dry the coal, 2) low severity thermal dissolution of the treated coal to obtain a very reactive coal-derived residual material amenable to upgrading, and 3) catalytic upgrading of the residual products to distillate liquids.

The objective of the present project is to perform the necessary experimental work and data analysis to acquire and understand, from a more fundamental physicochemical basis, the following detailed information related to mild chemical pretreatment of coal:

- types and extent of coal bond cleavage during pretreatment and subsequent low severity thermal dissolution
- effect of pretreatment on the coal's physical structure including surface area modifications
- relationships between bond cleavage, metal chloride formation, coal conversion kinetics, and liquid and gaseous yields
- liquid and residuum product characterization, including residuum reactivity towards catalytic or thermal upgrading to distillate liquid products

WORK DONE AND CONCLUSIONS:

During the first few months of this project, we have been concentrated on evaluating the effect of mild coal pretreatment on low severity dissolution reactivity of the eight pristine coals from the Argonne Premium Sample Bank. Pretreatment of these coal samples was performed by suspending 5 g of undried coal in 40 cm^3 of methanol and 0.1 cm^3 of concentrated hydrochloric acid in a 100 cm^3 round bottom flask and continuously stirring for 3 hrs. The flask was connected to a cooling water condenser to reduce solvent losses during pretreatment. After pretreatment, most of the methanol was decanted off and the moist coal sample washed with fresh methanol and water to remove residual acid. Any remaining solvent was recovered by roto-evaporation and vacuum drying (50 °C, 10-20 millitorr, 24 hrs.). Pretreatment experiments were also completed using hexane or acetone in place of methanol. Untreated coal samples were vacuum dried at the same conditions before liquefaction. After drying, all treated and untreated coal samples were stored at room temperature in a vacuum desiccator (0.1 torr) for less than 12 hours before analysis or liquefaction.

Liquefaction experiments were conducted in a 20 cm^3 tubing bomb reactor attached to an agitator arm and immersed in a fluidized sandbath. Low severity reaction conditions were set at 350 °C reaction temperature, 1000 psig initial cold hydrogen pressure, and 30 min. reaction time. Dihydrophenanthrene (DHP) was used as liquefaction solvent, and coal conversion was monitored using tetrahydrofuran (THF) solvent solubility measurements.

Pretreatment with methanol/HCl enhanced low severity liquefaction reactivity for all eight Argonne coals. The absolute increase ranged from 5.5 wt% for Blind Canyon coal to 31.5 wt% for Wyodak coal, and averaged 18.0 wt% for the eight coals (MAF basis). Interestingly, replacement of methanol with hexane or acetone during coal pretreatment also resulted in increased low severity liquefaction reactivity. Since hexane cannot participate in the coal/methanol alkylation chemistry proposed by Sharma (Fuel, 64, 449, 1985), other effects must also be contributing to the observed reactivity improvement. Some possibilities include: 1) leaching of calcium, magnesium, iron and perhaps other species from the coal mineral matter, and 2) formation of chlorinated mineral species such as $FeCl_3$ which are known coal dissolution catalysts.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Many economic and operational incentives exist for converting coal to liquid fuels at less severe reaction conditions than presently employed. The ability to significantly enhance coal liquefaction reactivity by pretreatment with common, inexpensive chemicals such as methanol and HCl will allow processes to operate at less severe reaction conditions and will have a positive impact on the commercial viability of low severity liquefaction processes. In addition, much of what is learned in this project will directly apply to development of similar low severity coal/oil coprocessing schemes.

PLANS FOR THE COMING YEAR:

During the second year of this project, we will continue to expand our baseline reactivity data set using additional mild pretreatment techniques and the eight Argonne coal samples. Portions of these samples will be analyzed using sophisticated techniques such as scanning electron microscopy (SEM) and x-ray diffraction (XRD) to begin studying the effect of our pretreatment technique on the physical and chemical nature of pretreated coals.

II. HIGHLIGHT ACCOMPLISHMENTS

We have shown that mild pretreatment of coal using methanol or other common organic solvent and hydrochloric acid enhances low severity liquefaction reactivity. Coal conversion levels are comparable to those obtained at high severity.

III. ARTICLES AND PRESENTATIONS

1. Miller, R.L., R.M. Baldwin, O. Nguanprasert, and D.R. Kennar, "The Effect of Mild Chemical Pretreatment on Liquefaction Reactivity of Argonne Coals," ACS Symposium Series No. 461, 1991.

2. Miller, R.L., K. Shams, and R.M. Baldwin, "Mild Coal Pretreatment to Enhance Liquefaction Reactivity," ACS Div. Fuel Chem. Preprints, 36, 1, 1, 1991.

TITLE: Rapid Pressure Swing Absorption Cleanup of Post-Shift Reactor Synthesis Gas

DATE: April 8, 1991

P.I.: Dr. K. K. Sirkar; SENIOR POST DOCTORAL RESEARCH ASSOCIATE: Dr. S. Majumdar

STUDENT(s) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Mr S. Bhaumik, M. Engg.

INSTITUTION/ORGANIZATION: Center for Membranes and Separation Technologies
Department of Chemistry and Chemical Engineering
Stevens Institute of Technology
Castle Point, Hoboken, NJ 07030

GRANT NO.: DE-FG22-90PC90300

PERIOD OF PERFORMANCE: 9/7/90 - 8/31/93

I. ABSTRACT

OBJECTIVE: This investigation is concerned with the separation of gas mixtures using a novel concept of rapid pressure swing absorption (RAPSAB) of gas in a stationary absorbent liquid through gas-liquid interfaces immobilized in the pore mouths of hydrophobic microporous membranes. The process is implemented in a module well-packed with hydrophobic microporous hollow fiber membranes. The specific objectives are (1) to develop a theoretical model which will provide guidelines for selecting an efficient RAPSAB process cycle which includes desorption; (2) to demonstrate the concept experimentally with a simple gas mixture (e.g., CO_2-N_2) and a simple absorbent liquid such as water, and (3) to extend the concept to reactive absorbent liquids for the separation of CO, CO_2 from the post-shift reactor synthesis gas.

WORK DONE AND CONCLUSIONS: A theoretical model containing a set of partial differential equations (PDE) in time and spatial dimensions has been developed to describe the dynamics of rapid pressure swing absorption (RAPSAB) of gases in the absorbent liquid lying stagnant on the hollow fiber module shell side while the feed gas flowed through the fiber lumina. For preliminary analysis, the model has been simplified with appropriate assumptions. Computer codes have been developed for a numerical solution of the model. Preliminary simulation results for CO_2-N_2 absorption with water illustrate the expected breakthrough of the gas species. A purification loop has also been built for experimental studies of CO_2-N_2-water system.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: After initial characterization of a RAPSAB system with simple gaseous mixture and simple absorbent liquid, we intend to study the purification of CO_2 from a model post-shift reactor synthesis gas mixture containing H_2, N_2, CO and CO_2 with aqueous amine solutions. Secondly, a mixture containing H_2, N_2 and CO will be purified to remove CO by a RAPSAB process to produce H_2-N_2 mixture, the synthesis gas used for ammonia manufacture. The process is expected to have the purification capabilities of absorption, adsorption processes. Further they are expected to have lower capital cost usually encountered with compact and efficient membrane modules with pressure drops lower than in conventional adsorption processes.

PLANS FOR THE COMING YEAR:
1. Determine an efficient process cycle from the model simulation results.
2. Study experimentally the removal of CO_2 from N_2-CO_2 mixture with pure water as an absorbent liquid.

3. Compare experimental results with model simulation.
4. Prepare for studying systems with chemical reactions.

II. HIGHLIGHT ACCOMPLISHMENTS

A simplified theoretical description of the novel rapid pressure swing absorption process has been developed. The absorption part of the pressure swing absorption cycle has been predicted for CO_2-N_2-water system. Numerical simulation of the model is being carried out for different operating conditions for selecting an optimum pressure swing cycle.

III. ARTICLES AND PRESENTATIONS

None so far.

ENGINEERING FUNDAMENTALS AND THERMODYNAMICS

Date: 4/1/91

TITLE: Configurational Diffusion of Coal Macromolecules

PIs: James A. Guin, Christine W. Curtis and A. Ray Tarrer

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Seongjae Kim (Ph.D.), Zen-Wen Chiou (M.S.), C. C. Chen (M.S.)

INSTITUTION/ORGANIZATION: Chemical Engineering Department
Auburn University
Auburn, AL 36849
(205) 844-2020

GRANT NO.: DE-FG22-86PC90504

PERIOD OF PERFORMANCE: 9-15-86 to 9-14-91

I. ABSTRACT

OBJECTIVE: The objective is to learn more about how coal macromolecules, e.g., asphaltenes, diffuse through small pores. This diffusion rate is dependent on the molecule size, shape, and pore geometry. This problem has applications in catalysis.

WORK DONE AND CONCLUSIONS: The bulk and effective diffusivities of coal macromolecules were measured using the diaphragm-cell technique with track-etched polyester membranes, and the relationship between effective diffusivities of coal macromolecules and pore size of a membrane was investigated, in order to obtain fundamental information concerning configurational diffusion phenomena occurring in coal liquefaction catalysts.

The coal macromolecules were prepared from a sample collected from the deashed residue stream of the ROSE-SR^{SM} unit at the Wilsonville coal liquefaction pilot plant (Wilsonville, Alabama), which was running Illinois No. 6 coal. The track-etched polyester membranes were prepared from irradiated polyester film using optimum etching conditions found in the current study. During the experiments, gel permeation chromatography was used to characterize the coal macromolecules and to analyze the diffusion experimental results. The experimental data were analyzed for six coal macromolecule fractions of narrow molecular size range, which were defined in the chromatogram.

Slightly stronger hinderance effects as compared to the theoretical curve were observed when the ratios of effective to bulk diffusivities of coal macromolecules were plotted against the ratios of average Stokes-Einstein radii to pore radii. Weak repulsive interactions between coal molecules adsorbed to pore walls and coal molecules diffusing through the pore were postulated to account for the differences between the experimental data and the theoretical curve.

Nc5/CONFIGUR

Several diffusion studies of model compounds and a diffusional boundary layer study were conducted prior to the coal diffusion study to test the performance of the experimental system and to provide information as to the effect of molecular size and the configuration on the effective diffusivity. It was found that the measured diffusion coefficients of model compounds were in agreement with the values estimated from the literature, that the measured effective diffusivities of a model macromolecule agreed with those predicted by a hydrodynamic theory with a minor modification, and that the diffusional boundary layer resistance was not affected by membrane properties.

<u>PLANS FOR THE COMING YEAR:</u> We plan to conduct diffusion experiments in actual porous media (catalyst pellets) to compare with diffusion in idealized membranes in the next phase of our work and to examine the effects of elevated temperature on the hindered diffusion phenomena.

II. HIGHLIGHT ACCOMPLISHMENTS

We have successfully measured hindered diffusion coefficients for coal macromolecules in track-etched polyester membranes at 25° C in ethyl acetate solvent.

III. ARTICLES AND PRESENTATIONS

1. Chiou, Zen-wen, "Preparation of an Anodic Aluminum Oxide Membrane and the Effect of Its Controlled Conditions", M.S. Thesis, Auburn University, 1989.

2. Kim, S. J., "Configurational Diffusion of Coal Macromolecules", Ph.D. Dissertation, Auburn University, 1990.

Nc5/CONFIGUR

Date: March 15, 1991

TITLE: SCALE-UP OF CIRCULATING FLUIDIZED BED COAL COMBUSTORS

PI's: Michel LOUGE and Michael TANCA

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

Jamaludin Mohd. Yusof (Ph.D. candidate)
D. Jeffrey Lischer (Ph.D. candidate)
Hong Der Chang (Ph.D., graduated 1/91)

INSTITUTION/ORGANIZATION: Cornell University, Dept. of Mechanical Engin.
Upson Hall
Ithaca, NY 14853
tel: (607) 255-4193

GRANT NO.: DE-FG22-88PC88929

PERIOD OF PERFORMANCE: September 1, 1988 - August 31, 1991

I. ABSTRACT

OBJECTIVE:

Circulating fluidization is a promising technology for designing efficient coal combustors with high solid throughputs. Unfortunately, limited understanding of circulating fluidized beds (CFB) renders design extrapolations of pilot reactors to full-scale plants both empirical and expensive. This project is aimed at quantifying the effects of scale-up upon the flow in CFB combustors and elucidating their hydrodynamics through models. For the experiments, we have constructed a cold CFB facility (diameter: 20cm; height: 7m) where gases are continuously recycled. In this way, the facility may be fluidized with mixtures of He and CO_2 with adjustable density and viscosity. Hydrodynamic analogy between the cold bed and a coal combustor is achieved by matching all relevant dimensionless parameters. Several choices of gas mixture composition and solid particle properties make the facility analogous to combustors of diameters in the range 30cm to 1m. Thus, direct quantification of scale-up is obtained in an ideal environment for detailed measurements.

WORK DONE AND CONCLUSIONS:

The present report summarizes the work accomplished during the first two years of this project. In the first year, the CFB facility was commissioned using FCC catalyst fluidized with air There, detailed measurements of voidage were carried out near the wall of the riser with a non-invasive capacitance probe. These measurement confirmed the presence of a denser layer of solids falling near the wall. Because this wall layer is in contact with the vertical tubes that control the combustion temperature, it governs two phenomena of crucial importance to designers: erosion and heat transfer [Louge, *et al. Powder Tech.* **62**, 267 (1990)].

After commissioning, scale-up experiments were carried out with plastic, glass, and metal particles with appropriate mixtures of helium and carbon dioxide [H. Chang, *PhD. thesis*, Cornell, 1991]. With these conditions, the CFB became analogous to coal combustors of 32, 47 and 100cm in diameter. For the first time, these experiments have shown that the vertical profiles of average pressure scale with the bed diameter, and that pressure fluctuations scale with the particle diameter. Other experiments have established that, if unchecked, electrostatics has significant effects on the flow. In this regard, we have found a powerful anti-static additive that virtually eliminates the problem. Finally, by

fluidizing two glass powders of identical characteristics but largely different surface Coulomb friction coefficients, we have also discovered that particle surface friction, which had previously been ignored in earlier CFB analyses, plays an important role in these flows perhaps through the dynamics of the dense wall layer. These effects of Coulomb friction demonstrate the importance of establishing the correct boundary conditions at the wall before carrying out any analysis of the dynamics of the particle phase.

To elucidate further the dynamics of particle suspensions in a CFB, we have also modelled the fully-developed pneumatic transport of relatively massive particles in a vertical pipe [Louge, *et al. J. Fluid Mech.* (1991), in press]. We have found that the velocity fluctuations of massive particles are produced by their collisions rather than by the gas turbulence. However, the turbulent energy of the gas is affected by the presence of the particles. A numerical solution of the resulting governing equations has provided velocity and turbulent energy profiles in good agreement with the measurements of Tsuji *et al.* [*J. Fluid Mech.* **139**, 417 (1984)]. In addition, we have used a similar model to predict the heat transfer to the wall in the pneumatic transport of massive particles [Louge, *et al. Int. J. Heat Mass Trans.* (1991), under review].

Finally, we are engaged in a joint project with Combustion Engineering, Inc to measure the radial profiles of voidage in a CFB coal combustor. The diagnostic technique is a water-cooled version of a capacitance probe developed at Cornell.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

The results from this project are directly relevant to the hydrodynamics and heat transfer of coal-burning CFB powerplants.

PLANS FOR THE COMING YEAR:

In the coming year, we will investigate further the role of the wall layer in the dynamics of CFB combustors through computer simulations, models and experiments.

II. HIGHLIGHT ACCOMPLISHMENTS

Principal accomplishments include:

- the construction of a CFB facility with recycled fluidization gases;
- the discovery of the importance of Coulomb friction in CFB dynamics;
- the completion of a series of tests that establish scaling rules for CFB combustors;
- the development of models for hydrodynamics and heat transfer in pneumatic transport.

III. ARTICLES AND PRESENTATIONS

- Louge, M., Lischer, D.J. & Chang, H.: *Powder Tech.* **62**, 267-74 (1990).
- Louge, M.Y., Mastorakos, M. & Jenkins, J.T.: *J. Fluid Mech.* (1991), in press.
- Louge, M. & Chang, H.: *Powder Tech.* **60**, 197 (1990).
- Louge, M., Yusof J.M. & Jenkins J.T.:*"A Model for Heat Transfer in the Pneumatic Transport of Large Particles"*, Annual Meeting of the AIChE, San Francisco, November 5-10, 1989. Also: *Int. J. Heat & Mass Trans.* (1991), under review.
- Chang H. & Louge M.: Proc 11th Int Conf on Fluid Bed Comb, ASME (1991), in press.

Date: April 1, 1991

TITLE: Supercritical Fluid Thermodynamics for Coal Processing

PIs: Prof. Frank van Swol
Prof. Charles A. Eckert* (subcontractor)

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Michael P. Ekart Ph.D. Frederic Pouillot M.S.
Barbara Knutson Ph.D. David L. Tomasko Ph.D.

INSTITUTION/ORGANIZATION: University of Illinois
Department of Chemical Engineering
Urbana, IL 61801

*Georgia Institute of Technology
School of Chemical Engineering
Atlanta, GA 30332-0100
(404) 853-9344

GRANT NO.: DE-FG22-88PC88922

PERIOD OF PERFORMANCE: September 1988 to September 1991

I. ABSTRACT

OBJECTIVE:

Because of their unusual solvating and mass transfer properties, supercritical fluids (SCF) show potential for a variety of coal processing applications. The main objective of this research is to develop a predictive equation of state so that SCF solvents can be tailored for the extraction and processing of coal. To meet this objective, we are carrying out a two pronged approach. First, a database containing the solubilities of coal model compounds in high temperature fluids, polar fluids, and fluid mixtures has been collected and is being extended. Second, we are looking at the intermolecular interactions between the solute and the solvent, cosolvent, and other solute molecules using spectroscopic techniques. All this information gives us the means to develop an equation of state that accurately reflects the true molecular makeup of the solution.

WORK DONE AND CONCLUSIONS:

Chemical forces can play an important role in phase equilibria, particularly in systems with cosolvents (such as methanol) where hydrogen bonding occurs. These type of interactions are important for many polycyclic aromatics containing sulfur, nitrogen and oxygen functional groups, representative of coal compounds, yet the current commonly used equations of state consider only physical forces between molecules. We have developed a model, therefore, that contains not only a physical term, but a chemical term to describe these specific interactions.

Although cosolvent modified SCF's show much promise in simplifying difficult separations, relatively little data exist on the effects of these modifiers. We have developed a chromatographic technique to measure these effects rapidly. We are also developing a complementary UV absorption technique to measure solubilities. These tools give us the means measure phase equilibria in a wide variety of systems.

Information on the strength of intermolecular interactions in SCF solutions has been obtained using high pressure fluorescence spectroscopy. Our results suggest the importance of solute/cosolvent interactions, even in dilute solutions. These measurements coupled with solubility studies of the same system will reap much insight on the nature of interactions on the molecular level and their macroscopic effect. The spectroscopic measurements will also be used to determine the parameters in the chemical portion of the association model so that they are based on actual observations rather than treated as adjustable parameters.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM

The primary purpose of the current studies is to gather pertinent experimental data to be used in the development of correlations and equation of state models that can be used for the design of coal treatment processes. The solubility studies will determine the ability of SCFs to extract and separate sulfur and nitrogen containing compounds from the coal matrix. We have also developed a chromatographic technique to fill important gaps in our database of solubilities. Finally, spectroscopic experiments will probe molecular interactions, information that is vital to the development of accurate phase equilibria models. All this information will guide the development of a new chemical-physical equation of state. With the experimental techniques we have developed and the new equation of state, SCF extraction and processing of coal can be researched rapidly and inexpensively.

PLANS FOR THE COMING YEAR

Future work will include further measurements of cosolvent effects on model compounds by the chromatographic technique. In addition, we are developing a UV absorbance technique to measure these effects that complements the chromatographic method. We will continue spectroscopic studies of sulfur, nitrogen, and oxygen aromatic heterocycles in SCFs. Information from both phase equilibria and spectroscopy experiments will be used in improving our equation of state model so that it will predict solubilities for the design of coal treatment processes.

II. HIGHLIGHT ACCOMPLISHMENTS

Supercritical fluids show potential for a variety of coal processing applications. To determine the phase behavior to be anticipated in these systems, we have developed new techniques to measure coal model compound solubilities in SCFs. The results are being used to test a new association model that we have developed. In addition, we have used fluorescence spectroscopy to determine the nature of the intermolecular interactions in systems of coal model compounds.

III. ARTICLES AND PRESENTATIONS

Brennecke, J. F., D. L. Tomasko, J. Peshkin, and C. A. Eckert, *I&EC Research*, 29, 1682 (1990).

Brennecke, J. F., D. L. Tomasko, and C. A. Eckert, *J. Phys. Chem.*, 94, 7692 (1990).

Brennecke, J. F., P. G. Debenedetti, K. P. Johnston, and C. A. Eckert, *AIChE J.*, 36 (1990).

Howell, W. J., M. M. Mayer, D. L. Tomasko, and C. A. Eckert, *J. Chem. Eng. Data*, 35, 446 (1990).

Karachewski, A. M., W. J. Howell, and C. A. Eckert, *AIChE J.*, 37, 65 (1991).

Van Alsten, J. G. and C. A. Eckert, *J. Chem. Eng. Data.*, in press.

Ekart, M. P., J. F. Brennecke, and C. A. Eckert, Supercritical Fluid Technology: Reviews in Modern Theory and Applications, ed. by J. Ely and T. Bruno, CRC Press, in press.

Brennecke, J. F. and C. A. Eckert, 2nd International Symposium on High Pressure Chemical Engineering, Erlangen, West Germany, September 25, 1990.

Karachewski, A. M., W. J. Howell, D. L. Bergmann, and C. A. Eckert, AIChE Annual Meeting, Chicago, IL, November 12, 1990.

Ekart, M. P., D. L. Tomasko, and C. A. Eckert, AIChE Annual Meeting, Chicago, IL, November 12, 1990.

Tomasko, D. L., B. L. Knutson, and C. A. Eckert, ACS National Meeting, Atlanta, GA, April 17, 1991.

Knutson, B. L., D. L. Tomasko, I. B. Petsche, P. G. Debenedetti, and C. A. Eckert, ACS National Meeting, Atlanta, GA, April 17, 1991.

Ekart, M. P. and C. A. Eckert, 2nd International Symposium on Supercritical Fluids, Boston, MA, May 20, 1991.

DATE: April 5, 1991

TITLE: MECHANICS/HEAT TRANSFER RELATION FOR PARTICLE FLOWS

PI: CHARLES S. CAMPBELL

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

DAVID WANG, PhD
KHURRAM RAHMAN, PhD

INSTITUTION: UNIVERSITY OF SOUTHERN CALIFORNIA
Los Angeles, Ca. 90089-1453

GRANT NO: DE-FG22-88PC88913

PERIOD OF PERFORMANCE: 10/1/88-9/30/91

I. ABSTRACT

OBJECTIVE: To understand the links between the mechanical behavior of a two phase mixture and its heat transfer behavior in a manner akin to Reynolds' analogy that has been long been established for simple fluids. The project studies two systems. The first is simple shear rheometers, which has clearly established a link between the apparent viscosity and thermal conductivity of dry particle flows. The second is to study fluidized beds with the intent to establish a link between the heat transfer behavior and an internal property called the "particle pressure". Unfortunately, no such link has been found for the latter problem and the investigation has turned toward examining the rheology of the particle pressure itself. It has been observed that bubbles generate the largest portion of the particle pressure in a gas-fluidized bed.

WORK DONE AND CONCLUSIONS:

The viscosity and thermal conductivity measurements are performed in an annular shear cell. The results indicate that, in a dry granular solid that is undergoing a rapid shearing motion, both the apparent thermal conductivity and viscosity of the mixture varies linearly proportional to the shear rate. This indicates that both can be attributed to the same internal transport mechanisms. In fact, it has been shown in computer simulations that the energy associated with the random motions of the particles - which, making an analogy with molecular motions in the kinetic theory of gases, has been dubbed the "granular temperature" - varies proportional to the square of the shear rate. Consequently, both the effective conductivity and viscosity vary as the square-root of the granular temperature much as the viscosity and conductivity of a hard sphere gas varies as the square root of the thermodynamic temperature.

The gas-fluidized bed project has succeeded both in developing a probe to measure the particle pressure and in making some preliminary measurements. (Even though this is a very simple measurement, these are the first measurements of the particle pressure that, to my knowledge, have been made.) The construction and experiments have bee submitted for publication in the references given below. Somewhat amazingly, we have found that all of our data collapses to a point in bubbling fluidized beds. Scaling the particle pressure, P_p, with the particle density, ρ_p, the gravitational acceleration, g, and the effective bubble diameter, D_E (the diameter of a spherical bubble with the same volume as that observed) yields:

$$\frac{P_p}{\rho_p g D_E} \simeq 0.08$$

throughout the bubbling and slugging regimes. This is a very important result in itself as this property has been linked to the stability of fluidized beds and is a fundamental parameter in multiphase flow modeling. Unfortunately, it now appears that there may be no relationship with the heat transfer as was originally speculated.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM: Nearly all of the processing of fossil fuels involves chemical reactions in particle-fluid systems of one form or another, whether they be synthetic fuel retorts or basic fluidized bed crackers. All chemical processes require the addition or removal of heat in order to maintain the reaction process, Hence, understanding the relationship between the state of motion of the multiphase system and its heat transfer properties could strongly influence future designs. Furthermore, the program studying particle pressures is relevant to many studies of multiphase systems that use such quantities in mathematical modeling.

PLANS FOR THE COMING YEAR: As the project terminates in October, our hopes lie in a proposed continuation.

II. HIGHLIGHT ACCOMPLISHMENTS

There have been two major accomplishments of this project. The first is to establish a link between the apparent viscosity and thermal conductivity within a granular shear flow. This should greatly ease heat transfer modeling efforts as they can borrow upon the extensive work done in modeling the constitutive behavior of granular systems. The second major accomplishment is the measurement of the particle pressures, itself. Even though it appears that there may be no relationship to the heat transfer, this quantity is significant towards understanding the attrition of particles, but more importantly, this paper has excited much interest as the constitutive nature of the particle pressure is important in many areas of fluidized bed modeling.

III. ARTICLES AND PRESENTATIONS

ARTICLES:

Campbell, C.S. and Wang, D.G., Particle pressures in gas-fluidized beds, Journal of Fluid Mechanics, in press

Campbell, C.S. and Wang, D.G., A particle pressure transducer suitable for use in gas-fluidized beds, Measurement Science and Technology, 1 (1990), 1275-1279

Wang, D.G., and Campbell, C.S., Reynolds Analogy for particle flows: the relationship between the apparent viscosity and thermal conductivity of a sheared granular material, J. Fluid Mech., submitted

TITLE: SiO_2 Membranes for H_2 Separation in Coal Gas Processing DATE: 4/9/91

PIs: G. R. Gavalas

STUDENT(S): S. Kim (PhD), M. Tsapatsis (PhD)

INSTITUTION/ORGANIZATION: California Institute of Technology
Caltech 210-41, Pasadena, CA 91125
(818) 356-4152

GRANT NO.: DE-FG22-89PC89765

PERIOD OF PERFORMANCE: 9-1-89 to 8-31-92

I. ABSTRACT

OBJECTIVE: To synthesize permselective ceramic membranes by chemical vapor deposition of SiO_2, TiO_2 and other pure or mixed oxides within the walls of porous support tubes, to characterize the membranes by permeability measurements and scanning electron microscopy, and to develop a mathematical model of the chemical vapor deposition.

WORK DONE AND CONCLUSIONS: Chemical vapor deposition of amorphous SiO_2, TiO_2, and Al_2O_3 layers on porous Vycor tube supports was carried out to prepare high-temperature membranes selective to hydrogen permeation. The deposition was carried out by reaction of the respective chlorides, $SiCl_4$, $TiCl_4$, $AlCl_3$ with water vapor at temperatures 200-800°C, depending on the chloride and the reaction geometry. Three modes of deposition were employed. In the opposing reactants mode, the chloride vapor and water vapor passed inside and outside the support tube respectively. In the one-sided mode both reactants were passed inside the support tube. In the alternating mode, alternating flows of the chloride vapor and the water vapor were used. Deposition of permselective SiO_2 layers was successful with both the opposing reactants mode at 700-800°C, and in the one-sided mode, at 400-800°C. The one-sided mode of deposition was much faster and gave membranes with hydrogen permeation coefficients as high as 0.3 cm^3/cm^2-min-atm at 450°C. The opposing reactants deposition was slower and gave membranes with hydrogen permeation coefficients of 0.1 cm^3/cm^2-min-atm at 450°C. The H_2-N_2 permeation ratios were between 1000 and 5000.

Deposition of TiO_2 and Al_2O_3 layers with selective permeation properties was not possible with one-sided deposition but was successful with opposing reactants deposition. Between the two oxides, TiO_2 yielded better permeation properties although slightly lower than those of SiO_2. For example TiO_2 deposited at 450°C yielded hydrogen permeation coefficients of 0.06-0.09 cm^3/cm^2-min-atm at 450°C and H_2:N_2 ratios of about 1000. Deposition of TiO_2 layers was also accomplished in the alternating deposition mode, but the permeation properties of the deposited layer were inferior.

Scanning electron microscopy on polished cross sections of the tubes showed that the deposited TiO_2 layer was located near the side exposed to the $TiCl_4$ flow. The profile of TiO_2 density across the cross section measured by electron microprobe analysis was highly asymmetric rising gradually from the side of $TiCl_4$ flow to a maximum and then declining sharply to zero. Similar profiles were obtained for the Al_2O_3 layers.

Predictions of an earlier mathematical model based on pseudosteady rate expressions were at variance with the measured SiO_2, TiO_2, Al_2O_3 profiles. A new model was developed that takes into account the reactions between the chloride vapor and water vapor with -OH and -Cl groups on the Vycor surface respectively:

$$\succ Si{-}OH + SiCl_4 = HCl + \succ Si{-}O{-}SiCl_3$$

$$\succ Si{-}Cl + H_2O = HCl + \succ Si{-}OH$$

$$Si{-}OH + \succ Si{-}OH = H_2O + \succ Si{-}O{-}Si \prec$$

$$Si{-}Cl + \succ Si{-}OH = HCl + \succ Si{-}O{-}Si \prec$$

The mechanism of TiO_2 deposition is somewhat uncertain but may involve reaction of $TiCl_4$ with Si–O–Si, Ti–O–Si, Ti–O–Ti groups on the surface. This model has yielded predictions in good agreement with the measured profiles of the deposited SiO_2 and TiO_2 layers.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The amorphous oxide membranes (SiO_2, TiO_2) are very selective to hydrogen permeation and are stable at high temperatures. These properties make them applicable to hydrogen production from coal gas for fuel cell power generation or chemical synthesis.

PLANS FOR THE COMING YEAR: Deposition experiments will continue seeking to improve the permeation rates and the thermal stability of the SiO_2 and TiO_2 membranes. Thermogravimetric experiments and IR spectroscopy will be carried out to obtain information about the mechanism and kinetics of deposition.

II. HIGHLIGHT ACCOMPLISHMENTS

One-sided deposition of SiO_2 was carried out successfully to prepare membranes with higher permeation coefficients than previously possible. TiO_2 deposition in the opposing reactants geometry was found to take place over a broad temperature range. A new deposition model was developed that gives good agreement with the measured SiO_2 and TiO_2 density profiles.

III. ARTICLES AND PRESENTATIONS

M. Tsapatsis, S. J. Kim, S. W. Nam and G. R. Gavalas, "Synthesis of Hydrogen Permselective Amorphous SiO_2, TiO_2, Al_2O_3, B_2O_3 Membranes from the Chloride Precursors," submitted to Industrial and Engineering Chemistry Research.

G. R. Gavalas, S. J. Kim, M. Tsapatsis, S. W. Nam, "Chemical Vapor Deposition of Permselective Oxide Films," presented at 1990 Annual Meeting of AIChE, Chicago, November 11-16, 1990.

TITLE: **NOVEL COAL FEEDER FOR LOW-SULFUR FUEL** DATE: April 8, 1991
P.I.(s): Soon-Jai Khang and Timothy C. Keener
STUDENT(s) AND THE DGREE FOR WHICH THEY ARE REGISTERED:
Linong Lin - PhD
INSTITUTION/ORGANIZATION: University of Cincinnati
Chemical Engineering Department/Civil & Civil Engr. Department
University of Cincinnati, Cincinnati, Ohio 45221
Phone - (513) 556-2789, FAX - (513) 556-3473
GRANT NO.: DOE-FG22-89PC89781
PERIOD OF PERFORMANCE: September 1, 1989 - August 31, 1992

I. ABSTRACT

OBJECTIVE: The project objective is to study the feasibility of an advanced coal desulfurization concept in a coal feeder. It is proposed to construct a novel coal feeder which contains dual screw tubes, the inner tube acting as a coal pyrolizer and the outer tube acting as a desulfurizer with hot calcined limestone pellets or other renewable sorbent pellets. The inner screw feeder pyrolyses coal particles in a reducing environment which produces sulfur-containing gases such as H_2S and COS. Hot calcined limestone pellets (or other renewable sorbent pellets) are added to the outer tube and react with sulfur components. Based on the experimental data on both the pyrolysis and the limestone-based desulfurization, the proposed system is expected remove between 50 and 80% sulfur from various high-sulfur coals.

WORK DONE AND CONCLUSIONS: Works under progress are (1) literature review on coal pyrolysis, (2) Computer/math modeling of the pyrolysis section, (3) Evaluation of pyrolysis kinetics, (4) Experimental pyrolysis in an auger feed tube. The conclusions are: (1) Pseudo-component approach for the pyrolysis kinetics, (2) A 48% desulfurization was achieved at residence times of 7 minutes for a pyrolysis temperature of 450°C, indicating a reasonable expectation for the goal of the project.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The acid rain resulting from burning sulfur-containing coal has become one of the main environmental issues in the decade. This project tries to solve the problem at the source: removing the sulfur before combustion while the sulfur containing compounds are converted to gaseous forms of product, mainly H_2S, during a mild pyrolysis and are still highly concentrated. The successful conclusion of this project will provide an economically feasible alternative to the conventional scrubbing methods. This project is also aimed at reducing the waste volume by maximizing the utilization of calcium-based sorbent particles and opening the possibility of regenerating spent sorbent and other renewable catalytic materials. The results of this project will have direct impact on many dry sorbent desulfurization processes such as LIMB currently under development.

PLANS FOR THE COMING YEAR:

- Continued experiments on devolatilization and desulfurization kinetics.
- Experiments with the double screw feeder -- Simultaneous Pyrolysis and Desulfurization.

- Evaluation of combustion characteristics of char and gas products.
- Economic evaluation and scale-up design.

II. HIGHLIGHT ACCOMPLISHMENTS

The system consists primarily of an auger feed tube which is used to both convey and provide desulfurization of a high sulfur coal feedstock. The coal is conveyed at temperatures ranging from 350 to 550 °C and under normal atmospheric pressure. Under these mild processing conditions, the coal partially pyrolizes and emits sulfur in the form of hydrogen sulfide while maintaining a relatively high heating value in the char product. The evolved gases are evacuated from the reactor (the feed tube) to another absorbing bed where H_2S reacts with the sorbent, usually lime or limestone. The resultant sorbent utilization is substantially higher than the values found in current dry scrubbing system and the produced low-sulfur char may then be used in a conventional steam boiler.

Based on the results of a limited number of tests on an Ohio No. 8 coal, the values of the total mass of coal tested (M_i) and recovered (M_f) as well as percent sulfur in the product char are recorded first for the various coal residence times. The kinetics of desulfurization and devolatilization are assumed to be proportional to the amount of "escapable" sulfur or volatiles remaining in the char at any time. Thus, a modified form of linear rate form may be written as

$$-\frac{dS}{dt} = k_S(S - S_\infty) \qquad (1)$$

$$-\frac{dM}{dt} = k_V(M - M_\infty) \qquad (2)$$

where,

t is the reaction time

k_S and k_V are the desulfurization rate constant and the devolatilization rate constant, respectively, and

the subscript ∞ represents the total escapable amount of sulfur or volatile at infinite reaction time.

It is not known at this time if the sulfur loss can be solely attributed to organic sulfur loss, or from some other mechanism such as the decomposition of ferric sulfide (pyrite) to ferrous sulfide (troilite) in the inorganic sulfur fraction.

From the Arrhenius plot, activation energies for desulfurization and devolatilization are calculated. These are 13,452 cal/mol for desulfurization and 33,400 cal/mol for devolatilization. These values indicate more temperature dependency for devolatilization. We will revise these values as more experimental values are obtained.

III. ARTICLES AND PRESENTATIONS

Yu, X. L., T. C. Keener "A Novel Coal Feeder For the Production of Low Sulfur Fuel," Air & Waste Management 83rd Annual Meeting, June 1990, Pittsburgh.

TITLE: Predictive Models for Circulating Fluidized Bed Combustors

DATE: April 16, 1991

PIs: Dimitri Gidaspow

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Aubrey L. Miller and Umesh Jayaswal, Ph.D. Candidates

INSTITUTION/ORGANIZATION: Department of Chemical Engineering,
Illinois Institute of Technology, Chicago, IL 60616; 312/567-3045

GRANT NO.: DE-FG 22-89PC89769

PERIOD OF PERFORMANCE: 9-1-89 to 8-30-93

I. ABSTRACT

OBJECTIVE:

The overall objective of this investigation is to develop experimentally verified hydrodynamic models for circulating fluidized bed (CFB) combustors.

Hydrodynamic models were developed for bubbling fluidized bed reactors by the U.S. Department of Energy and by IIT. The IIT code is being used by several former IIT graduates at two national laboratories by M. Syamlal Ph.D., (1985) at Morgantown Energy Technology Center and by J. Bouillard, Ph.D. (1986) and others at Argonne National Laboratory who have a joint DOE-Industry sponsored project on computation of tube erosion in bubbling fluidized bed combustors. No hydrodynamic models, except for a steady state, one dimensional model by R.W. Breault of Riley Stoker Corporation, are available in the open literature for CFBs.

WORK DONE AND CONCLUSIONS:

II. HIGHLIGHT OF ACCOMPLISHMENTS

Flow regimes of dense phase vertical pneumatic transport of solids, referred to in the literature as circulating fluidized beds, have been computed using a generalization of the Navier-Stokes' equations for two fluids. In the less dense regime corresponding to volume fractions of solids of about one percent, the flow consists of centrally upward moving solids and downward moving clusters. The computations agree with observations made by high speed movies and with measurements of radial solids concentrations and velocities. In the dense regime, corresponding to volume fractions of about ten percent, a core-annulus type of regime is obtained with solids descending down at the wall. The computed voidage distributions and velocity profiles agree with measurements done at the Institute of Gas Technology (Tsuo and Gidaspow, 1990).

As an example of the capability of our computer code, flows with and without reaction through a cross-section of a commercial circulating fluidized bed combustor were simulated. The volume fraction of solids in the riser part of the combustor was high near the inlet and then reached a fully-developed flow condition as expected. The system has large asymmetries, downflow of solids near some walls and operates in an oscillatory mode which promotes good heat and mass transfer. The discharge rate from the standpipe into the riser corresponds to critical flow of solids with a velocity of about one meter per second, as experimentally observed in such systems (Gidaspow, et al. 1990).

In a Ph.D. investigation being completed Aubrey L. Miller measured particle concentration profiles using an x-ray probe and flux profiles using an extraction probe for three sections of a CFB. Using these data and pressure drop information he computed particulate viscosities as a function of volume fraction of solids. The viscosities measured in the CFB are being compared to kinetic theory predictions which were obtained this year for the reasonably dilute CFB regime. Preliminary results indicate that in order to obtain a match between the kinetic theory and the measurements, the restitution coefficient of particles must be very close to unity.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

The purpose of these models is to help American industry design and scale-up CFB combustors that are capable of burning U.S. Eastern high sulfur coals with low SO_x and NO_x emissions.

PLANS FOR THE COMING YEAR:

The extension of the kinetic theory of Ding and Gidaspow (1990) to the dilute regime will be compared to the measurements done by Aubrey Miller in the CFB. Later we plan to add to the model the reaction kinetics of coal, dolomite with SO_2 and perhaps NO_x reactions to obtain a complete CFB model.

III. ARTICLES AND PRESENTATIONS

J. Ding and D. Gidaspow, "A Bubbling Fluidization Model Using Kinetic Theory of Granular Flow," AIChE Journal 36, 523-538 (1990).

D. Gidaspow, J. Ding and U.K. Jayaswal, "Multiphase Navier-Stokes Equation Solver in "Numerical Methods for Multiphase Flows," FED-Vol. 91, 47-56, American Society of Mechanical Engineers (1990).

Tsuo, Y.P. and Gidaspow, D., "Computation of Flow Patterns in Circulating Fluidized Beds." AIChE Journal 36, 885-896 (1990).

TITLE: COAL PLASTICITY AT HIGH HEATING RATES AND TEMPERATURESDATE: APRIL, 1991

PIs: Prof. Jack B. Howard and Dr. William A. Peters

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Sarakorn Gerjarusak, Ph.D., Chemical Engineering

INSTITUTION/ORGANIZATION: MIT, Energy Laboratory and Dept. of Chemical Engineering
Cambridge, MA 02139
Tel.: (617) 253-4574 (JBH); -3433 (WAP)

GRANT NO. DE-FG22-89PC89773

PERIOD OF PERFORMANCE: 9/1/89 - 8/31/92

I. ABSTRACT

OBJECTIVE: Our objective is to obtain improved, quantitative understanding of the transient plasticity of softening coals under high heating rates and other reaction and pretreatment conditions of scientific and practical interest. To these ends, the softening and resolidification behavior of two U.S. bituminous coals will be measured with a rapid-heating, fast response, high-temperature coal plastometer. Apparent viscosity, softening temperature, plastic period, and resolidification time will be measured for molten coal as a function of independent variations in reaction conditions (e.g. temperature, heating rate). Intra-coal inventory and molecular weight distribution of pyridine extractables will also be measured using a rapid quench, electrical screen heater coal pyrolysis reactor. The yield of extractables is taken as representative of the intra-coal inventory of plasticing agent (metaplast) within the coal at the instant of quenching. Coal plasticity kinetics will be mathematically modeled from generation and depletion rates of extractables, by taking advantage of a correlation between the viscosity of a suspension and the concentration of deformable medium (here extractables) in that suspension.

WORK DONE AND CONCLUSIONS: A rapid heating rate, high temperature coal plastometer was previously developed in our laboratory [Fong, W.S., Sc.D. Thesis, Chem. Eng. (1986), et. al., Rev. Sci. Instr. 56, 586-591 (1985)]. During the past year this equipment has been modified to improve both accuracy and precision. With a parallel plate shearing disk, friction between mechanical parts, and misalignment of the disk can affect the observed viscosities. By performing runs at two different shear rates these effects were accounted for, and good agreement was then found between the measured apparent viscosity of a highly viscous liquid standard and the apparent viscosity quoted by the supplier. However, to reduce frictional and misalignment effects a shearing disk with a double cone-and-plate geometry has been designed, installed, and calibrated. This configeration has the additional benefit of providing a simple mathematical relationship between apparent viscosity and torque, even for a non-Newtonian fluid. These improvements are expected to provide additional flexibility and reliability in c systematic studies of coal plasticity.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM: Softening coals are candidate or actual feedstocks in metallurgical coke manufacture, coal gasification, and liquefaction, and combustion. Their thermoplastic behavior can result in caking and agglomeration of the coal particles during process applications, which may in turn contribute to desirable process performance: e.g. generation of a strong and reactive product in metallurgical coke manufacture, or to undesirable operating behavior: e.g. bed bogging in fixed or fluidized bed gasifiers, and

swelling and agglomeration during pulverized coal combustion resulting in larger diameter char particles requiring longer burnout times. Plasticity effects can be more pronounced at elevated pressures and in the presence of hydrogen. Plasticity may also affect the extent of intraparticle secondary reactions of newly formed pyrolysis volatiles during coal devolatilization and, hence, the offgas composition and extent of carbon utilization in gasification and combustion. Transient plasticity may also influence coal liquefaction behavior including hydrogen transfer and conversion reactivity. Better fundamental understanding of coal plasticity kinetics, will thus aid process design and optimization, including selection of pretreatment and operating procedures to enhance or inhibit plasticity, as desired.

The project will benefit fundamental coal science by contributing new data and kinetic models on the temperature-time variation of the plasticity of different coals, at rapid heating rates. The work is also expected to determine if molten coal exhibits significant non-Newtonian behavior, and to elucidate the effect of physical and chemical processes on transient extractables inventories and plasticity kinetics. Data on apparent viscosities of molten coal are useful for estimating the corresponding diffusivities of extractables in molten coal. These diffusivities are in turn of value for estimating and modeling transport rates for tar-like species within molten coal.

PLANS FOR THE COMING YEAR: The plastometer will be used to measure effects of temperature and heating rate on the apparent viscosity of softening coal (e.g. Pittsburgh No. 8 and Illinois No. 6), and of certain softening polymers that may give insights on the thermal softening behavior of coal itself (e.g. polystyrene).

II. HIGHLIGHT ACCOMPLISHMENTS

- A high temperature high heating rate plastometer has been modified to improve instrument reliability, and facilitate data analysis.
- A double cone-and-plate geometry shearing disk has been designed, installed, and calibrated.

III. ARTICLES AND PRESENTATIONS

1. Howard, J.B., Darivakis, G.S., Gerjarusak, S., Peters, W.A., "Coal Plasticity at High Heating Rates and Temperatures", presented by J.B. Howard at the USDOE Office of Program Analysis, evaluation of Project DE-FG22-89PC89773, Coraopolis/Pittsburgh, October (1990).

DATE: March 27, 1991

TITLE: Chemical Kinetics and Transport Processes in Supercritical Fluid Extraction of Coal

P.I.s: Ben J. McCoy, J. M. Smith
STUDENT AND THE DEGREE REGISTERED: Mr. Ming Wang (Ph.D. program)
INSTITUTION/ORGANIZATION:
Department of Chemical Engineering
University of California, Davis, CA 95616
(916) 752-6923

GRANT NO.: DOE DE-FG22-90PC90288
PERIOD OF PERFORMANCE: 8/10/90-8/8/92

I. ABSTRACT

OBJECTIVE: Investigate the supercritical fluid extraction, both catalytic and noncatalytic, of hydrocarbons from coal.

WORK DONE AND CONCLUSIONS: Continuous-flow extraction experiments have been conducted on Montana lignite and Illinois No. 6 coal with supercritical tert-butanol. The fraction extracted and the aromatic content of the extract increased with temperature. Insight into the chemical nature of the extract, and the effect of solvent interaction with coal, was obtained by detailed GC-MS analysis of the extract, both liquid and gas. The results indicate that tert-butanol, a hydrogen donor solvent, enhances the thermal degradation of coal, and that higher conversion of supercritical extraction can be achieved with tert-butanol than with toluene under the same conditions.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: Supercritical extraction of coal has been proposed for the production of liquid fuels and chemical feedstocks. Information on coal structure and thermolytic (or non-thermolytic) kinetics and mechanisms may also be obtained with supercritical processing.

PLANS FOR THE COMING YEAR: We are presently conducting experiments on supercritical extraction of coal that allow continuous monitoring of the extract concentration as a function of time. To describe this data, mathematical models for the chemical reaction kinetics and mass transfer processes are being developed for realistic models of coal extraction.

II. HIGHLIGHT ACCOMPLISHMENTS

We have adapted existing supercritical fluid apparatus in our laboratory, used previously for extraction of oil shale and biomass, to the extraction of coal particles. Our initial studies have provided the data and information for the article and presentation listed below.

III. ARTICLES AND PRESENTATIONS

1) C. Zhang, J. M. Smith, B. J. McCoy, "Supercritical Fluid Extraction of Lignite and Bituminous Coal with tert-Butanol," March (1991); submitted to I&EC Research.
2) C. Zhang, M. Wang, B. J. McCoy, "Extraction of Bituminous Coal with Supercritical Butanol," February (1991); to be presented at the 2nd International Symposium on Supercritical Fluid Processes, Boston, May 1991.

TITLE: Combustion Fume Structure and Dynamics DATE: April 8, 1991

P.I.: Richard C. Flagan

STUDENTS AND THE DEGREES FOR WHICH THEY ARE REGISTERED:

Donald Dabdub: Ph.D. student in Chemical Engineering
Melissa Richmond: Ph.D. Student in Mechanical Engineering

INSTITUTION/ORGANIZATION:

California Institute of Technology 210-41
Pasadena, CA 91125
(818) 356-4383

GRANT NO.: DE-FG22-90PC90286

PERIOD OF PERFORMANCE: 8/15/90-4/8/91

I. ABSTRACT

OBJECTIVE:

This comprehensive study of the dynamics of pyrogenous fumes is designed to develop and validate a model of the formation and evolution of fine particles from minerals volatilized during coal combustion. Of particular interest is the the structure that results when particles do not coalesce immediately upon agglomeration, the influence of sintering kinetics on that structure, and the influence of that structure on agglomeration kinetics. Focussing on the fundamental physics that govern the particle structure, size, and composition of fume particles formed in coal combustion, the experimental program is based upon model systems that have been designed to minimize the experimental uncertainties.

WORK DONE AND CONCLUSIONS:

Simulations

Diffusion limited aggregation (DLA) and cluster--cluster aggregation (CCA) simulations yield particles with substantially different structures. DLA clusters are formed by the addition of small, highly mobile structures to a much larger particle. The small particles can penetrate deep within the larger agglomerate so the resulting structures are relatively dense. For diffusion limited aggregation to occur in flame, the small particles must be continuously generated by nucleation and consumed by coagulation with previously formed particles. On the other hand, when similarly sized agglomerates coagulate, interpenetration is unlikely, and low density agglomerates result. An early burst of nucleation followed by extensive agglomeration will lead to such structures. The fractal dimensions of such agglomerates may be expected to increase if the primary particles that comprise the agglomerate sinter together. Intermediate fractal dimensions may also result if new particles are continuously added to a coagulating aerosol. In a coal flame, this could result from mineral matter volatilizing throughout the burn time of the coal char particle. Because of the large composition and temperature gradients immediately surrounding the hot char particle, vapors released at the char surface will nucleate before they diffuse more than a few radii away. Thermophoresis will tend to drive the new nuclei and any previously formed particles away from the char particles, thus bringing new and old particles together so that they may agglomerate. The influence of this intermediate growth environment on particle structure has not previously been explored.

We have undertaken simulations of one such condition with dual purposes: (*i*) to understand the relationship between the relative rates of new particle formation and agglomeration on particle structure; and (*ii*) identification of a method for synthesis of particles with controllable fractal dimension would add an important degree of freedom to our experimental design. The diffusion limited aggregation case, while theoretically interesting, is extremely difficult to realize in the laboratory. Through numerical simulations of agglomeration, we seek to define physically realizable systems that can produce particles with a spectrum of fractal dimensions. With such an agglomerate source, we can rigorously probe the influence of fractal dimension on agglomerate aerodynamics and coagulation kinetics.

A conceptual experiment would be to feed the effluent from a source of fine particles into a stirred reactor where the particles would continuously be exposed to more aged particles. Coagulation would then proceed between particles of dissimilar sizes as well as between particles of comparable size. Because the collision frequency between particles of substantially different sizes is much larger than that between particles of the same size, it is anticipated that the small particles will rapidly deposit on those large particles that are present. Preliminary two dimensional simulations for particle growth in a stirred reactor indicate that agglomerates with fractal dimensions approaching that of DLA can be generated with appropriate control of the residence time distribution , suggesting that a relatively simple experimental system that approaches DLA can be built. Moreover, by using reaction schemes that alter the residence time distribution, a continuum of agglomerate sources can be developed for studies of agglomerate dynamics.

Experimental

The experimental program is based upon model systems that allow precise control of the aerosol concentrations and properties to promote a fundamental understanding of the dynamics of agglomerate aerosols. By avoiding the complications of heterogeneous coal minerals and the associated property variations and uncertainty in fume source rates, precise measurements of fume evolution becomes possible. Metal alkoxides are being pyrolyzed to produce single component metal oxide fumes. Initial experiments have employed a small reactor to synthesize TiO_2 fumes by pyrolysis of titanium tetraisopropoxide. The aerosols produced in this low residence time reactor will be allowed to agglomerate at room temperature to make coagulation rate measurements. During the start-up phase of this research, the nature of the particles produced by this small reactor have been probed using the scanning electrical mobility spectrometer (SEMS) developed at Caltech. Preparations are also being made for the characterization of the particle structures by in situ small angle light scattering and electron microscopy.

II. HIGHLIGHT ACCOMPLISHMENTS

An approach has been developed that should allow particles of controllable fractal dimension to be synthesized, enabling direct probing of the relationship between fractal structure and the dynamics of the aerosol.

III. ARTICLES AND PRESENTATIONS

Richard C. Flagan, "On the Structure of Pyrogenous Fumes," presented at Kerr McGee Corporation, Oklahoma City, OK, April 16, 1991.

Date: April 8, 1991

TITLE: Equilibrium and Volumetric Data and Model Development of Coal Fluids

P.I.(s): R. L. Robinson, Jr.
K. A. M. Gasem

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED: S. Srivatsan, M.S.
A. Sura, M.S.
X. Yi, M.S.

INSTITUTION/ORGANIZATION: Oklahoma State University
Stillwater, OK 74078
(405) 744-5280

CONTRACT NO.: DE-FG22-90PC90302

PERIOD OF PERFORMANCE: 1 October 1990 - 30 September 1993

I. ABSTRACT

OBJECTIVE: The specific objectives of the work proposed herein include:

- Development of an experimental facility having the capability to provide data on equilibrium phase compositions (solubilities) and liquid densities, and doing so with greater accuracy and speed than our previous facility.
- Measurement of equilibrium phase properties for systematically-selected mixtures - specifically those containing important solute gases (such as hydrogen, carbon monoxide, carbon dioxide, methane, ethane, carbonyl sulfide, ammonia) in a series of heavy paraffinic, naphthenic and aromatic solvents (e.g., n-decane, n-eicosane, n-triacontane, n-tetracontane; cyclohexane, decalin, perhydrophenanthrene, perhydropyrene; benzene, naphthalene, phenanthrene, pyrene).
- Testing/development of correlation frameworks for representing the phase behavior of fluids of the type encountered in coal-conversion processes.
- Generalization of parameters in the correlation frameworks to enable accurate predictions for systems of the type studied, permitting predictions to be made for systems and conditions other than those for which experimental data are available.

WORK DONE AND CONCLUSIONS: During the past period, measurements have been made for the solubility of methane in n-hexane (n-C_6), n-dodecane (n-C_{12}), and toluene (C_6). Similar data were obtained for carbon monoxide in n-eicosane (n-C_{20}). In general, these measurements were over the temperature range 323 to 423 K, pressures to 10 MPa and solute mole fraction to 0.30.

The methane and carbon monoxide solubilities can be described accurately with cubic equations of state such as the Soave or Peng-Robinson equation. The precision of these descriptions varies; average errors are about 0.002 mole

fraction when a single interaction parameter, k_{12}, is used for each isotherm and 0.001 when two parameters, k_{12} and l_{12}, are employed for each isotherm. The experimental data provided by this project can serve as an excellent basis for determining parameters in any selected model to describe phase behavior. Moreover, our systematic studies of selected solutes in a series of solvents from the same molecular class will facilitate generalization of model parameters.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The ultimate goal of this work is to improve the abilities of predictive models for representation of vapor-liquid phase equilibria in mixtures typical of those encountered in production and processing of coal-derived fluids. Since accurate prediction of such phase behavior is critical to the design of all steps in the process in which multiple phases occur, adequate models for phase behavior predictions are of value in many process design and optimization calculations.

PLANS FOR THE COMING YEAR: In the coming period, measurements will be completed for the solubility of carbon monoxide in a series of paraffinic, naphthenic, and aromatic solvents. In addition, generalized-parameter descriptions, using selected equations of state, will be extended to the carbon monoxide / hydrocarbon mixtures.

II. HIGHLIGHT ACCOMPLISHMENTS

Experimental solubilities have been measured for the following mixtures:

- methane + n-hexane: 37.3, 71.1, 104.4°C
- methane + n-dodecane: 50.0, 100.0°C
- methane + toluene: 40.0, 65.5, 150.0°C
- carbon monoxide + n-eicosane: 50.0, 100.0, 150°C

TITLE: Characterization of Multiphase Flow during Air-Sparged Hydrocyclone Flotation by X-Ray CT

DATE: 21 March, 1991

P.I.: J. D. Miller, Professor of Metallurgical Engineering

STUDENT AND THE DEGREE FOR WHICH THEY ARE REGISTERED: Avimanyu Das, Ph.D. Metallurgical Engineering

INSTITUTION/ORGANIZATION:
Dept. of Metallurgical Engineering
University of Utah
216 W. C. Browning Bldg.
Salt Lake City UT 84112

(801) 581-6386

GRANT NO.: DE-FG22-90PC90311

PERIOD OF PERFORMANCE: 8/14/90 through 8/13/93

I. ABSTRACT

OBJECTIVE:

Recent research carried out at the University of Utah indicates that x-ray computed tomography (CT) can provide a new dimension in the analysis of multiphase fluid-flow behavior. With such measurements, dispersed-phase concentration gradients in the swirl layer and froth phase of the air-sparged hydrocyclone can be determined during the actual flotation process. In this regard, the phenomenological details of multiphase flow in the air-sparged hydrocyclone are to be examined by x-ray computed tomography. In this program it is anticipated that time-averaged density variations can be established as a function of design and operating variables in order to more fully explain the observed flotation response of coal slurries and the extent to which ash and sulfur can be eliminated.

WORK DONE AND CONCLUSIONS:

Discussions with the operators of the x-ray CT facility were held to determine the procedures to be followed for making the necessary CT measurements.

Preliminary measurements have been made to determine the effect of air-sparged hydrocyclone orientation on flotation behavior and fluid-flow characteristics. The results indicate that the system can be studied in the horizontal position without significant change in fluid-flow behavior.

Earlier x-ray CT measurements have been analyzed to make some initial estimate of the effect of process variables in a water/frother-only system. It was observed that, with an increase in either frother level or air flowrate, the air core on the axis of the air-sparged hydrocyclone significantly increased in size. These x-ray CT data support earlier speculations based on high-speed video measurements.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Air-sparged hydrocyclone (ASH) technology shows promising potential for high-capacity flotation in the coal industry. This position is supported by the results from a two-inch air-sparged hydrocyclone test program just completed in 1989 by Penelec at the EPRI/CQDC facility in Homer

City, Pennsylvania, as part of a DOE/PETC-sponsored proof-of-concept project. The distinctive feature of air-sparged hydrocyclone flotation is its high specific capacity, 100 times the specific capacity of conventional mechanical or column flotation equipment.

A complete understanding of the multiphase fluid flow and flotation phenomena inside the air-sparged hydrocyclone is essential for further advances in the design, operation, and scale-up of the air-sparged hydrocyclone. The fundamental studies in this area have achieved only partial success, mainly due to experimental limitations. It is expected that as a result of this research program improved design criteria and better operating conditions can be established for more effective rejection of mineral matter, particularly pyritic sulfur, during ASH flotation of fine coal.

PLANS FOR THE COMING YEAR:

Plans for the coming year include detailed experimentation to measure, by x-ray CT, density gradients that exist during air-sparged hydrocyclone flotation. This research will begin with experiments involving only air/water/frother and advance to the more complex case involving both hydrophilic and hydrophobic particles.

II. HIGHLIGHT ACCOMPLISHMENTS

1. Made arrangements for use of x-ray CT facilities.
2. Reviewed preliminary x-ray CT data to determine procedure for future detailed experimentation.
3. Established procedure and codes necessary to display x-ray CT images on supergraphics workstation and do 3-D reconstruction for scientific visualization of the time-averaged multiphase flow.

III. ARTICLES AND PRESENTATIONS

S. Gopalakrishnan, Y. Ye, and J. D. Miller, "Dimensionless Analysis of Process Variables in Air-Sparged Hydrocyclone (ASH) Flotation of Fine Coal," Coal Preparation: An International Journal, 9, to be published (1991).

J. D. Miller, C. L. Lin, and A. B. Cortes, "Review of X-Ray Computed Tomography and its Applications in Mineral Processing," Mineral Processing and Extractive Metallurgy Review, 7, 1-18 (1990).

J. D. Miller, Y. Ye, and S. Gopalakrishnan, "Preliminary Comparison of the Performance of the ASH-2C with the ASH-6C for Fine Coal Flotation," Presented at the Engineering Foundation Conference, Palm Coast, Florida, December 1-5 (1990).

Y. Ye, S. Gopalakrishnan, and J. D. Miller, "Scale-up and Design of Large Diameter Air-Sparged Hydrocyclones," 21st Annual Meeting of the Fine Particle Society, San Diego, California, August 21-25 (1990).

Y, Ye, S. Gopalakrishnan, and J. D. Miller, "Scale-up and Design Considerations in Air-Sparged Hydrocyclone Flotation of Fine Coal," 1991 SME Annual Meeting, Denver, Colorado, February 25-28 (1991).

J. D. Miller, "The Status of Air-Sparged Hydrocyclone Flotation Technology," 4th Asian Symposium on Mineral Processing, Manila, Philippines, April 9-11 (1991).

ENVIRONMENTAL SCIENCE

Date: April 9, 1991

TITLE: PLASMA ASSISTED NO_x REDUCTION
IN EXISTING COAL COMBUSTORS

PI's: Professors S.C. Yao and Professor T. Russell

STUDENTS: Ms. Q. Zhou, Ph.D. Student
Mr. J. Boyle, Ph.D. Student

INSTITUTION: Department of Mechanical Engineering
Carnegie Mellon University
Pittsburgh, Pennsylvania 15213
Telephone: (412) 268-2508 or (412) 268-3614

GRANT NO.: DE-FG22-88PC88932

PERIOD OF PERFORMANCE: 9/1/88 - 8/31/91

I. ABSTRACT

OBJECTIVE: To explore the feasibility of using plasma produced chemical radicals to interact with the coal combustion processes to reduce NO_x emissions.

WORK DONE AND CONCLUSIONS: A complete analysis of the chemical kinetics of ammonia and the radicals derivatives of ammonia has been performed. Additional species can favorably modify the kinetics to increase radical lifetimes and process efficiency. The chemical model is being altered to model the freezing the reactions by rapid expansion through a nozzle. Modeling of nitrogen plasma injection,unlike ammonia, has been shown to be ineffective chemically and energetically.

CMU combustion facility modification has been completed and inductively coupled plasma system has been converted for the present application. A series of tests has been performed which have supported the computational results. Additional methods, and optimization of current methods, are being studied to increase process effectiveness.

These results, which are supported by those found at the PETC facility, show that NOx reduction by the injection of molecular radicals is effective. The reduction is less sensitive to combustion gas temperature and less susceptible to ammonia slip than thermal $deNO_x$.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The use of ammonia plasma in NO_x reduction appears as feasible for the injection at the downstream of the combustor, considering both the chemical kinetics and energy efficiency. Other practical factors need be considered to make a more definitive statement. Tests show that using NH_2 radical injection upstream and within the combustion zone can also reduce NO.

PLANS FOR THE COMING YEAR: Analytical and computational study of the transport involving the plasma radicals in the fluid flow will be performed to fully understand the fundamental mechanisms of this process. Extensive tests on the low power plasma process will be performed. Consideration of additional plasma carrier gases, such as nitrogen, will be included to improve energy efficiency. Search for the optimal scheme of injection will be conducted together theoretical analysis of the database.

Enhanced chemical kinetic studies will explore the possibility of using compounds, in addition to NH_3, for injection. Computational results and experiments indicate methane is a good candidate. However, optimal conditions have not been found.

II. HIGHLIGHT ACCOMPLISHMENTS

1. Numerical modeling has shown that the reduction of NO by the injection of the NH_2 radical is very promising. The NH_2 radical injection scheme functions remarkably well, even at transient local temperatures as high as 4000 K.

2. Chemical Kinetic modeling is progressing which will allow for modeling of rapid temperature and pressure changes to simulate flow through a supersonic nozzle. The numerical code is being altered to accept expressions defining transient thermodynamic conditions.

3. A complete analysis of the reduction of NO by the injection of the N radical was found to be ineffective in the presence of excess oxygen and carbon dioxide for typical post-combustion conditions. The reaction of the N radical with stack gases creates more NO than is consumed because of the excess oxidizing potential of the mixture at any practical temperatures.

4. A new chemical mechanism has been constructed which more completely define the complex reaction system found in post-combustion gases containing C/H/O and N.

5. Modeling of the mixing of plasma jet and fuel jet are in progress. The coal particles are modeled using a newly invented "Group" approach; the transport and diffusion of plasma pockets with highly variable properties have been considered.

6. Test results from both CMU and PETC show that downstream plasma injection for NO_x reduction is effective. Although the facilities and plasma generators were substantially different, the results were very similar.

7. A laboratory scale facility at CMU has been constructed and a series of tests have been performed. A reduction of 86% in initial NOx has been achieved by the injection of ammonia radicals. Plasma injection is more effective than the thermal deNOx process at the same conditions.

8. Test results at CMU showed NO_x reduction increases when ammonia flow rate and argon flow rate increase and when plasma power and the amount of excess air in the combustion gases decrease.

9. A combined chemical and transport model has been postulated to explain the mechanism of NO_x reduction by plasma injection. Investigation of the fluid and chemical dynamics of this process is in progress.

10. Downstream radical injection tests performed at the DoE-PETC facility have produced up to 90% NOx reduction by the injection of ammonia in argon plasma. Reduction is achieved at temperatures substantially lower than thermal $deNO_x$ and with insignificant ammonia slip.

III. PUBLICATIONS

1. "Reduction of NO_x Employing Chemical Radical Species", John Boyle, Qian Zhou, Ted Russell, S.C. Yao, presented at 5th Annual Coal Preparation, Utilization and Environmental Control Contractor Conference. July 31-August 3, 1989.

2. "The Effect of Plasma Injection on the NO_x Control of Pulverized Coal Combustors", Qian Zhou Ph.D. Thesis, Carnegie Mellon University, 1991.

3 "Radical Injection Test Report", PETC-DoE, John M. Boyle, 1990,1991.

Date: April 10, 1991

Title: Indirect Electrolysis Process for Removal of Pollutants from Coal Liquids

PI's: Carl A. Koval and Richard D. Noble

Students: Steven Drew, Naceur Jemaa and Doug Wedman (Ph.D.),Kenan Ozekin (M.S.)

Institution: University of Colorado, Dept. of Chemistry (Koval) or Dept. of
Chemical Engineering (Noble) Boulder, CO 80309 (303) 492-5564

Grant No.: DE-FG22-88PC88916

Period of Performance: 10-1-88 through 9-31-91

I. ABSTRACT

OBJECTIVE: We are exploring a novel separation process for the removal of nonvolatile nitrogen and sulfur pollutants from coal liquids. The process involves the binding of the pollutants to metalloporphyrin carriers. The binding is reversed by electrochemical oxidation of the carrier and the active form of the carrier is regenerated by reductive electrolysis. The efficiency of the process is evaluated by investigating the removal of a representative set of pollutants from solutions of iso-octane. Separations involving individual pollutants and mixtures of pollutants will be examined. Mathematical models which utilize the physical properties that are relevant to the separation process have been developed. These models will be used to determine conditions that produce optimal separation efficiencies.

WORK DONE AND CONCLUSIONS:

Experimental studies with iron porphyrins and ion-exchange polymers.

Initial experimentation focused on demonstrating the validity of the chemical process proposed for the reversible complexation of nitrogen compounds to iron porphyrins within an ion-exchange polymer. The critical steps in this process involve the electrochemical redox steps and the extraction/release steps. The electrochemical redox step has been demonstrated for iron tetra(N-methyl)pyridyl porphyrin (FeTMPyP) exchanged into a Nafion polymer membrane. Eu(II) ion was used for the reduction of Fe(III)TMPyP. Subsequent exposure of the membrane to air oxidizes the Fe(II)TMPyP/Nafion within about a minute. This series of redox steps can be cycled up to five times with only about five percent loss of absorbance due to porphyrin degradation. The extraction/release steps have been shown to occur for various nitrogen compounds. This was demonstrated by placing an Fe(II)TMPyP-Nafion membrane under inert atmosphere into an aqueous solution of imidazole. This series of reactions was also demonstrated for isoquinoline when extracted from an iso-octane solution.

Development of Mathematical Models

The cyclical process for the removal of pollutants from a hydrocarbon phase using ion-exchange polymers was analyzed. In the analysis, there are three main steps: adsorption of the pollutant into the polymer containing the complexing agent in the active form; contacting the polymer with a chemical mediator that results in oxidation of the complexing agent and release of the pollutant; and, contacting the polymer with a second chemical mediator that results in reduction of the complexing agent to its active form. In the first step, which involves diffusion of the pollutant into the polymer followed by a fast reversible reaction, the system can be described by a non-linear partial differential equation which describes an ordinary differential equation on the boundary. This equation is solved with the appropriate computer code and the results give the distribution of the pollutant in the polymer bead and in the hydrocarbon phase. In the second step, as the mediator diffuses into the polymer the complexation reaction is reversed and there is countercurrent diffusion of the pollutant out of the polymer. This is a moving boundary problem which can be described by a partial differential equation. By assuming low concentrations of mediator in the contacting solution, the equation can be solved analytically using the steady state assumption. The results show the pollutant distribution in the bead and at the reaction front. In the third step, the second mediator diffuses into the particle and reactivates the complexing agent. The solution to this problem is similar to step one

Investigation of Redox Polymers on Electrodes.

Based on calculations, two problems with the initially proposed process were identified. The density of sites commercially available in ion-exchange polymers limits the amount of complexing agent that is incorporated and thereby limits the amount of pollutant that can be adsorbed. The models described above indicate that modulation of the redox state of the complexing agent will be time consuming and the use of these materials is also somewhat cumbersome. In order to circumvent these difficulties, we are investigating complexing agents that can be polymerized on the surface of high surface area electrodes.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

In order to develop a focused national and regional program of university research on coal science, the Department is particularly interested in innovative, fundamental research pertinent to coal conversion and utilization including Environmental Science.

Sulfur and nitrogen compounds contained in crude oil and synthetic fuels are a source of many water and air pollution problems. Present technology requires high pressure catalytic hydrogenation to reduce their levels. This process is expensive, requires large reactor and catalyst volumes, and is not specific. Hydrogenation saturates C-H bonds as well as heteroatom sites. Furthermore, the entire fluid volume must be processed. This project is an attempt to develop a new technology for selective removal of nitrogen and sulfur compounds from crude fuels.

In addition, the application requirements and eligibility for this grant state that "The involvement of professors and students to generate fresh research ideas and ensure a future supply of coal-scientists and engineers is a key purpose of this program."

PLANS FOR THE UPCOMING YEAR:

1. Complete mathematical analysis of stages process.
2. Develop procedures for obtaining high surface loadings of aminoporphyrins, incorporate metals such as Fe(III) and CO(III), show that the oxidation states of these metals can be electrochemically modulated, examine the extraction of various pollutants.

II. HIGHLIGHT ACCOMPLISHMENTS

1. We have demonstrated the validity of the proposed reaction scheme in an ion-exchange membrane by proving that the necessary redox and binding processes can occur.
2. We have developed mathematical models describing the three main stages of the cyclical process.
3. We are investigating the use of aminoporphyrins for the formation of polymer coatings directly on electrode surfaces.

III. ARTICLES AND PRESENTATIONS

C.A. Koval, S.M. Drew, Y. Jianhan, R.D. Noble, "Electrochemistry of Axial a Water-Soluble Iron Porphyrin and Its Exploitation for Selective Removal and Concentration of Environmentally Hazardous Materials Via Electrochemically Modulated Complexation," Inorg. Chem., (1990) 29, 4708-14.

N. Jemaa, J. Yu, R.D. Noble, S.M. Drew, D.E. Wedman and C.A. Koval, "Two Methods to Study the Aggregation of Complexing Agents Used to Alter Solute Partitioning Between Phases," I & EC Res., submitted.

K. Ozekin, "Removal of Sulfur and Nitrogen Compounds from an Organic Phase Using Ion-Exchange Polymer, M.S. Thesis, University of Colorado, Boulder, CO , 1991.

S.M. Drew, "The Electrochemistry and Coordination Chemistry of Water Soluble Iron Porphyrins and Their Application to Novel Separation Processes" Ph.D. Thesis, CU, 1989.

R.D. Noble, "Electrochemically Modulated Complexation to Separate and Concentrate Solutes," A.I.Ch.E. Nat. Mtg., November 12, 1990, Chicago, IL.

Date: April 9, 1991

TITLE: Mechanistic and Kinetic Studies of High-Temperature Coal Gas Desulfurization Sorbents

PIs: Adel F. Sarofim, Maria Flytzani-Stephanopoulos

STUDENT(S) AND THE DEGREE FOR WHICH THEY REGISTERED:
Susan Lew (Ph.D.)

INSTITUTION/ORGANIZATION:
Massachusetts Institute of Technology
Department of Chemical Engineering
Rm 66-466; (617) 253-4566
Rm 66-471; (617) 253-3178

GRANT NO.: DE-FG22-88PC88927

PERIOD OF PERFORMANCE: July 27, 1988 to July 27, 1991

I. ABSTRACT

OBJECTIVE: The objectives of this project are to: (i) carry out kinetic measurements of the reduction of Zn-Ti-O mixed oxides to determine the optimum sorbent in terms of composition and chemical phases which yield the desired resistance to zinc loss by reduction, (ii) carry out kinetic measurements of the sulfidation reactions including intrinsic reaction rate and product layer diffusion measurements for both Zn-Ti-O and ZnO materials, and (iii) determine structural changes and chemical phase transformations during sulfidation.

WORK DONE AND CONCLUSIONS: The sulfidation of bulk mixed oxides of zinc and titanium of various compositions and Zn-Ti-O crystalline phases in H_2S-H_2-H_2O-N_2 gas mixtures was investigated in a thermogravimetric apparatus over the temperature range of 400-800°C. Comparative sulfidation experiments with ZnO were also performed. In comparison to ZnO, the use of Zn-Ti-O solids allows raising the operating temperature for desulfurization of hot coal-derived fuel gas, e.g. by as much as 94 degrees Celsius for solids with $(Zn/Ti)_{atomic}=2/3$. The initial sulfidation rate of Zn-Ti-O solids with $(Zn/Ti)_{atomic}\leq 3$ was approximately 1.5-2 times slower than for ZnO. Different zinc titanate phases (i.e. Zn_2TiO_4, $ZnTiO_3$ and $Zn_2Ti_3O_8$) had the same initial sulfidation rate. Similar activation energies (9-10 kcal/mol) were measured for ZnO and Zn-Ti-O sulfidation. No effect of H_2 or H_2O was observed on the initial sulfidation rate. However, at high conversions, rates were decreased as the H_2 concentrations were increased. Fine particles and cracks were observed in sulfided ZnO as a result of ZnO reduction and subsequent vapor phase reaction between Zn and H_2S to form ZnS. These structural effects were largely absent in Zn-Ti-O solids.

The overlapping grain model which allows for randomly overlapping grains successfully predicts the sulfidation profiles of ZnO and Zn-Ti-O sorbents in the

temperature range 400-700°C where the resistances to reaction are due to diffusion through the product layer and the surface reaction. For Zn-Ti-O sorbents, a discrete bimodal grain size distribution was used in the model while for ZnO, a single grain size was used. The activation energies of the product layer diffusion coefficient for ZnO and Zn-Ti-O sulfidation were similar, 26.6 kcal/mol. However, as the relative content of titanium in the solids increased, the pre-exponential factor decreased. Because diffusion in TiO_2 was at least ten times slower than in ZnS, the product layer diffusion in zinc titanate solids was dominated by diffusion through ZnS. The presence of TiO_2 in the product layer merely reduces the cross-sectional diffusion area and increases the tortuosity of the diffusion path. Thus, the product layer diffusion coefficient decreases as the TiO_2 content of the product layer increases.

From this year's results along with the earlier reported data on reduction of Zn-Ti-O solids, it is concluded that the optimum sorbent composition for desulfurization should be based only on the amount of reduction tolerated and the sulfur loading desired. In the absence of H_2O, the best sorbent composition for operation in a fixed-bed reactor is one with an atomic ratio of $(Zn/Ti)_{atomic} \leq 3/1$. A higher percentage of titanium yields no improvement in decreasing the reduction rate and decreases the sulfur loading. However, in the presence of H_2O or for operation in a fluidized bed reactor, a higher percentage of titanium will decrease the reduction rate.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: This project is aimed at measuring kinetics of reduction and sulfidation and identifying reaction-induced structural effects on mixed oxide sorbents of zinc and titanium, presently under development for coal gas desulfurization at high temperatures. As such, the project is significant to the DOE Fossil Energy Program because it directly impacts the development of the Hot Gas Cleanup Technology, which is now recognized as crucial for the efficient and economic coal utilization in coal gasifier-based power plants.

PLANS FOR THE COMING YEAR: This project is scheduled to terminate on July 27, 1991.

II. HIGHLIGHT ACCOMPLISHMENTS

- The use of Zn-Ti-O solids in hot gas desulfurization allows raising the operating temperature above that of ZnO.

- TiO_2 was found to eliminate reaction sites on ZnO in both reduction in wet hydrogen streams and sulfidation. However, above 25 mol % Ti (based on Zn-Ti stoichiometry) no further decrease in initial sulfidation rates took place.

- Sulfidation kinetics were similar for different zinc titanate phases (i.e. Zn_2TiO_4, $Zn_2Ti_3O_8$, and $ZnTiO_3$).

- High hydrogen contents in the sulfidation gas mixture at 800°C produced adverse structural effects on ZnO, as evidenced by development of cracks and fissures. No such effects were observed on Zn_2TiO_4.

- TiO_2 in the Zn-Ti-O sorbents limits sintering of ZnS. Water vapor enhances the sintering of both ZnO and Zn-Ti-O sorbents.
- A discrete bimodal grain size distribution with the random overlapping grain model successfully predicted the sulfidation profiles of Zn-Ti-O sorbents.
- The product layer diffusion coefficient, De, decreased as the TiO_2 content in the product layer increased. Although a drawback of Zn-Ti-O sorbents over ZnO is their lower De, at high temperature and with high sorbent surface area, product layer diffusion is relatively fast compared to the intrinsic sulfidation kinetics.

III. ARTICLES AND PRESENTATIONS

1. S. Lew, K. Jothimurugesan and M. Flytzani-Stephanopoulos, "High-Temperature H_2S Removal from Fuel Gases by Regenerable Zinc Oxide-Titanium Dioxide Sorbents". *I&EC Research*, 1989, 28, 535.
2. M. Flytzani-Stephanopoulos, S. Lew and A.F. Sarofim, "Kinetic and Structural Studies of ZnO and ZnO-TiO_2 in High Temperature Reduction-Sulfidation". Presented at the Annual AIChE Mtg., San Francisco, Nov. 5, 1989.
3. M. Flytzani-Stephanopoulos, S. Lew and A.F. Sarofim, "Hot Gas Desulfurization by Zinc Oxide-Titanium Dioxide Regenerable Sorbents". *ACS Div. Fuel Chemistry Preprints*, 1990, 35 (1), 77.
4. S. Lew "High Temperature Sulfidization and Reduction of Zinc Titanate and Zinc Oxide Sorbents", Ph.D. Dissertation, Massachusetts Institute of Technology, October 1990.
5. S. Lew, A.F. Sarofim and M. Flytzani-Stephanopoulos, "The Reduction of Zinc Titanate and Zinc Oxide-Solids". *Chem. Eng. Sci.* (submitted).
6. S. Lew, A.F. Sarofim and M. Flytzani-Stephanopoulos, "The Sulfidation of Zinc Titanate and Zinc Oxide Solids". *I&EC Research* (submitted).
7. S. Lew, A.F. Sarofim and M. Flytzani-Stephanopoulos", Modeling of the Sulfidation of Zinc-Titanium Oxide Sorbents with Hydrogen Sulfide". *AIChE J.* (submitted).
8. M. Flytzani-Stephanopoulos, S. Lew and A.F. Sarofim, "Hot Coal Gas Desulfurization by Zinc Titanate and Zinc Oxide Solids". To be presented at the Annual AIChE Mtg., Los Angeles, CA, Nov. 17-22, 1991.
9. S. Lew, A.F. Sarofim and M. Flytzani-Stephanopoulos, "Electronic and Geometric Effects of TiO_2 on the Reduction and Sulfidation of ZnO". (in preparation).

April 9, 1991

TITLE: PULSED ELECTRON BEAM PRECHARGER

PI's (Authors): W. Neil Shelton and Wright C. Finney

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

1. Chris Oswald, B.S. in Electrical Engineering, 1991.
2. Mushtaq Sarwar, B.S. in Electrical Engineering, 1991.
3. John Blair, M.S. in Electrical Engineering, 1992.
4. Arnnie Gibson, B.S. in Electrical Engineering, 1992.

INSTITUTION/ORGANIZATION:

Aerosol Physics Group, Department of Physics
The Florida State University, Tallahassee, FL 32306-3016
(904) 644-6552, (904) 644-2878.

GRANT NUMBER: DE-FG22-89PC89768.

PERIOD OF PERFORMANCE: September 1, 1989 - August 31, 1991.

I. ABSTRACT

OBJECTIVE: The specific objective of the Pulsed Electron Beam Precharger project is to further develop the technology of efficiently collecting high resistivity fly ash using a two-stage system composed of an electron beam precharger coupled with an electrostatic precipitator. High resistivity fly ash, produced by burning low sulfur coal in power plant and industrial boilers, limits the operating parameters of conventional electrostatic precipitators by initiating debilitating "back corona". If the particle charging and collecting functions are optimized separately in a two-stage configuration, higher removal efficiencies can be obtained and the back corona problem can largely be avoided.

The process of electron beam ionization of air molecules produces a bipolar plasma of ions and electrons in the precharger. One monopolar fraction (usually negative) is used to charge the dust particles to very high levels nearing the saturation limit. After precharging, the aerosol is removed in a downstream electrostatic collector operated in a back corona-free electrical condition. The superior charging performance of electron beam prechargers is due to the combined effects of space charge enhancement of the charging electric field, and a much superior particle charging by available free electrons.

Pulsed operation of the particle charging electric field is the subject of the present contract research. The advantage of pulsing the electric field lies in the fact that pulsed electric fields can be achieved which are much larger than the breakdown electric field for DC operation, provided that the pulse duration is sufficiently short (200 ns). The direct result is an increase in particle charge due to the increase in electric field during the pulse, and an enhancement of the charging field due to ionic space charge which would persist for some time after the pulse in the presence of a DC bias.

WORK DONE AND CONCLUSIONS: *A laboratory scale closed circuit wind tunnel has been constructed for the test of various experimental electron beam prechargers in two stage operation with an electrostatic precipitator. The electrostatic precipitator acts as a low current collector downstream from the electron beam precharger. The most advanced electron beam precharger design to date (the Mk. III-B) using a 100 keV electron beam source provided the ionization for particle charging. High concentrations of very fine, monodisperse hydrated alumina dust was injected into the wind tunnel. Experiments consisted of establishing the test aerosol baseline concentration, measuring the removal with the electrostatic precipitator alone, and then measuring the removal efficiency while operating the combined two-stage E-beam precharger/electrostatic precipitator. DC voltage of up to 70 kV and pulsed voltage of as high as 80 kV are delivered to the precharger anode using a T-R set and a rotating spark gap power supply, respectively. Pulse characteristics are 60 Hz frequency, 200 ns pulse width, and 20 ns rise time. The charge and mass of individual particles exiting the electron beam precharger was measured using an FSU-developed laser illuminated/oscillating electric field charge vs. radius (Q/A) recording system.*

In one set of particle collection efficiency experiments using a dc electric field in the precharger, an aerosol of fine, high resistivity hydrated alumina dust was removed at an efficiency of over 40 times greater than that using the collector-alone. This was accomplished despite the fact that the particle charge level was lower than either the saturation or predicted charge levels.

Another experiment consisted of comparing the effectiveness of the electron beam precharger with equal levels of dc voltage, pulsed voltage, and pulsed plus dc bias voltage. From a collector-alone particle collection efficiency of 93.2%, the application of 66 kV dc to the precharger increased the efficiency to 99.3%. As before, pulsing the precharger anode reduces the efficiency to 53.5%, but the imposition of a dc bias caused an immediate jump in efficiency to 96.2% at 10 kV dc bias and 99.5% at 20 kV dc bias. As evidenced by these preliminary experiments, the performance of the E-beam precharger when the anode is pulsed with no dc bias is poor. This is probably because a continuous electric field across the charging zone is needed to separate out the negative ion and electron portion of the ionized plasma. The short duration of the pulses does not allow this to occur. Once a small dc bias is present in the precharger, the maximum electric field which can be achieved with pulsing is much greater than the dc breakdown limit; therein lies the advantage of using pulsed power instead of a high dc electric field.

Using the single particle charge vs. radius ratio apparatus, charge and mass data was obtained from particles sampled just downstream from the precharger. Experimental particle charge levels were acceptably high, but they were found to be somewhat lower than the saturation charge predicted by ionic field charging theory. Optimization of the precharger electrical energization schedule should improve these already high particle charge levels.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: *The project currently under contract with the Pittsburgh Energy Technology Center, U.S. DOE, addresses the pressing problem of more efficiently controlling the emission of fine, high resistivity fly ash from low sulfur coal-burning power plants. As such, the project is an integral part of the DOE mission to advance technologies which provide for the safe and economically viable utilization of the nation's large but potentially polluting coal resources. Reducing the emission of particulate matter from coal fired boilers is in the national interest from a respiratory health standpoint, while improved power efficiency of the removal process serves the goals of lowered energy consumption.*

PLANS FOR THE COMING YEAR: *The particle collection efficiency experiments using monodisperse aerosol in the electron beam precipitator wind tunnel will be completed by testing the E-beam precharger at several energization frequencies and a range of pulse heights. Further investigation will be conducted into the role of dc bias on the charging and collection efficiency of the E-beam precharging process. Optimum values for all of the electrical parameters affecting electron beam precharging, including pulse voltage, frequency, width, rise time, and the dc bias voltage will be determined. A series of measurements will be made of the particle collection efficiency and the charge vs. radius ratio for polydisperse, high* *resistivity fly ash. Finally, a practical assessment of the results and data analysis from the entire body of pulsed electron beam precharging experiments will be formulated, including economic considerations and future directions for research.*

II. HIGHLIGHT ACCOMPLISHMENTS

1. *A rotating spark gap pulsed power supply has been modified extensively in order to deliver pulsed voltage to the electron beam precharger. Pulse characteristics are as follows: pulse voltage = 80 kV maximum, pulse frequency = 60 Hz, pulse duration = 200 ns, pulse rise time = 20 ns.*
2. *Using dc voltage only on the electron beam precharger anode, system particle collection efficiency levels of up to 99.7% were achieved for a moderately high concentration of high resistivity hydrated alumina dust.*
3. *The α - value quantifies the improvement in collection efficiency due to the effect of the E-beam precharger over the effect of the collector alone; collection efficiency increases of up to a factor of 40 (α = 40) have been achieved.*
4. *While precharger pulsed power alone does not increase system collection efficiency, the addition of a small dc bias voltage to the precharger anode along with pulsed energization produces very high particle removal efficiencies.*
5. *Particle charge and mass measurements made on individual particles after passing through the pulsed electron beam precharger show that experimental particle charge falls below but is close to the charge predicted by the ionic saturation field charging theory.*

III. ARTICLES AND PRESENTATIONS

1. *W. C. Finney, J. S. Clements, and R. H. Davis. Particle Charging and Collection Efficiency in a Laboratory Scale Electron Beam Precipitator. In: Proceedings of the 7th Symposium on the Transfer and Utilization of Particulate Control Technology, Volume 1, Particulate/SO_2 Control with Electrostatic Precipitators. Sponsored by the Electric Power Research Institute (EPRI) and the U.S. EPA. EPRI GS-6208, Vol. 1, pp 29-1 -- 29-16, 1989.*

2. *D. B. O'Hara, J. S. Clements, W. C. Finney, and R. H. Davis. Aerosol Particle Charging by Free Electrons. Journal of Aerosol Science, Volume 20, Number 3, pp. 313-330, 1989.*

3. *W. C. Finney and W. N. Shelton. Pulsed Electron Beam Precharger -- PEER Review Assessment. Presented at the PEER Review Conference of Research Projects in the Fossil Energy Advanced Research Programs, U.S. Department of Energy. Sponsored by the Office of Program Analysis and the Pittsburgh Energy Technology Center, U.S. DOE. 57 pp. Bethesda, MD, August 21-23, 1990.*

4. *A. Q. Mizuno, J. S. Clements, and R. H. Davis. Use of an Electron Beam for Particle Charging. IEEE Transactions on Industry Applications, Volume IA-26, No. 1, pp. 29-35, January/February, 1990.*

5. *W. C. Finney. Air Pollution Control Technology Using Energetic Electrons for Coal Fired Power Plants. Presented at the Chemical Engineering Colloquium, Department of Chemical Engineering, Florida State University, Tallahassee, FL., October 17, 1990.*

6. *W. C. Finney, J. S. Clements, and R. H. Davis. Electron Beam Precharging in a Laboratory Scale Electrostatic Precipitator. Submitted to the IEEE Transactions on Industry Applications, 1990.*

7. *R. H. Davis, W. C. Finney, J. S. Clements, A. Q. Mizuno, and M. X. Sato. Removal of Fly Ash, SO_2, and NO_x from Coal Smoke by Energetic Electrons. Submitted to Energy Systems, 1990.*

Date: April 9, 1991

TITLE: BINDING AND CATALYTIC REDUCTION OF NO BY TRANSITION METAL ALUMINOSILICATES

PIs: Kamil Klier and Richard G. Herman

STUDENT: Shaolie Hou, Ph.D.

INSTITUTION: Lehigh University
Department of Chemistry and
Zettlemoyer Center for Surface Studies
Sinclair Laboratory, #7
Bethlehem, PA 18015
(215) 758-3577

GRANT NO.: DE-FG22-89PC89784

PERIOD OF PERFORMANCE: September 1, 1989 to August 31, 1992

I. ABSTRACT

OBJECTIVE: To provide the scientific basis for processes that actively and selectively disproportionate or reduce NO in dilute exhaust streams, as well as in concentrated streams, to N_2. Experimental studies of NO chemistry in transition metal-containing aluminosilicate catalysts will be carried out with the aim of determining the patterns of reactivity in activating NO. Electronic and orbital calculations will be carried out to deduce the chemical rules for NO reduction on non-precious metals.

WORK DONE AND CONCLUSIONS: Catalysts prepared and analyzed include cobalt(II) exchanged A zeolites having 1.3 and 3.9 Co(II) ions per unit cell. These samples have been analyzed by high resolution electron spectroscopy for chemical analysis (HR-ESCA) for uniformity of Co(II) site symmetry and purity and by optical diffuse reflectance spectroscopy before and after dehydration and after quantitative adsorption and desorption of NO. The adsorption experiments confirmed the accessibility of the trigonally held transition metal cations and that NO adsorption is strong and reversible. Interpretation of optical spectroscopy and CO, O_2, and NO adsorption data for a Fe(II) A zeolite having 3.33 Fe(II) ions per unit cell has been carried out. An understanding of the electronic structure and bonding scheme in the zeolite-held complexes was provided by semi-empirical extended Hückel calculations. Ligand field stabilization energies were calculated for the first row transition series monovalent and divalent metals, as were the reducibilities, i.e. $M^{2+}(D_{3h}) \rightarrow M^{1+}(C_{3v})$. It was shown that the transition metal cations on the right hand side of the periodic table should form strong complexes with NO.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The benefit of this research rests in providing a foundation for developing non-noble metal catalysts for the active and selective disproportionation or reduction of NO from both dilute and concentrated gas streams such as produced by coal conversion processes. Active non-noble metal exchanged zeolites could handle large throught-puts of exhaust gas and would allow control of polluting NO_x emissions.

PLANS FOR THE COMING YEAR: Transition metal ion exchanged zeolites, including Co(II), Fe(II), Mn(II), and Cu(II) A zeolites having metal cation contents on the order of 1 and 4 M(II) ions/unit cell, will be tested in a batch reactor for disproportionation and for reduction of NO. The reactor system, having an attached quadrupole mass spectrometer for gas analysis, allows *in situ* optical spectroscopy by diffuse reflectance to be carried out to determine the oxidation state and symmetry of the transition metal ions prior to and after the interaction with NO. Appropriate reaction conditions will be found for the disproportionation and reduction of NO.

II. HIGHLIGHT ACCOMPLISHMENTS

Divalent transition metal exchanged A zeolite samples, including Co(II) exchanged A zeolites having 1.3 and 3.9 Co(II) ions per unit cell, as well as Fe(II), Mn(II), and Cu(II) A zeolites, have been prepared and characterized. A reaction system that is capable of being evacuated and containing an *in situ* diffuse reflectance cell and a quadrupole mass spectrometer has been assembled and is being used for the NO disproportionation and reduction studies that are being carried out with these zeolites. It has been demonstrated that the ion exchange process can be quantitatively monitored by HR-ESCA analysis. In addition, the valence band spectra, as well as HMO calculations, indicate that there is significant bonding overlap of the 3d orbitals of the Co ions with the zeolite O 2p-based lattice orbitals.

III. ARTICLES AND PRESENTATIONS

"UV-VIS-NIR Study of Fe(II)-A Zeolite: Dehydration, Adsorption, and Redox Behavior," J.-P. Lange and K. Klier, Twelfth North American Meeting of the Catalysis Society, Lexington, KY, May 5-9, 1991; Abstract No. A06.

"UV-VIS-NIR Studies of Fe(II)-A Zeolite: Dehydration, Adsorption of Probe Molecules, and Redox Behavior," J.-P. Lange and K. Klier, manuscript under revision.

TITLE: Molten Iron Oxysulfide as a Superior Sulfur Sorbent **DATE:** 3/11/91

P.I.(s): Malcolm T. Hepworth and Kenneth J. Reid

STUDENT: Shaolin Zhong (registered for PhD degree).

INSTITUTION: University of Minnesota
c/o Department of Civil and Mineral Engineering
500 Pillsbury Drive, SE
Minneapolis, MN 55455
(612) 625-3344 & (612) 625-5522

GRANT NO.: DOE/DE-FG22-89PC89778

PERIOD OF PERFORMANCE: September 1, 1989 to August 31, 1992

I. ABSTRACT

OBJECTIVE: Examine the thermodynamics and kinetics of the molten phase in the iron-oxygen-sulfur system to determine the optimum operating conditions to run a slagging-desulfurizing burner. Compare the potential for use of this system with lime-based systems for desulfurization.

WORK DONE AND CONCLUSIONS: Slagging combustors with injected lime or limestone are being considered as replacements for conventional coal burners. They have advantages in that they can be staged to reduce NO_x and SO_x emissions. Iron oxide, as an alternative to lime or limestone may be effective not only as a desulfurizing agent, but under the right conditions of oxygen potential and after combination with sulfur, the reaction products of coal gases with iron oxide can act as a flux to produce a fluid phase. The thermodynamic conditions for determining the most effective operating conditions of the first stage of a combustor are calculated for several Illinois coals. The conditions which were studied this year include contact of a coal gas with the phase combinations $CaO/CaSO_4$, CaO/CaS, Fe/FeO/Liquid for the temperature range of 950° to 1300° C.

Additionally, the liquid iron oxysulfide phase was studied in contact with iron at 1200°C, a temperature for which data in the literature were available. The results are reported in terms of the expected pounds of SO_2 per million Btu of heat evolution calculated for complete combustion of the coal. The calculations indicate that for the Fe-O-S system, higher temperatures give better results, approaching 96% sulfur removal from a coal containing 4.2% sulfur in the phase combination Fe/FeO/Liquid at 1200°C. Under these conditions the off-gas emerging from the second stage of combustion under stoichiometric conditions would contain 0.36 pounds of SO_2 per million BTU's of heat generated. For the system Fe/Liquid, results indicate that the lowest sulfur levels in the off-gas occur

for the gas in contact with iron and a liquid phase containing 49.0 atom% iron, 29.5 atom% oxygen and 21.5 atom% sulfur. Under these conditions, the stack gas emerging from the second stage of combustion under stoichiometric conditions would contain 0.59 pounds of SO_2 per million BTU's of heat generated.

The results of the calculations are reported both in tabular form and in three-dimensional representation. Lowest values of SO_2 occur as a "trough" on the iron-oxygen-sulfur isotherm at compositions at the phase boundary of the oxysulfide liquid region in equilibrium with iron.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The results of these studies would enable a designer of a slagging combustor system to determine the theoretical degree of desulfurization which could be achieved and the necessary operating conditions which would be required to burn coal in a two-stage combustor. With the first stage operating under sub-stoichiometric conditions which maximize sulfur capture and minimize NO_x emissions, it is possible to enter the coal composition into an interactive computer program to determine the optimum conditions for sulfur capture. The calculated conditions are being verified by thermodynamic and kinetic experiments.

PLANS FOR THE COMING YEAR: The experimental program is about to generate the necessary information to check the previously calculated conditions. The temperature range will be expanded to higher temperatures than 1200°C to include temperatures up to 1450°C, which is the limit of the available furnace equipment. The results of these measurements will be used in a parallel study in which sulfur-laden simulated coal gases will be contacted in a controlled vortex burner with magnetite injected particles to produce liquid iron oxysulfide.

II. HIGHLIGHT ACCOMPLISHMENTS

An interactive computer program has been developed which enable the optimum conditions for desulfurization to be determined in the following phase combinations for the staged-combustion of a range of coal compositions:

CaO/CaS/gas
$CaO/CaSO_4$/gas
Fe/FeO/liquid iron oxysulfide/gas
Fe/liquid iron oxysulfide/gas.

III. ARTICLES AND PRESENTATIONS

Hepworth, M. T., Reid, K. J., Wang, J. C. and Zhong, S.: "Thermochemistry of the Fe-O-S System as a Desulfurizer in Coal Combustion Atmospheres: Part I - Fe-FeO-Liquid Equilibrium", *Proceedings of Clean Coal Technology Symposium*, Amer Chem Soc, Pittsburgh, August 29, 1990, pp 1433-1437.

Hepworth, M. T. and Zhong, S.: "Comparison of Lime as a Desulfurizer with Iron in Coal Combustion Atmospheres: Fe-FeO-Liquid Equilibrium," *Energy and Fuels*, Vol 5, No 2, March/April, 1991.

TITLE: Comparison of Lime and Iron Oxide for
High Temperature Sulfur Removal **DATE:** 4/7/91

P.I.(s): Kenneth J. Reid, Malcolm T. Hepworth

STUDENT: Dongming Zhu (M.S.)

INSTITUTION: Mineral Resources Research Center
University of Minnesota
56 East River Road
Minneapolis, MN 55455
(612) 625-3344

GRANT NO: DE-FG22-89PC89779

PERIOD OF PERFORMANCE: 09/01/89 to 12/31/91

I. ABSTRACT

OBJECTIVE: To examine the sulfur removal behavior of both lime and iron oxide sorbents under carefully controlled sulfur and oxygen potentials in a novel double vortex combustor.

WORK DONE AND CONCLUSIONS: The design, installation and commissioning of the burner test facility turned out to be a larger task than originally planned and although significant progress was made the test facility was not available for the experimental program at the end of the first year. A no cost extension to the project was therefore requested to 12/31/91. After preparation of a suitable test location in the MRRC furnace bay a gas feed console and off-gas treatment stream acquired second hand from IITRI were installed and tested.

Preliminary tests on the novel dynamic containment burner indicated the potential benefits of being able to visually observe flame stability and operating characteristics. A glass burner model was therefore built and proved to be extremely helpful in developing vortex drive systems and defining operating variable ranges for the test burner proper. Many photos of different operating conditions have been obtained and a short video tape has been prepared to demonstrate basic operating modes. During the glass model tests two fundamental burner geometries were identified and the comparative fluid dynamic characteristics examined.

The sorbent testwork requires the controlled introduction of relatively small flowrates of very fine solids. This is not an easy task and considerable time was spent in developing a suitable solution to this problem. A feeder design with an air assisted discharge cone and a discharge stream proportional cutter has been developed and permits stable flow rates at the levels required for the desulfurizing testwork.

Preliminary testwork to observe the solid sorbent trajectories in the glass model burner has been carried out and has indicated melting of the very fine particles of magnetite (-5 μm) can be achieved under reducing conditions. With higher oxygen content oxidation of magnetite (Fe_3O_4) to hematite (Fe_2O_3) was observed.

Based on the glass model testwork design, details for the stainless steel test burner were established. The burner body and outer drive system have been constructed.

Control of the flame fluid dynamics and the trajectories of injected solids have been shown to be critically dependent on the inner drive system, particularly with respect to the vorticity component. Inner drive designs are under review to achieve the required overall desulfurizing system fluid dynamic control.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The reduction of sulfur emissions is a primary target of the fossil energy program and this project relates both to a novel sorbent (iron oxide) and a novel combustor system (double vortex combustor). If iron oxide can be substituted for lime in a multistage burner, then it may be possible to improve the degree of desulfurization which can be accomplished over that encountered with lime as a sorbent. At the same time, a low-melting point slag should be the product which has the potential to be less reactive to atmospheric conditions of water-leaching than calcium sulfide, which would be the product of lime-desulfurization under reducing conditions.

The new combustor system also has the potential to reduce dust loading in the boiler and flue gas system.

PLANS FOR THE COMING YEAR: Completion of detailed test program including:

- Mineralogical characterization of sorbents and product.
- Influence of gas phase sulfur content.
- Determination of absorption capacity as a function of particle size, exposure time, fuel sulfur content and operating energy level.
- Comparison of lime, limestone and taconite concentrates as sorbents.

II. HIGHLIGHT ACCOMPLISHMENTS

- A highly sophisticated second hand gas train control system and off gas treatment unit was acquired at a favorable cost and is now installed as part of the overall double vortex burner test rig.
- A glass burner model has been constructed and has provided many critical insights into flame stability and operating characteristics.
- A fine particle feeder system has been developed and calibrated for feeding fine taconite concentrate material.

III. ARTICLES AND PRESENTATIONS

A. Articles:

None

B. Presentations:

July 17-19, 1990 DOE Peer Review Assessment Meeting

TITLE: Selenium Transformation in Coal Mine Spoils: Its Environmental Impact Assessment

DATE: June 25, 1991

P.I.(S): Asmare Atalay and Kurtis J. Koll

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

Kurtis J. Koll - Ph.D.
Douglas W. Weirick - Ph.D.
Hualiang Zhang - M.S.
Dharamvir Maggon - M.S.
Srinivas Chaluvadi - M.S.

INSTITUTION/ORGANIZATION:
University of Oklahoma
Civil Engineering & Environ. Science
202 W. Boyd, Room 334
Norman, OK 73019
(405) 325-5911

GRANT NO: DE-FG22-89PC89782

PERIOD OF PERFORMANCE: September 1989 - September 1991

ABSTRACT

OBJECTIVES:

1. To develop an Ion Chromatograph procedure for analysis of selenium.
2. To conduct field lysimetry study to monitor the transformation of selenium from coal mine spoils.
3. To assess the impact of selenium from coal mine spoils on the environment.

WORK DONE AND CONCLUSIONS: Ion chromatography procedures were developed that permitted the measurement of selenate and selenite (the two major forms of selenium) in water samples. The detection limit for each specie was close to 10 ppb. The investigation reveled that high levels of chloride and nitrate interfered with selenite measurement whereas high level of sulfate interfered with selenate measurement. Most of the groundwater in Oklahoma was found to contain selenium above the allowable limit (10 ppb Se) set by the U.S. EPA. Preserving water samples with dilute nitric acid reverted selenate to selenite instantly. Unpreserved spiked deionized water samples stored at 4 °C showed no significant changes in either selenate or selenite levels when analyzed after 4 weeks. The addition of barium on equivalent basis to samples containing as much as 500 ppm sulfate effectively precipitated most of the interfering sulfate.

Results from the lysimetery study indicated that the spoil at the abandoned coal mine site has equilibrated for such a long time (over 40 years) that the selenium may have either leached,

transformed or volatilized. Samples collected from the site indicated very low levels of selenium, even lower than was found in some groundwater samples. Oxidation reduction potential (ORP) studies indicated that $HSeO_3^-$ (mainly), SeO_4^{2-} and SeO_3^{2-} were the species found in the spoil. A pE vs pH plot of the result showed that these species were stable between pH 5 and 8. Results from column studies revealed that selenate and selenite are readily adsorbed by the spoil material.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The importance of selenium speciation in fossil fuel energy program is associated with the stringent regulation of the U.S. EPA for the level of selenium in drinking water and irrigation water. Because of similarities in chemistry between selenium and sulfur, much of the selenium in the earth's crust occurs in sulfide minerals. Therefore, during the excavation of coal, sulfide minerals such as pyrite, FeS_2, chalcopyrite, $CuFeS_2$, pyrrhotite, $Fe_{n-41}S_n$, and many others, are displaced and brought to the surface. If the environment is conducive, these minerals undergo oxidation-reduction reactions that release the sulfide and associated selenium. All abandoned coal mine spoils are potential sources of selenium contamination of groundwater. Selenium contamination of irrigation water caused genetic abnormalities in waterfowl in San Joaquin Valley, California.

PLANS FOR THE COMING YEAR: (1) Complete the current project. (2) Continue research on selenium, its microbial transformation. (3) Investigate the usefulness of fly ash for the treatment of acid mine water from abandoned mine sites.

II. HIGHLIGHT ACCOMPLISHMENTS

The ion chromatograph procedure developed for measuring selenium from water samples was extended to look at selenium in soils and plant materials. The method was also useful in analyzing other anions such as arsenate, arsenite, nitrate, chloride, and sulfate. The Lysimetry set up can be used to study the redox chemistry of other metals in the aqueous soil environment. The environmental impact assessment conducted revealed that selenium and other mobile pollutants may not be a problem in older spoil sites that have equilibrated long enough.

III. ARTICLES AND PRESENTATIONS

1. Atalay, A. and Cahoon Cecilia, "Development of Ion Chromatography procedure for analysis of oxyanions in water and soil samples". In preparation.
2. Maggon, Dharamvir and Atalay, A. "Selenium in Oklahoma ground water and soils" Oklahoma Academy of Science, Tulsa, Oklahoma, October, 1990.
3. Atalay, A. and Kurtis J. Koll, "Selenium Transformation in Coal Mine Spoils" DOE Peer Review, Dallas, TX, December 12, 1990.

TITLE: Synergistic Capture Mechanisms for Alkali and Sulfur Species from Combustion

P.I.'s: Thomas W. Peterson, Farhang Shadman and Jost Wendt

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Edward Olsen (M.S. Chemical Engineering)
BaoChun Wu (Ph.D. Chemical Engineering)

INSTITUTION:
Chemical Engineering
University of Arizona
Tucson, AZ 85721 (602) 621-6044

GRANT NO.:
DE-FG22-90PC90285

PERIOD OF PERFORMANCE:
9-1-90 to 8-31-93

I. ABSTRACT

It is proposed to conduct a systematic study to elucidate mechanisms governing both the effect of sulfur on the capture of alkali and trace metals on sorbents during combustion, and the converse effect of alkali/trace metals on the capture of sulfur. This study is motivated by existing data which indicate that the speciation of alkali compounds in the gas phase profoundly influences the mechanism of alkali capture on alumino-silicate sorbents, and by results from other laboratories demonstrating enhanced sulfur capture by lime contaminated by alkali or trace metals. We propose to utilize these synergistic mechanisms to develop novel bi-functional sorbents, suitable for the simultaneous capture of alkali/trace metals and sulfur during combustion. Such a dual sorbent might be bauxite or alumina impregnated with lime.

The research involved bench scale experimental studies, laboratory combustor studies and theoretical modeling to relate the two. Bench scale experiments, utilizing a thermogravimetric furnace, focus on kinetics and mechanisms of alkali/trace metal interactions with individual sorbent flakes under simulated flue gas conditions. Laboratory combustor studies, utilizing a 17kW downflow combustor, focus on synergistic mechanisms as the occur in real, but well defined, combustion environments, with the sorbent in a disperse phase. Additional synergistic effects caused by combustion modifications for NOx abatement will also be examined. In each case attention is centered on synergistic interactions during condensation and capture on sorbents. Results from this research should lead to novel "designer" sorbents which will allow coal to be burned with minimum alkali/trace metal, sulfur and nitrogen oxide emissions.

OBJECTIVE:

The objectives of this research are twofold: first, through a systematic study, to gain an understanding of mechanisms of the interactions between alkali metal capture and sulfur capture on sorbents during combustion, and second, to exploit synergistic interactions between these processes in order to optimize combustion modifications that minimize emission of alkali metal compounds, sulfur compounds and fixed nitrogen compounds. Fundamental understanding gained will be used in at least two different ways: 1) to develop novel sorbent chemistry that enhances simultaneous capture of both alkali and sulfur, and 2) to exploit modifications in the gas phase chemistry caused by low NOx combustion conditions to further augment the Na and S capture efficiency of these novel sorbents.

WORK DONE AND CONCLUSIONS:

Work on this project is following two approaches at the present time. The first development of a quartz reactor to study sorbent behavior in the presence of alkali vapor and SO2. The second is development of an aerosol reactor to study the particle size evolution of aerosol formed in the presence of alkali vapor, sulfur oxides and sorbent materials.

The experimental plans include design and set up of a small quartz reactor which allows for the generation of alkali vapor at a controlled rate and exposure of sorbents under study. A new reactor system is under design and construction for study of combined SO2 and alkali capture. The reactor system consists of four parts: simulated flue gas preparation, reactor, the furnace with capability for both steady and transient thermal conditions, and the gas analysis section.

The aerosol reactor currently being designed will provide for both particle and gas extraction and analysis. As with the quartz reactor above, the relative rates of reaction among selected sorbents, alkali species and sulfur oxides will be examined.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

During the combustion or gasification of coal, alkali and trace metals partially vaporize and subsequently condense either to form a fume of very small particles which are difficult to capture, or around existing ash particles which then become sticky and likely to adhere to heat transfer surfaces. Sulfur and nitrogen oxides are other unwanted by products of reaction. It is known that alkalis (Na and K) can be chemically reacted on certain sorbents such as bauxite or kaolinite. It is also known that the presence of sulfur affects the speciation of the alkali complex captured on the sorbent surface. Conversely, the presence of Na and Cr has been shown to affect the capture of sulfur on other sorbents (namely lime or calcined limestone). Both capture processes are strongly influenced by the local gas phase environment which may have been modified for the purpose of NOx control. Although there already has been significant research activity on sulfur capture and, to a much less extent, on alkali capture, there has been so far no systematic study which focuses on mechanisms that can be exploited for the simultaneous capture of both alkali metals and sulfur on novel sorbents.

Research proposed here is designed to fill this gap. In addition, it is also designed to take advantage of additional complications caused by modifications in gas phase chemistry to enhance further the alkali, trace metal and sulfur capture capability of novel bifunctional sorbents arising from the work.

PLANS FOR THE COMING YEAR:

The study is conducted on three levels of complexity. The first set of experiments utilize a bench scale thermogravimetric furnace and an aerosol reactor to obtain fundamental information on kinetics and mechanisms related to alkali/sulfur interactions and capture on sorbents. This set of experiments will yield a novel dual sorbent in which calcium oxide for sulfur capture is impregnated on a Bauxite or kaolinite support both to allow alkali capture and to enhance sulfur capture by preventing pore closure. It is expected that synergistic effects of alkali on sulfur capture and of sulfur on alkali capture will make this approach especially attractive.

The second set of experiments expands the study to relate the bench scale results to a well defined laboratory combustor system. The operating temperature window for sorbent injection will be defined, and mechanisms, which now involve aerosol dynamics in addition to the sorbent reactions will be elucidated. The new bifunctional sorbent will be tested under these clean combustor conditions.

The third set of experiments involve the combustion of solid fuels. These tests will involve a well defined coal which is low in sulfur and low in ash but high in sodium. The purpose of these tests is to expand our knowledge of mechanisms to a fairly well defined coal combustion system in which the effects of certain variables, such as S content and sorbent injection location can be explicitly determined without being obscured by the complications caused by coal ash particles. Finally, these results are expanded to test the application of dual sorbents to a more normal pulverized coal combustion system in which normal coal ash may be a factor.

II. HIGHLIGHT ACCOMPLISHMENTS

Preliminary efforts have started to work on the preparation of multifunctional sorbents. The sorbents are aluminosilicate substrate. Currently, we are characterizing their physical structure including porosity, area and pore-size distribution.

The project has just begun, and while significant progress in the experimental design and construction has been made, no quantitative results are available as yet.

III. ARTICLES AND PRESENTATIONS

None to date.

TITLE: Improved Utilization of Coal Derived Fly Ash in Concrete

DATE: 4/5/91

P.I.(s):Dr John W. Liskowitz
Dr. Anthony E. Cerkanowicz
Dr. Methi Wecharatana

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

Mr. Chai Jaturapitakkul	PhD Civil Eng.
Mrs. Poorna R. Ratnaweera	MS Civil Eng.
Mr. Arunkumar Sripathi	MS Environmental Eng.
Mrs. Lin Wang	MS Environmental Sci.

INSTITUTION/ORGANIZATION:
The Foundation at New Jersey Institute of Technology
Civil and Environmental Engineering
323 Martin Luther King Blvd.
Newark, New Jersey 07102
(201) 596-3432

GRANT No:DOE-DE-FG22-90PC90299

PERIOD OF PERFORMANCE: 9/1/90 to 8/31/93

I. ABSTRACT

OBJECTIVE:
Successful use of coal derived fly-ash in the formulation of concrete currently depends on long term testing of the suitability of sample ash-concrete formulations prior to ash acceptance. Existing tests have proven unreliable and have not provided correlation between formulated concrete strength and fly-ash/combustor/coal characteristics. This program represents a study of the interrelationship between the ash formation process, the ash properties, and the concrete quality. Given the coal type, and the combustion and ash collection conditions, we expect to predict the optimum use of the captured ash in concrete formulation. We further intend to use these results to develop an innovative ash quality test.

WORK DONE AND CONCLUSIONS:
Our initial studies are directed to identifying ash with the desired properties and quality for use in concrete mixtures. For this purpose, we have gathered and characterized fly-ash from various coal fired utilities of Public Service Electric and Gas Company of New Jersey. Ash particle size, and surface and bulk composition have been determined. Since leaching can influence the ash character, we have subjected some of the collected dry ash to water washing. To the end, we have also collected ponded ash which has undergone long term leaching. The ash sample were used as a partial and complete replacement for cement in formulating two-inch cubic test specimens. Fly ash percentages ranged from 0 to

35%. Test specimens were monitored for compressive strength changes over a 180 day period.

Fly-ash particle size distribution was found to be a significant correlating factor in cement strength. Increased percentages of fly-ash at and below about 10 microns led to increased strength throughout the 180 day curing period. Results for ponded fly-ash were influenced by the high chloride content present in the pond due to the use of brackish river water in the ponding operation. Other experiments involving the use of clean water for leaching are currently being performed.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:
The proposed study will provide an innovative understanding of the influence of the combustion process, coal composition and type on the pozzolanic properties of the generated fly-ash and the resultant effect on the quality and properties of concrete using this ash. New guidelines and recommended on-line measurements to characterize and predict ash pozzolanic quality are being sought. It is expected that this effort will lead to a significant increase in fly-ash utilization in the concrete industry. This results because the utilities generating the ash would be able to predict and quickly test for pozzolanic activity and provide quality assurance as to the performance of the ash in the concrete. The increasing costs facing the utilities for the disposal of the fly-ash as a waste material would be minimized and the attractiveness of coal as a cost effective source of energy maintained.

PLANS FOR THE COMING YEAR:
Research directed at delineating the important fly-ash properties for high strength concrete formulation will continue. Wet and dry bottom boiler ash will be air classified into a number of size ranges to further identify and quantify the effect of ash particle size. Continued studies of the influence of leaching by means of clean water washing will continue. A neural networking model will be applied to the fly-ash/concrete strength data as well as accumulated literature data. The objective of the model will be to correlate concrete strength against ash properties, ash collection means, combustor conditions, and coal type.

II. HIGHLIGHT ACCOMPLISHMENTS

Significant quantity of commercially generated coal fly-ash employing different combustion and collection processes has been obtained for evaluation. The influence of ash particle size, particle size distribution, surface and bulk chemical composition, and leaching treatments on fly-ash/concrete strength are being evaluated as a function of curing time.

III. ARTICLES AND PRESENTATIONS

None

TITLE: Anion-Exchange Resin-Based Desulfurization Process

DATE: April 5, 1991

P.I. (s): Atul C. Sheth

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:
Sterling D. Strevel - M.S. in Engineering Science & Mechanics

INSTITUTION/ORGANIZATION: The University of Tennessee Space Institute
Energy Conversion Research & Development Programs
B.H. Goethert Parkway
Tullahoma, Tennessee 37388
(615) 455-0631, Ext. 427

GRANT NO.: DE-FG22-90PC90309

PERIOD OF PERFORMANCE: August 9, 1990 to August 8, 1993

I. ABSTRACT

OBJECTIVE: To further develop the anion-exchange, resin-based desulfurization concept that has been developed and tested on a limited scope for feasibility at UTSI.

WORK DONE AND CONCLUSIONS: To date in the project, the following activities have been carried out -

- Completed computer-based literature search and acquired publications of interest.
- Contacted resin manufacturers and suppliers and acquired samples of eleven candidate resins.
- Developed an experimental screening procedure to evaluate candidate resins in relatively easy and quicker (than fixed bed mode) batch mode tests.
- Prepared a schematic of the semi-automated fixed-bed unit and arranged (either salvaged or ordered) for the necessary parts and components.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: From the economic and environmental viewpoints, it is necessary to regenerate (desulfurize) and recycle the spent alkali metal sorbents (mainly sulfates). The need for a simple, low-cost and readily acceptable sorbent regeneration option to desulfurize such alkali metal sulfates can be satisfied by the anion-exchange resin-based UTSI concept.

PLANS FOR THE COMING YEAR: As a result of the batch mode screening tests, three candidate resins will be selected for further screening tests in a fixed-bed setup. We shall then complete the bench scale process variables study using these three resins to select the one resin for optimizing the resin regeneration step and to evaluate the effect of performance enhancers. We also plan to test the mathematical model used by the previous investigators at UTSI to satisfy the bench scale process variables study data, and if necessary, make appropriate modifications.

II. HIGHLIGHT ACCOMPLISHMENTS

In order to develop the experimental procedure to test candidate resins in a batch mode, several experiments were carried out using IRA-68 resin in which major variables such as ammonia concentration (for resin regeneration), mixing time (for exhaustion and regeneration steps), resin sample size and carbonation time (at a CO_2 flow rate of 2 SCF/hr) were varied one at a time. From this study the following conclusions were derived:

- Concentration of sulfate ions retained by the resin at the end of the regeneration cycle (which indicates the efficiency of resin regeneration step) initially decreases significantly with the ammonia solution concentration and then levels off around 4 wt % strength. This means that for complete regeneration of the exhausted resin, ammonia concentration in excess of 4 wt % should be adequate.
- Mixing time during the exhaustion cycle, when varied from 15 to 30 minutes, does not affect the amount of sulfate ions removed from the bulk solution by the active resin sites.
- Resin sample size, when varied from 10 to 100 ml., does not affect the performance during the exhaustion and/or regeneration cycle.
- Amount of sulfate ions removed by resin (i.e. exchanged with the resin-active sites) increases with the carbonation time at near atmospheric pressure at a CO_2 flow rate of 2 SCF/hr, but then appears to level off between 30 and 60 minutes.

Based on these results, the desirable conditions for the batch mode screening experiments would be as follows:

- Mixing time for exhaustion and regeneration ~ 15 minutes
- Ammonia solution concentration for regeneration ~ 3.5 wt %
- Carbonation time (at a CO2 flow rate of 2 SCF/hr) ~ 30 minutes
- Resin sample size ~ 25 ml., and
- Solution-to-resin ratio ~ 2:1

III. ARTICLES AND PRESENTATIONS

As soon as the screening tests and process variables study are completed, we will present the results in an appropriate professional conference.

HIGH TEMPERATURE PHENOMENA

DATE: April 3, 1991

TITLE: PYRITE THERMOCHEMISTRY, ASH AGGLOMERATION, AND CHAR FRAGMENTATION DURING PULVERIZED COAL COMBUSTION

PI: Professor Stephen Niksa

STUDENT: Reuben Diaz (Ph.D.)

INSTITUTION/ORGANIZATION: High Temperature Gasdynamics Laboratory
Mechanical Engineering Department
Stanford University
Stanford, CA 94305
415/723-1745

GRANT NO.: DE-FG22-87PC79909

PERIOD OF PERFORMANCE: September 15, 1987 to September 4, 1991

I. ABSTRACT

OBJECTIVE: During p.f. firing of coal, the evolution of particulate ash from extraneous mineral matter is determined by thermochemistry, agglomeration of molten inclusions as the char is consumed, and fragmentation of the char into finer particulates. The transformation of pyrite inclusions into iron oxide ash is the primary focus of this program, including pyrite thermochemistry, the average number of ash particles per char particle, and the relation between the size distributions and compositions of mineral inclusions and ash particles.

The proposed research utilizes synthetic chars with monodisperse pyrite inclusions and a range of controlled pore structures, including the mesosphere structures common to p.f. firing. Studies with the synthetic char establish an essential reference condition for analyzing the behavior of coal char. The size distributions and compositions of ash particulates from both the synthetic chars and coal chars will be monitored during simulated p.f. firing in our new radiant coal flow reactor.

WORK DONE AND CONCLUSIONS: Having perfected the synthesis of carbons with controlled macrovoids and pyrite loadings earlier in the program, we focused on developing reproducible experiments for pyrite thermochemistry under a broad range of simulated p. f. firing conditions throughout the past year. The laboratory reactor is a novel radiant flow system in which technologically relevant heating rates and temperatures are achieved without the complications of gas preheating. This system has the additional advantages of no convective mixing phenomena at the injector, so thermal histories are less uncertain, and radiant transfer in the optically thin limit, so individual particles experience the same heat flux. In addition, the process gases remain relatively cool, so products recovered in the gas phase more closely represent the primary reaction products. The system is equipped with a rapid quench for time resolution on a 10 ms scale, and a scheme to recover particulate and aerosol samples for subsequent chemical characterization.

Chemical compositions of recovered solid samples are based on x-ray diffraction (XRD). Mass concentrations of FeO, Fe_3O_4, $Fe_{1-x}S$, FeS_2, and Fe_2O_3 have been assigned from calibration curves developed with an intrinsic standard, on a relative basis. Synthetic mixtures spanning broad ranges of the species populations have been reproduced within a relative uncertainty of 5%. Gas phase compositions will be based on FTIR, which is now being calibrated.

All aspects of the experimental procedures were evaluated in pyrolysis experiments with pyrite particles for furnace temperatures from 1100K to 1500K at a fixed nominal residence time of several hundred milliseconds. In a separate study at 1560K, the transient evolution of the iron ash constituents was completely determined. Experiments of iron ash oxidation have also been conducted. These results have been evaluated in a preliminary way by comparing them to thermochemical equilibrium compositions assigned in house, using a modified version of Prof. Reynold's STANJAN solver. Several reaction models have also been formulated to screen for various rate limiting mechanisms.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: The experiments are aimed at two advances. First, the pyrite thermochemistry studies will identify any kinetic constraints among the iron-bearing compounds during p.f. firing, as an important step toward predicting ash compositions from mineral matter compositions. Second, the fragmentation studies promote a fresh approach to modeling the size distribution of ash known as the percolate fragmentation model. While this model has distinct conceptual advantages over deterministic pore models, experiments of the sort proposed here are essential to realizing the model's full potential for utility boiler applications.

PLANS FOR THE COMING YEAR: The term of the contract is expired.

II. HIGHLIGHT ACCOMPLISHMENTS

A novel radiant flow reactor has been used to prepare particulate samples of iron ash from simulated p. f. firing conditions. Technologically relevant heating rates, temperatures, and oxygen levels are achieved. This system also features time resolution on a 10 ms time scale, so the reaction dynamics are accessible. Iron ash compositions are determined in house using x-ray diffraction. Mass concentrations of FeO, Fe_3O_4, $Fe_{1-x}S$, FeS_2, and Fe_2O_3 have been assigned from calibration curves developed with an intrinsic standard, to a relative uncertainty of 5%. Pyrolysis experiments with pyrite particles for furnace temperatures from 1100K to 1500K and the transient evolution of the iron ash constituents at 1560K have been conducted. Experiments of iron ash oxidation have also been demonstrated. The observed compositions have been compared to thermochemical equilibrium compositions assigned in house.

III. ARTICLES AND PRESENTATIONS

Akan-Etuk, A. and Niksa, S., WSS/CI 1989 Fall Mtg., Paper No. 89-82, Sandia Laboratories, Livermore, CA.

Diaz, R. and Niksa, S., WSS/CI 1990 Spring Mtg., Paper No. 91-4, Univ. Colorado, Boulder, CO.

Date: April 29, 1991

TITLE: Thermally Induced Structural Changes in Coal Combustion

PIs: G. R. Gavalas and R. C. Flagan

STUDENT(S): M. Choi (PhD), X. Li (PhD), B. A. Wong (PhD)

INSTITUTION/ORGANIZATION: California Institute of Technology
Caltech 210-41, Pasadena, CA 91125
(818) 356-4152

GRANT NO.: DE-FG22-88PC88911

PERIOD OF PERFORMANCE: 9-1-88 to 8-31-91

I. ABSTRACT

OBJECTIVE: Measure thermally induced structural changes occurring at temperatures and times typical of pulverized combustion and determine the changes in the intrinsic combustion rate caused by these structural changes.

WORK DONE AND CONCLUSIONS: All experimental work was conducted with a Pittsburgh seam coal (hvbA, PSOC 1451). Devolatilization and combustion experiments were conducted in an electrically heated entrained flow reactor at 1600 K. The coal particle size was 45-53 µm, the gaseous atmosphere was N_2, 1% O_2-N_2, and 5% O2-N_2. The residence times were 100, 200, 300 ms. The product char + ash were collected on a filter at the base of a probe cooled by N_2 injection, and water circulation. The solids collected were completely burned in a muffle furnace to determine total ash content which was used to calculate conversion. Partially burned samples were oxidized in a thermogravimetric analyzer (TGA) to characterize their reactivity. The TGA experiments were conducted at 500°C using flow of 5% O_2-N_2 mixture at 150 ml/min. The reactivity results can be summarized as follows. The reactivity of chars produced in pure N_2 (devolatilized only) increases with the devolatilization time (time in the entrained flow reactor). For the chars collected in 1% O_2-N_2 and 5% O_2-N_2, the reactivity declines with the residence time in the entrained flow reactor. For fixed residence time, the reactivity is in the order $N_2 > 1\%\ O_2\text{-}N_2 > 5\%\ O_2\text{-}N_2$. This decline of reactivity with increasing oxygen content, i.e. with increasing conversion can be attributed to the heterogeneity of the organic material in the char with the more reactive material reacting at the beginning. Another possibility is thermal annealing, especially in the presence of oxygen.

Another series of experiments was carried out with the quadrupole electrodynamic balance described in an earlier report. In these experiments single particles of char from the Pittsburgh seam coal were charged and suspended at the center of the electrodynamic balance in air. The particles were then heated from top and bottom by two opposing IR beams from a CO_2 laser. After heating for a certain period at some constant temperature between 600 and 700°C, the particle size was measured photographically and the particle mass was determined by measuring the settling velocity. At this time, the most interesting finding is the relation between conversion and particle size. For the range of temperatures and particle sizes examined, calculations indicate Thiele moduli small enough for intraparticle diffusion not to be rate limiting. These conditions normally suggest oxidation at constant size. Such was, in fact, the case for the char produced by devolatilization at

1600 K. However, the chars produced at 1200 and 1400 K displayed significant shrinking with conversion.

Modeling studies continued focusing on the effect of particle shape on combustion. Numerical calculations carried out using a boundary integral technique showed that particles become increasingly nonspherical with conversion. The combustion rate of nonspherical particles was close to that of a spherical particle of equal surface area.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: This research is focused on two poorly understood features of particle combustion. One is the changes in intrinsic reactivity with conversion, changes that may be due to thermal annealing or to an initial nonuniformity in reactivity. The second feature is the role of particle size and shape. Attention is focused on the role of initial shape as well as on the evolution of shape with conversion. Information on both these issues will be useful for quantitative models of particle combustion.

PLANS FOR THE COMING YEAR: The remaining few months of this project will be used to complete the experimental and modeling tasks of the project.

II. HIGHLIGHT ACCOMPLISHMENTS

An important trend of declining reactivity with conversion during char combustion was established. It was also found that chars produced by devolatilization at temperatures below 1400 K undergo significant shrinking upon oxidation, even at temperatures at which pore diffusion is not limiting.

III. ARTICLES AND PRESENTATIONS

M. K. Choi and G. R. Gavalas, Gas-Solid Reaction on Nonspherical Particles, submitted to Chem. Eng. Sci.

G. R. Gavalas, Thermally Induced Structural Changes in Coal Combustion, presented in the UCR Contractors Review Meeting, Pittsburgh, July 17-20, 1990.

April 8, 1991

TITLE: CORROSION AND ARC EROSION IN MHD CHANNELS

PIs: Richard J. Rosa
Richard J. Pollina

STUDENT(S) AND THE DEGREE FOR WHICH THEY ARE REGISTERED:

Gaurav Venkatramana, Ph.D.

INSTITUTION/ORGANIZATION: Department of Mechanical Engineering
Montana State University
Bozeman, Montana 59717
(406) 994-6284

GRANT NO.: DE-FG22-88PC 88928

PERIOD OF PERFORMANCE: 9-30-88 through 9-30-91

I. CORROSION AND ARC EROSION IN MHD CHANNELS

OBJECTIVE: The objective of this work is to study the corrosion and arc erosion of MHD materials in a cooperative effort with the MHD topping cycle program of DOE. Materials tested in the Avco Research Laboratory/Textron facility, or materials which have significant MHD importance, will be analyzed to document their physical deterioration. Conclusions shall be drawn about their wear mechanisms and lifetime in the MHD environment with respect to the following issues: sulfur corrosion, electrochemical corrosion, and arc erosion. The impact of any materials or slag conditions on the level of power output and on the level of leakage current in the MHD channel will also be noted, where appropriate.

WORK DONE AND CONCLUSIONS: Last year a method for determining leakage current was developed and applied to a large quantity of test data from the DOE MHD facility in Butte MT. This data reduction task continues as test results become available. The primary effort this year has been to understand the mechanisms responsible for leakage and how they effect electrode lifetime. To this end, by comparing data from many runs, we have sought correlations between the leakage values and various duct operation parameters. The resulting correlations have suggested three mechanisms plus a possible fourth which may together be responsible for most of the observed leakage.

A major conclusion is that axial current leakage correlates only weakly with axial electric field, but strongly with transverse current density. This relegates to a minor role the leakage mechanism previously thought by the MHD community to be the dominant one. The mechanisms now thought to play a role, and their contribution to a typical total apparent leak of 140 amperes are as follows.

1. Normal segmentation (Due to the finite size of each electrode)..20 A.
2. Resegmentation (Due to cathodes shorting in groups of three or four as a result of slag polarization)............40 A.
3. Normal slag leakage (Expected axial current flow due to known electrical conductivity of slag).....................25 A.
4. Arc streamers, analytical problems, etc....................55 A.

The first three are reasonably well understood while the third is not. Several possibilities are currently being explored. One of these is that arcs may stream for a distance of several centimeters off the downstream edges of electrodes (probably the cathodes). At the other extreme, we are asking hard questions as to whether or not either measured or calculated input parameters could possibly deviate from true values by enough to make the fourth mechanism dissapear. And if so, how? In either case a greater understanding of the MHD generation process and electrode wear process results.

The most serious gas side erosion of anodes, which takes place on the leading or upstream corner, appears to be a thermal erosion process caused by localized heating of the platinum surface by the anode arcs. Using Auger spectroscopy, sulfur and potassium have been identified at the base of arc erosion tracks in exposed platinum and grain boundary attach has been observed both on the active anode corner and on the platinum top cap of the anode. The dominant loss mechanism on the Pt corner piece is arc melting with some chemical attack. The attack is a surface or liquid phase attack which leaves no tell-tale reaction zone. On the top cap grain boundary attack is the most serious loss mechanism. The corroding species are sulfur in the gas and K_2CO_3, the seed material used to enhance the efficiency of the MHD process, and KOH. On the cathode wall the recession rate of tungsten cathodes at their upstream corner is also thermally activated erosion due to the presence of strong electrical activity on the cathode leading edge in a high water vapor environment, though it is more difficult to associate a specific electrical process to its cause at this time.

Electrochemical and chemical wear of the waterside materials is also a factor in the choice of MHD materials. Using scanning electron microscopy, here has been observed a loss of tungsten from the surface of 75% W-Cu alloy from tests at the CDIF together with a pitting corrosion. The pitting is less severe with the bar wall design than it is with the peg wall design because of the lower interelement leakage currents through the connecting hoses in a bar wall in contrast with the small (<1mm) distance between peg wall elements with an o-ring seal. At the water surface the W reacts to form an oxide-hydroxide layer which dissolves leaving little(<1 micron) scale. Work is currently being done to determine the severity of this corrosion.

<u>SIGNIFICANCE TO FOSSIL ENERGY PROGRAM</u>: The MHD development program of DOE has the objective of providing cleaner and more efficient conversion of coal to electricity. One of the most serious issues facing the MHD program is the identification of materials and structural designs which will give the required 2000 hour lifetime in the MHD channel environment. Currently both metallic and ceramic materials are being tested in the MHD program and both types of materials, as well as their attachments, are susceptible to sulfur corrosion, to electrochemical corrosion, and to arc erosion. The final choice of materials and

designs may impact the operating parameters of the MHD power train in order to meet the goal of a 2000 hour lifetime.

PLANS FOR THE COMING YEAR: This grant terminates this year on 9/30/91. Until then current activity will continue and summary of the three year effort will be prepared.

II. HIGHLIGHT ACCOMPLISHMENTS

1. Discovery of correlation functions linking apparent axial leakage current to transverse current and Hall parameter.
2. Determination of three mechanisms contributing to apparent leakage current.
3. The identification of the chemical species at the base of a cleaved arc groove using Auger spectroscopy means that not only sulfur appears to play a role in the loss of platinum but also the MHD seed material, K_2CO_3, and KOH attacks platinum. So for the anode, at least, the question of eastern vs. western coal becomes less important from a sulfur corrosion point of view since it is not the only culprit in Pt wear.
4. The first observation of grain boundary attack on platinum MHD anodes is a major step forward in understanding the nature of the surface wear and the limitations of using platinum in that environment. Subsequent to this observation, an oxide (zirconia) stabilized platinum was tested with a noticeable reduction in arc tracking due to the more grain boundary attack-resistant structure of the oxide dispersed material.
5. The recession rate of tungsten cathodes at their upstream corner is attributed to the presence of strong electrical activity in a high water vapor environment. This explains why Mo wears faster than W (it is more reactive to water vapor) and why no corrosion products are ever observed (the oxides are volitile in this environment).
6. The identification of the waterside corrosion mechanism of the primary candidate for the wide wall makes progress much more focussed towards learning how to use the material or in deciding to rule it out altogether.

III. ARTICLES AND PRESENTATIONS

Papers given since the last contractors meeting are:

Pollina, R. J., W. Simpson, L.C. Farrar, R. J. Rosa, D. L. Douglass, "MHD Channel Element Errosion - Corrosion Studies," 28'th Symposium on the Engineering Aspects of MHD, Chicago, June 26-28, 1990, pp. VI 6.1.

Rosa, R.J., "Leakage Resistance and Current Inferred from CDIF Operating Data," 28'th Symposium on the Engineering Aspects of MHD, Chicago, June 26-28, 1990, pp. VI 4.1-4.5.

Rosa, R.J., "Leakage Current and Electrode Wear Processes," 29'th Symposium on the Engineering Aspects of MHD, New Orleans, June 18-20, 1991.

Pollina, R.J., and N. Anderson, (Ceradyne Inc.), Advanced Aerospace Materials/Processes Conference, May 20-23, 1991, Long Beach, CA.

Pollina, R.J., S.W. Petty, C. Pian, E.W. Schmitt, J. Reich, A. Dunton, and L. Farrar, "Materials Corrosion and Confirmation Test Results for 1A4 50 MW(th) Proptotypical MHD Channel", 29th SEAM, June, 1991, New Orleans, LA.

Pollina, R.J., S.W. Petty, C. Pian, E.W. Schmitt, J. Reich, A. Dunton, and L. Farrar, "Materials Corrosion and Confirmation Test Results for 1A4 50 MW(th) Proptotypical MHD Channel", Institut de Mecanique de Grenoble, Sept. 1991, Cadarache, France.

Pollina, R.J., E.W. Schmitt, A.W. McClaine, C.C.P. Pian, J. Reich, and L.C. Farrar, "Engineering Design and Performance Calculations for a 50 MWt Coal-Fired MHD Generator", 28th SEAM, June 26-28, 1990, Chicago, IL.

In addition a presentation was given before a DOE peer review panel on September 20, 1990, in Knoxville Tennessee.

Date: April 5, 1991

Title: Effects of Catalytic Mineral Matter on CO/CO_2 Ratio, Temperature and Burning Time for Char Combustion

P.I.s: John P. Longwell
Adel F. Sarofim

Students: Zhiyou Du, ScD (1/90)
Chun-Hyuk Lee, PhD candidate

Institution: Massachusetts Institute of Technology
Cambridge, MA 02139 (617) 253-4534

Grant No.: DE-FG22-89PC89774

Period of Performance: 9/1/89 - 8/31/92

I. ABSTRACT

Objective

The objective of this program is to determine the CO/CO_2 ratio generated at or near the surface of burning char as a function of temperature gas composition and char properties with a special emphasis on the effect of catalytic mineral constituents.

Work Done and Conclusions

The electrodynamic balance, developed in our laboratory, is being used to study the oxidation of 200µm spherocarb char particles. The weight, oxidation rate, and surface area of individual char particles are measured. CO/CO_2 ratio produced by oxidation was determined by gas chromatography.

The electrodynamic balance has been built to allow operation at pressures up to 25 atm. Surface areas are measured by CO_2 adsorption and calculated from the Dubinin-Polany relationship. The higher pressure gave a substantial improvement in accuracy.

CO/CO_2 ratio for uncatalyzed spherocarb was measured over a temperature range of 750-1400 K for steady-state conditions where little oxidation took place in the surrounding cold gas. Above this temperature significant oxidation of CO to CO_2 took place in the gas phase. The CO/CO_2 ratio increased from 0.1 at 700 K to approximately 1.0 at 1400 K for a 20% oxygen atmosphere. Increasing oxygen decreased the CO/CO_2 ratio.

A model of char oxidation has been developed which takes into account the distribution of oxygen chemisorption energies on the char surface and which asumes that CO and CO_2 are formed on different chemisorption sites. Catalysis by calcium was found to increase the number of CO_2 sites with little effect on the CO producing sites. So far, the model results are quite consistent with the measurements.

Significance to Fossil Energy Program

The burnout of char particles in pulverized coal combustion depends on particle temperature and reactivity. The CO/CO_2 ratio strongly effects particle temperature. Both this ratio and reactivity depend on catalyses by calcium and other inorganic coal components. Direct determination of CO/CO_2 ratio and reactivity will allow more accurate modeling of the coal burnout process and of the requirements for efficient coal combustion.

Plans for the Coming Year

Attention is now being shifted to measurement of the effects of calcium and irons catalysis on the CO/CO_2 ratio. Modeling of the oxidation proces will be extended to take into account the effects of gas phase oxidation and mass transport limitations.

II. HIGHLIGHT ACCOMPLISHMENTS

1. Improved accuracy for determination of single particle surface areas.
2. The first measurements of CO/CO_2 ratio, produced at the char surface, as a function of temperature.
3. An oxidation model which promises to provide an excellent framework for dealing with the effects of catalysis and temperature.

III. ARTICLES AND PRESENTATIONS

Du, Z., Sarofim, A.F., Longwell, J.P., and Mims, C.A., "Kinetic Measurement and Modeling of Carbon Oxidation" *Energy and Fuels*, Vol. 5, p 214-222 (1991).

Bar-Ziv, E., Longwell, J.P. and Sarofim, A.F. "Determination of Surface Area Single Particles from High Pressure CO_2 Adsorption--Desorption Measurements in an Electrodynamic Chamber" *Energy and Fuels*, 5, 227-228 (1991).

April 18, 1991

TITLE: Mineral Transformations and Fragmentation in Coal Combustion

PI: Boyd F. Edwards

STUDENTS AND THE DEGREE FOR WHICH THEY ARE REGISTERED: Yao Dan (Ph. D.), Xiaopei Guo (M. S.), Jie Huang (Ph. D.)

INSTITUTION/ORGANIZATION: West Virginia University Department of Physics, Morgantown, West Virginia 26506, (304) 293-3422

GRANT NO.: DE-FG22-89PC89791

PERIOD OF PERFORMANCE: October 1, 1989 to September 30, 1992

I. ABSTRACT

OBJECTIVE : Our goal is to use a rate equation approach to understand mineral matter transformations and fragmentation during pulverized coal combustion.

WORK DONE AND CONCLUSIONS : We have studied fragmentation of pure char using a rate equation modeling approach. This fragmentation arises from oxidation in the char macropores leading to widening and fusion of pores, and finally to loss of integrity and to fragmentation as final bridges between different regions of a particle are consumed. The rate equation gives the particle mass distribution $n(x,t)$ (the number of particles of mass x at time t) based on a fragmentation rate $a(x)$, a reaction (mass loss) rate $c(x)$, and a distribution $\bar{b}(x|y)$ of "daughter" particle masses x produced by fragmentation of a parent particle of mass y.

Several exact analytical solutions and numerical solutions have been obtained to the rate equation. These involve the general power-law forms $a(x) = Ax^{\alpha}$, $c(x) = \epsilon x^{\gamma}$, and $\bar{b}(x|y) = f(y)x^{\nu}$ of the kernels, with $f(y) = (\nu+2)/y^{\nu+1}$ following from mass conservation. A general solution for random mass removal with $\gamma = 1$ and arbitrary α, ν, and ϵ shows a wide range of physical behavior reflecting a range of combustion temperatures, coal ranks, and oxygen concentrations as the arbitrary parameters are varied.

It is not known whether real experimental particles obey these power-law forms. Since available experimental data sets typically involve ensembles of particles of all sizes, it is difficult to extract information about the kernels from the data. As an important first step in identifying the kernels for actual physical particles, we have obtained these kernels for random bond removal from percolation clusters near the percolation threshold. Percolation clusters are numerically generated spatially random porous objects which have been shown to adequately model many aspects of real coal particles. We find that, for large clusters, $a(x)$ and $c(x)$ obey the power-law forms with $\alpha = \gamma = 1$, whereas $\bar{b}(x|y) = y^{-\phi}g(x/y)$ differs from the power-law form, with ϕ depending on the dimensionality of the lattice ($\phi = 1$ and $g(r) = 2$ in one dimension, whereas $\phi = 1.6$ and $g(r) = Br^{-w}(1 - r^{-w})$ in two dimensions, etc.). An exact scaling law giving the value of ϕ in all dimensions is also derived. That $\bar{b}(x|y)$ can be written as a function $g(r)$ of the daughter/parent mass ratio $r = x/y$ indicates that $\bar{b}(x|y)$ is scale invariant for large clusters.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM : Strict regulations on particulate smokestack emissions have threatened the competitive position of energy production by

pulverized coal combustion. Fragmentation and mineral-matter transformations during coal combustion can reduce the sizes of fly-ash particulates, making them more difficult to remove from the exit gas stream. Thus, understanding the processes of formation of these particulates is important to pollution abatement.

PLANS FOR THE COMING YEAR : It is important to study the implications of mineral matter during combustion. Since it is doubtful that exact analytical solutions can be obtained when mineral matter is included in the rate equation approach, we intend to focus on numerical solutions. Knowledge about the forms and implications of the kernels gained from the analytical solutions and from the studies of percolation clusters will be used to postulate initial guesses at kernels appropriate to experiments. Using an iterative procedure, these kernels will be adjusted until the best fit between the predicted time evolution and the experimental data is obtained, thereby obtaining best estimates of the kernels for the experimental data.

II. HIGHLIGHT ACCOMPLISHMENTS :

We have obtained analytical and numerical solutions to a rate equation for pure char fragmentation which illuminate various regimes of behavior. We have also calculated the kernels relevant to percolation clusters as a first step toward comparison with experiments. These results deepen the understanding of fragmentation needed to extend the models to include mineral matter.

III. ARTICLES AND PRESENTATIONS :

1. "Exact and Asymptotic Scaling Solutions for Fragmentation with Mass Loss", M. Cai, B. F. Edwards, and H. Han, Phys. Rev. A **43**, 656 (1991).
2. "Fragmentation of Percolation Clusters - Criticality and Scaling", M. F. Gyure and B. F. Edwards, Bull. Am. Phys. Soc. **36**, 769 (1991).
3. "Dynamic Behavior of Fragmentation with Mass Loss", X. Guo and B. F. Edwards, Bull. Am. Phys. Soc. **36**, 769 (1991).
4. "Rate Equation and Scaling for Fragmentation with Mass Loss", B. F. Edwards, M. Cai, and H. Han, Phys. Rev. A Rapid Communications **41**, 5755 (1990).
5. "General Solution and Simulations of Linear Fragmentation with Mass Loss", B. F. Edwards, J. Huang, and D. Yao, Bull. Am. Phys. Soc. **35**, 201 (1990).
6. "Rate Equation and Scaling for Fragmentation with Mass Loss," B. F. Edwards, M. Cai, and H. Han, Proc. 17th IUPAP International Conference of Thermodynamics and Statistical Mechanics - STATPHYS 17, Rio de Janeiro, Brazil, 4 August (1989).
7. "General Solutions and Scaling Violation for Fragmentation with Mass Loss", J. Huang, B. F. Edwards, and A. D. Levine, submitted to J. Phys. A.
8. "Fragmentation of Percolation Clusters near the Percolation Threshold", M. F. Gyure and B. F. Edwards, submitted to Phys. Rev. Lett.
9. "Numerical Simulation of Fragmentation with Mass Loss", D. Yao, B. F. Edwards, and X. Guo, submitted to Phys. Rev. A.
10. "Exact General Solution for Fragmentation with Random Mass Loss", X. Guo and B F. Edwards, to be submitted to Phys. Rev. A.

TITLE: **High-Temperature Membranes for H_2S and SO_2 Separations**

P.I.: Jack Winnick DATE: 4/9/91

STUDENTS AND DEGREE FOR WHICH THEY ARE REGISTERED:
Dennis McHenry PhD
Steven Alexander PhD

INSTITUTION/ORGANIZATION: Georgia Institute of Technology
School of Chemical Engineering
Atlanta, Georgia 30332-0100
(404) 894-2839

GRANT NO.: DE-FG22-90PC90293

PERIOD OF PERFORMANCE: 09/01/90 to 08/31/93

I. ABSTRACT

OBJECTIVE:
To develop a high temperature membrane separation technique which can be applied to gas mixtures involved in coal utilization. For coal gasification, H_2S is removed from the syn-gas stream, split into hydrogen, which enriches the syn-gas, and sulfur, which can be condensed from an inert gas sweep stream. For coal combustion, SO_2 is separated from the flue gas, with concentrated SO_3 produced as a by-product. Both processes appear economically viable, but each requires fundamental improvements: more efficient membranes and a more efficient anode for the H_2S cell.

WORK DONE AND CONCLUSIONS:
Investigated different binder systems for tape casting of membrane matrix materials. Best results were obtained when the ceramic material was milled with the binder/solvent system and the ensuing slip was poured onto a polyethylene glycol coated substrate to facilitate removal of the tape once the solvent had evaporated.

Particle sizes for the different matrix materials were investigated to determine the pore size distribution in the resulting tapes and to optimize the ceramic loading in the slip. Matrix materials investigated include MgO, borosilicate glass, silicon carbide and silicon nitride. Particle size analyses for the SiC and Si_3N_4 were obtained from Phillips Petroleum, the manufacturer of these high purity ceramics.

With the SO_2 removal process, a new electrode is undergoing testing for improved chemical stability and surface area characteristics. Lithiated nickel oxide holds great promise for this purpose and requires some final corrosion testing and X-ray diffraction analysis to determine its stability in the 5 wt% V_2O_5 in potassium pyrosulfate ($K_2S_2O_7$) electrolyte.

The SO_2 removal process has completed a sucessful full cell test using lithiated NiO electrodes and a membrane of tape cast Si_3N_4. This test showed 5 mA/cm^2 at 1.5 V cathodic overpotential, compared to 1 mA/cm^2 at 1V cathodic for previous electrode/membrane combinations. This cell obtained stable operation for two weeks, an improvement over previous runs which yielded quality data for 2-3 days. This run was also stable at current densities of 10 mA/cm^2; however, due to cell design, the requisite flow rate to support this current density had insufficient residence time and was entering the cell cool, preventing proper conversion of SO_2 to SO_3, impeding removal and increasing concentration polarization. Redesign has been completed.

For the H_2S removal process, work has centered around polishing applications of the process (H_2S levels below 100 ppm) and development of a gas impermeable membrane to prevent the cross-over of H_2 from the process gas side to the sweep gas side.

Full cell tests have been performed with success in both areas. For the polishing application tests, two mats of zirconia cloth ZYW-30A, from Zircar Fibrous Ceramics, soaked with molten salt electrolyte $(Li_{0.62}K_{0.38})_2CO_3$, were used as the membrane between a porous carbon cathode and a porous CoS_2 anode. 85% of the H_2S was removed from a simulated process gas with an H_2S level of 100 ppm and a CO_2 level of 1.5%. However, hydrogen cross-over allowed corresponding CO_2 removals of 50%. Still, considering that the CO_2 concentration in the process gas was two orders of magnitude higher than the H_2S concentration, removal is still highly preferential for H_2S.

For the prevention of hydrogen-crossover, zirconia cloth was layered with MgO tape made using an acrylic binder. The overpotential data from this experiment suggest that hydrogen was not present at the anode. Completely selective removal of H_2S was recorded, but high overpotentials at the anode eventually led to oxidation of the CoS_2 anode and breakdown of the cell performance.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:
Replacement of current scrubbing technology and Claus plants with one step removal/conversion processes which generate saleable by-products at attractive economic rates.

PLANS FOR THE COMING YEAR:
For the SO_2 removal process: Optimize ceramic loading in the tape casting process, evaluate the stability of the lithiated NiO electrodes for use at the cathode and anode, and to increase the current density of the system to the design criteria of 50 mA/cm^2 at 1 V total overpotential.

For the H_2S removal process: Continue optimization of the ceramic membrane, evaluate electrolyte activity coefficients and study oxidation reactions at the anode.

II. HIGHLIGHT ACCOMPLISHMENTS

Particle size determinations led to initial optimization of ceramic loading in tape cast membranes. Coating of substrate material with polyethylene glycol solutions enhanced removal of the dried "green" tapes.

SO_2 removal cell: Identified possible replacement electrode material, lithiated NiO. Increased current density from 1 mA/cm^2 to 5 mA/cm^2 (sustained) at 1.5 V cathodic overpotential. Reached 10 mA/cm^2 for short periods of time, but was limited by heating of inlet gas.

H_2S removal cell: Used to polish natural gas streams with low concentrations of H_2S. Prevented transport of H_2 from cathode to anode and subsequent oxidation of carbonate supporting electrolyte.

III. ARTICLES AND PRESENTATIONS

S. Alexander, AIChE 1990 Nat'l Mtg, Chicago, November, 1990.
D. McHenry, ACS Nat'l Mtg, Atlanta, April, 1991.
S. Alexander, ACS Nat'l Mtg, Atlanta, April, 1991.
J. Winnick, Electrochem. Soc. Mtg, Wash., DC, May, 1991.

TITLE: Combustion of Dense Streams of Coal Particles
PRINCIPAL INVESTIGATOR: Kalyan Annamalai
STUDENT(s) AND DEGREE FOR WHICH THEY ARE REGISTERED:
W. Ryan,,(PhD)
K. Esam, (MS)
INSTITUTION/ORGANIZATION: Mechanical Engineering
Texas A&M University
College Station, TX 77843-3123
(409)-845-2562
GRANT NO: DE-FG-22-90PC90310
PERIOD OF PERFORMANCE: Aug. 29,1990 to Aug 28,1992

I.ABSTRACT

OBJECTIVE(s):

1.Develop a group combustion approach in modeling transient combustion for both the cylindrical and spherical clouds of high volatile coal particles.

2.Use video-imaging of flame,obtain experimental data on combustion intensity and compare the experimental data with the predictions.

WORK DONE AND CONCLUSIONS:

1.Group Model

A. A **generalized group combustion model** applicable to planar,cylindrical and spherical clouds has been developed.

B. Preliminary results on **ignition time have been generated for cylindrical clouds** and the results for ignition time are qualitatively similar to the results obtained with the spherical cloud model.

C. The **model has been modified to include backward reactions so that dissociation can be included.** The results with dissociation for a spherical cloud show existence of double flame in the initial periods: inner flame (Flame-M) propagating into premixed volatiles and oxygen in the cloud and outer diffusion flame (Flame-D).After complete consumption of oxygen in the cloud, the Flame-M disappears leaving only diffusion flame. Such a result of double flame is unique to coal dust clouds since volatiles are released at relatively higher temperatures compared to liquid drop clouds.The existence of double flame may promote more NOx emission.

D. The **combustion rate of hot char particles in the cloud has been obtained for spherical clouds.** It is found that the combustion rate of the hot char particles in the cloud is controlled by the diffusion into the cloud rather than by the diffusion rate to the individual particle.

2.Experimental Verification

A. In order to improve the optical accessibility a flat flame burner is being acquired.

B. A Video imaging system including i) Videocamera,ii) VCR, iii)Image Processing Board and Software,iv) High resolution Video Monitor is in the process of being acquired.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM:

Data is generated for the effect of cloud denseness on the combustion rate.For eg, as the load is increased in a boiler, fuel input rate must be increased. The increased solid fuel flow through the same impeller plate causes increased coal denseness with reduced combustion intensity.Further the improved pulverization does not necessarily improve combustion intensity if particles are entrained as a cluster and burn as a cluster. A state supported parellel program on a small scale boiler burner (swirl burner)is underway . The know how generated from the fundamental studies will be used to improve the burner operation and design.

PLANS FOR THE COMING YEAR:

Generate model results for cylindrical clouds for the actual geometric and operating conditions of the burner.Obtain experimental data on the double flame positions and the har burn out rate under dense conditions. Compare the experimental data with predictions.

II.HIGHLIGHT ACCOMPLISHEMENTS

The cloud model results have been generalized for planar,cylindrical and spherical clouds since the small scale experiments my involve a batch of particles (approximately spherical),cylindrical stream of particles through a circular slot and and planar stream through a rectangular slit.Cylindrical cloud results have already been obtained for ignition time.

A two part comprehensive review article has been written which reviews the literature on Interactive Transport Processes in Gasification and Combustion in Drop Arrays and Clouds (Part I) and Coal/Char Arrays and Clouds (Part II) . Part I has been reviewed and it will be published. Part II will be submitted in Summer 1991.

The experimental work will begin in Fall 1991.

III. ARTICLES AND PRESENTATIONS

Annamalai K.,and Ryan,W., " Interactive Processes in Gasification and Combustion Processes, Part I : Liquid Drop Arrays and Clouds," J.of Prog.in Energy and Combustion Sc.(1991).

Annamalai K., Ryan W. and Caton,J.," -ibid-Part II: Coal/Char Arrays and Clouds," Prog.Energy and Comb.Sc.,to be submitted in Summer (1991).

Annamalai K. and Anand V., " Group Effects on NOx Emission," to be submitted to ASME,WAM, (1991)

Laster, W.R. and Annamalai, K., " Ignition Delays of Liquid Drop Clouds: Group Combustion Theory," Chem.Engineering Communications, accepted,(1991).

Ryan W and Annamalai K.," Group Ignition of Coal Particles," Journal of Heat Transfer, accepted (1991).

Annamalai,K. and Ryan,W. " Evaporation Characteristics for Arrays, " to be presented ,Central States of Combustion Institute, Nashville, TN., April 22-24 (1991).

Ryan,W. and Annamalai," Group Combustion of Coal:Double Flame," to be submitted to Journal (1991).

Annamalai,K. and Ruiz,M., " Lcally Fluidizing Feeder for Powder Transport," to be submitted to Journal (1991).

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