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Undergraduate Research Studies Program at Participating Institutions of the HBCU Fossil Energy Consortium

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Final Report

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ABSTRACT

The primary objective of this research program is to expose students in the Historically Black Colleges and Universities (HBCU) Fossil Energy Consortium Institutions to energy and fossil fuels research, to stimulate their interest in the sciences and engineering and to encourage them to pursue graduate studies. The long-range goal is to ensure a future supply of coal scientists and engineers. This project has been valuable in providing research opportunities in the respective Universities as well as at various Fossil Energy operational units.

This report provides the research accomplishment of the various students who participated in the program. The students gained valuable experience through this program and a number of them are currently pursuing their graduate programs in various areas of science and engineering.

UNDERGRADUATE RESEARCH PROJECTS

RESEARCH TITLE: Energy enhancement and pollutant reduction in coal by cryogenic diminution

PRINCIPAL INVESTIGATORS: Sunnie A. Aburime and William Knuth

STUDENT/DEGREE PROGRAM: Bubacarr Barrow

INSTITUTION: Alabama A & M University

OBJECTIVES:

To ascertain if coal at liquid nitrogen temperature (-196°C) will shatter to ultrafine, submicron particles if it is suddenly expanded to atmospheric pressure. It is expected that the project will pave the way for more cost-effective commercial production of ultrafine coal particles. Such a process may also result in coal desulfurization since the non-porous pyrites and minerals in the coal will not shatter.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS:

Prior work has indicated that freezing coal to cryogenic temperature results in significant microfracture development. It is anticipated that the process will work effectively when the coal is brittle. It has been demonstrated that abrupt decompression of coal fines that have been saturated with superheated water results in further size reduction of the coal when the water flashes to steam in the pores of the coal particles. These experiments were carried out at high temperature (over 700° F) in order to produce the superheated water effects. At such a high temperature, the coal has begun to soften and gain toughness. Arrangements have been made to conduct such chilling experiments with dry coal powder as well as with powder that has been pre-soaked in water. It is expected

that the cryogenically chilled coal will show substantial microfracturing when viewed by SEM. It is the presence of the micro-fracturing that will give rise to the anticipated fine powder.

A preliminary economic assessment has been completed. This assessment shows that the process will have to be a recuperative refrigeration cycle, so that a substantial level of refrigeration (on the order of 80%) is recuperated in the cycle. If the incoming raw coal is chilled by the recuperation process, it appears that the cost of preparing submicron coal fines will be about $6.00 to $10.00 per ton. However, savings in coal and process cleanup, and higher energy production per ton, are equal to or higher than the process cost, so a net cost savings can be postulated. As more information is developed, it may be found that the cost balance is more or less favorable. Nevertheless, the important fact is that there is not a major cost impact of using this process.

RESEARCH TITLE: Competition of NO and SO_2 for OH generated within electrical aerosol analyzers

PRINCIPAL INVESTIGATOR: Arthur W. Stelson

STUDENTS/DEGREE PROGRAM: Roselyn Strong

INSTITUTION: Atlanta University Center

OBJECTIVES:

To apply Electrical Aerosol Analyzer (EAA) to accurate measurements of aerosol distributions in the flue gas.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS:

Pure sulfur dioxide and nitric oxide were mixed with dried and filtered, compressed room air in a two stage rotameter dilution system. The diluted concentrations of SO_2 and NO were 1300 ppm and 500 ppm, respectively. The

dilution system was of teflon and stainless steel construction (Stelson). Two 47 mm filter holders (Gelman 2220 with Gelman A/E glass fiber filter) were placed between the gas cylinder regulators (SO_2 and NO) and their respective rotameters. The first stage of dilution included the mixture of SO_2, NO, and air regulated by rotameters. The pressure of the mixture was controlled by a value which insured the pressure within the dilution system to be over 1 atm. During the second dilution, the dilute mixture was allowed to mix with filtered and dried, compressed room air. The sample was then drawn through a Thermo Electron Model 40 Pulsed Fluorescence SO_2 Monitor, after having passed through another 47 mm filter holder (Gleman 2220 Gelman A/E glass fiber filter). The $S0_2$ monitor, which has a sample intake capacity of 6 1/min, was used to directly measure the SO_2 concentration.

The dilute mixture was then drawn through the aerosol inlet stream of Thermo System, Inc. Model 3030 Electrical Aerosol Analyzer (EEA) and the Thermo Electron Model 10 A/R Chemiluminescent NO/NO_x Monitor; the EAA and the Chemiluminescent NO/NO_x Monitor have a sample intake capacity of 4 1/min and 1.5 1/min, respectively. All excess volumes were vented and sample from the EAA was removed by a vacuum pump. In addition, a calibrated Honeywell Electronik 194 Dual Channel Recorder was connected to the EAA and SO_2 Monitor to observe the signal outputs of the instruments. A Linear Instruments Model 225/MM Chart Recorder was used to record the NO signal. For improved accuracy, the analog signal from the SO_2 Monitor was read using a Hewlett Packard Model 3466A Digital Voltmeter instead of the analog meter supplied with the instrument. The EAA signal output indicated the formation of artifact aerosol particles which decrease with the presence of NO.

Based on the analysis of the signal outputs of the instruments, NO competition with SO_2 for OH radicals has been demonstrated; even though, exact quantification has not been attained. Verification of the aerosol composition has

not been performed because our laboratory currently does not have the required instrumentation. With sulfur dioxide in room air, the aerosol composition could be an sufuric acid-water mixture or $NOHSO_4$ formed by the reaction of nitrous acid with sulfur trioxide.

Further, observations made with the NO/NO_x monitor show a significant SO_2 interference, (100 ppm NO for 1300 ppm SO_2 and 500 ppm NO) which was confirmed in the absence of NO (30 ppm NO for 1300 ppm SO_2). The presence of NO in an SO_2-dried room air mixture significantly decreases the amount of artifact aerosol formed within the electrical Aerosol Analyzer.

RESEARCH TITLE: Dispersed iron catalysts for coal gasification

PRINCIPAL INVESTIGATOR: Godfried M.K. Abotsi

STUDENT/DEGREE PROGRAM: De'Awna McMahon

INSTITUTION: Clark Atlanta University

OBJECTIVES:

The primary objective of this research program is to expose students in minority institutions to energy and fossil fuels research, to stimulate their interest in the sciences and engineering, and to encourage them to pursue graduate studies. The research goal is to determine the effects of coal surface charge on the adsorption of iron and magnesium, representative coal gasification catalysts, from aqueous solution.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS:

A subbituminous coal was used for the study. Two types of analysis were performed. These were zeta potential measurements (electrophoresis) and atomic absorption spectrophotometric analysis. The zeta potential results show that as the medium became more alkaline, the zeta potential became more negative,

indicating that the coal acquired a more negative surface charge. Atomic absorption analysis of the filtrates from the adsorption studies show that as the medium became more neutral, most or all of the metal ions were adsorbed onto the surface of the coal, whereas adsorption was negligible in very acidic solutions. It was observed that the coal acquires the most negative charge when the medium is alkaline. This can be attributed to the negatively charged functional groups that result when functional groups such as carboxylic acid and hydroxyl groups lose their acidic protons, resulting in exposed, negatively charged oxygens. Since the catalyst precursors are positively charged metal ions, the most favored interaction between the coal surface and the catalysts would occur when the coal surface has a large negative charge density. The high level of adsorption in alkaline medium is attributed to this.

It can be concluded that in order to obtain the most efficient catalyst impregnation, the catalyst solution should be near neutral so that maximum adsorption would occur. The medium for magnesium adsorption may need to have a higher pH relative to the medium needed for iron adsorption. This may be due to the magnesium ion being divalent (Mg^{2+}), whereas the iron (III) ion is trivalent (Fe^{3+}), resulting in greater attraction for the negative surface of the coal. In strongly alkaline media, insoluble iron or magesium compounds may be produced.

The student investigator is currently pursuing graduate studies in Chemistry at the Georgia Institute of Technology. Thus, the research and the educational objectives of encouraging the student to undertake graduate studies has been achieved.

RESEARCH TITLE: NQR/NMR studies of copper-cobalt catalysts for syngas conversion

PRINCIPAL INVESTIGATORS: A.N. Murty and Frank Ohene

STUDENTS/DEGREE PROGRAM: George Jones
Tracy Hill
B.S. Chemistry

INSTITUTION: Grambling State University

PROJECT NO. 1

OBJECTIVES:

The goals of this project are to:

(i) prepare a series of copper-cobalt catalysts with or without a third component - chromium or titania,

(ii) investigate changes in the metallic charge distribution through a study of NMR spectra of cobalt and NQR spectra of copper,

(iii) investigate the magnetic character of the catalysts by examining its hysteresis properties,

(iv) evaluate the relationship between catalytic and magnetic properties.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS

Copper-cobalt catalysts were prepared by coprecipitation of the nitrates of the metals in the presence of sodium carbonate solution maintained at pH 7-8 and 80° C. The precipitate was thoroughly washed, dried at 100° C, calcined at 350° C for 20h and the oxide reduced in hydrogen at 350° C for 18h. Magnetic susceptibility measurements on the samples show that the susceptibility increased with increased in the copper concentration of the catalysts. However, the contribution of cobalt oxides to the magnetic moment was insignificant. A Hysteresis in the data is attributed to the existence of cobalt in the spinel structure which renders its reduction to the metallic state difficult. Another important observation is an appreciable increase in the coercive field value as the

temperature was reduced from ambient conditions to liquid nitrogen temperature. The catalyst particle sizes were estimated to be in the 20-50 nm range.

Nuclear quadrupole (NQR) and Nuclear magnetic resonance (NMR) studies of the catalysts gave a consistent occurrence if high frequency lines in the 222.5 - 226.5 MH_2 range for all the samples. It was concluded that significant changes occurred in the metallic charge distribution of the copper-cobalt clusters. The modifications were sensitive to the ratio of the metals and the method of catalyst preparation.

PROJECT NO. 2

OBJECTIVES:

To investigate the effects of coal particle size distribution, temper-ature and shear on the rheology of coal water slurries (CWS).

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS

The coal used for this study was PSOC 1475. The coal samples were ground to various distributions and screened to obtain size fractions of: -400 mesh, +400/-325 mesh, +325/-270 mesh, +270/-200 mesh and +200/-100 mesh using standard U.S. sieve screens. Slurries were prepared from blended distributions using either an ammonium naphthalene sulfonate (A-23) for Igepal 990 as an additive. Each slurry was made using a dosage of 0.3% dispersant based on dry coal and at a pH of 10. The packing concentrations were calculated from particle size distribution measurements obtained by using a Microtrac Particle Size Analyzer Model 2600, and a program based on truncated log-normal distribution which has been developed at the Adelphi Center for Energy Studies. The packing concentrations calculated increased with increase in the number of fines (-325 mesh) to a value of 49% fines by weight. Above a value of 40% fines, the packing

concentration decreased. The particle size distribution was obtained from slurries containing 65% solids content and 0.3% A-23 dispersant.

Rheological analyses of the flow curves show that the flow behavior changed from dilatant to pseudoplastic as the packing concentration increased. Also, the viscosity was found to decrease with increase in the packing concentrations of the slurries. This is an indication that a wider distribution is indeed necessary for more efficient packing. The particle size distribution measurements together with the calculated packing concentrations reveal that, the packing concentrations increase as the percentage of fines (<325 mesh) increase to a value of 40%. Above 40%, the packing concentration decreases.

The viscosity of CWS was found to decrease with increase in temperature between 19° C and 50° C. However, with Igepal 990 as an additive, there was an increase in viscosity between 45° C and 60° C. It is apparent that the flow behavior of the slurry in the low temperature range is governed by the behavior of water. Above 45° C, the flow behavior is dependent on the additive. The change in flow behavior can be caused by changes in the solubility behavior or changes in the interaction of the additive with the coal particles at higher temperature. This may explain the increase in viscosity with increase in temperature when Igepal 990 was used as a dispersant. The high temperature behavior of CWS is of interest with regard to their atomization behavior. Thus, CWS prepared using Igepal 990 as an additive will require special handling techniques at higher temperatures.

RESEARCH TITLE: Catalytic gasification of coal chars by potassium sulfate and ferrous sulfate mixtures

PRINCIPAL INVESTIGATORS: Jale F. Akyurtlu
Ates Akyurtl and
Adeyinka A. Adeyiga

STUDENTS/DEGREE PROGRAM: Evangeline Clendenning
Kilby Williamson and
Jonathan Acquaye
B.Eng; Chemical Engineering, all three

INSTITUTION: Hampton University

OBJECTIVES:

To evaluate the catalytic activity of (K_2SO_4 + $FeSO_4$) mixtures in the steam gasification of coal chars and to compare it with that of K_2CO_3. The research has been planned such that the effects of chemical and physical properties of char upon gasification rate and product composition will be evaluated quantitatively.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS:

One of the physical properties under investigation is the surface area of coal chars, both reacted and unreacted. The surface area of the char is measured by CO_2 - adsorption using a 'Quantasorb' surface analyzer. CO_2 is used as an adsorbate because with it, adsorption equilibrium is reached in a short time even at low relative pressures. The Dubinin-Polanyi theory with modifications by Medek is employed to calculate the surface area of chars from the experimental measurements.

The surface areas of the chars were underestimated by N_2-adsorption because their very fine pores hinder the adsorption of N_2 molecules. The surface areas ranged from about 1 to 12 m^2/g. Therefore, CO_2-adsorption will be employed for further surface area determination. The large variance in N_2-adsorption results is due to the low N_2-uptake. The effect of sample size on the measurements on the

helium pycnometer has also been studied; the results show that there is no sample size effect on density measurements obtained on the helium pycnometer.

RESEARCH TITLE: A new method for cleaning and beneficiation of ultrafine coal

PRINCIPAL INVESTIGATOR: Joseph Okoh

STUDENTS/DEGREE PROGRAM: Michael Holder
Amy Roberts
B.S. Chemistry

INSTITUTION: University of Maryland
Eastern Shore

OBJECTIVES:

To assess new, cost-effective methods for cleaning and beneficiating ultrafine coal by increasing its surface hydrophobicity. Determination of the zeta potential, contact angle, wettability and floatability of coals which have been subjected to various treatments.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS:

A Laser Zee Model 500 was used for the zeta potential measurements of both treated/untreated coal samples. In all cases, the zeta potentials were measured using potassium nitrate as the supporting electrolyte, and the pH was adjusted by the addition of HNO_3 or NaOH. The extraction of surface hydrophobic groups was performed on ground coal samples (treated/untreated). A 50/50 (by volume) mixture of chloroform and ethyl acetate was prepared. 1 gm. of coal sample and 20 mls. of the above solution were mixed and stirred for ten minutes at room temperature. The mixture was filtered through #42 filter paper. The absorbance of the filtrate was read as is on a uv/visible. spectrophotometer at 400 nm. The carboxylic groups in the coal samples were determined by refluxing 125

mg. of coal in air with calcium acetate (0.1N solution, 50 mls., pH = 8.25,) for four hours. The acid that was released was titrated potentiometrically under nitrogen in the presence of the coal, with alkali (0.O5N) until the pH value of 8.25 was restored. A glass-calomel electrode combination in conjunction with a pH meter served as the measuring device. The total acidity of the coal sample was determined by reacting the coal with excess barium at high pH, namely with a solution of 0.2N barium hydroxide plus 0.8N barium chloride under nitrogen. After treatment, the excess barium hydroxide as determined by backtitration with 0.1N HCl. From the titration results, the total acidity of the coal samples was determined.

The concentration of the phenolic groups was obtained by subtracting the concentration of the carboxylic functionality from the total acidity. Approximately 3.0 grams of coal powder, treated and untreated respectively, were loaded into a glass tube with a fritted end. The tube was always very carefully filled to the same height by tapping over two hundred times. The packed tube was placed in the appropriate wetting liquid, and the wetting height was measured as a function of time. From such measurement and by the use of Washburn's equation, the packing constant was calculated from the slope of a graph of the square of the wetting height in meters against time in seconds. By using the calculated packing constant, the contact angles of treated and untreated powdered coal samples were calculated. One gram of treated or untreated coal was added to 60 mL of deionized-distilled water. After one minute of mixing, methyl isobutyl carbinol (MIBC), was added as a frother - collector at a dosage of 0.015kg/mt. The slurry was conditioned for one minute and air was introduced for flotation. Airflow rate was maintained constant for different flotation experiments by the use of a rotometer. Coal froth was collected for three minutes at most, dried to a constant weight with an infrared lamp and weighed.

Through the study of electrical effects, surface phenomena which reflect the conditions at the solid - liquid interface such as adsorption density and zeta potential can be correlated directly with surface phenomena like contact angle and froth flotation that reflect conditions at the solid-liquid-gas interface. Using ethene treated coal sample for example, the zeta potential exhibited a decrease in the magnitude of negative potential compared to untreated coal. The zeta potentials in aqueous solution (pH 2.0 to 10.0) of the ethene treated and untreated Illinois #6 coals reveals that: 1) the zeta potential of the untreated coal is more negative up to pH ~ 6.0 than that of the treated variety. ii) the curve of the zeta potentials of the treated coal exhibits an isoelectric point at pH 3.3, while the untreated does not. These trends can be explained via adsorption and or ionization. If one assumes that the untreated coal surface consists of phenolic (pKa = 10), carboxylic pKa = 4 ~ 5) and sulfonic acid (pKa = 1 ~ 2) functionalities, increasing pH will lead to their deprotonation, in addition to adsorption, causing the coal surface to acquire negative potential from pH 2.0 to 10.0. The response of treated coal to pH changes is quite different. As a result of gaseous phase reaction, the phenolic functionalities are converted to ether functional groups, while the carboxylic and sulfonic acids are converted to esters. Up to pH 3.3, the ester and ester groups become protonated at their oxygen atoms, confering a positive potential on the coal surface. Surface enhanced hydrophobicity has been demonstrated in oxygen functional group analysis. Using the calcium acetate method, the acidity of untreated Illinois #6 coal was computed to be 2.00 meq. H^+/gm. The nitrogen treated Illinois #6 caol had acidity of 1.20 meq. H^+/gm. Olefin (ethene, propene and butene) treated Illinois #6 generally had 0.00 meq. H^+/gm acidity. Using the barium hydroxide method, the quantity of standard acid that was needed to back titrate excess base was determined. From this backtitration, the total acidity of the

coal samples viz untreated, nitrogen, ethene, propene and butene treated samples were computed.

The results demonstrate reduced surface acidity (carboxylic plus phenolic) as a result of gaseous phase treatment. Coal surface hydrophobicity tends to be inversely related to an increase in the content of the carboxylic and phenolic groups in coal. Carboxylic groups exert their effect through ionization in aqueous solution, thereby affecting the magnitude of the electric charge on the coal surface. Apart from the former, the hydrogen ions of both the phenolic and carboxylic functionalities may attract water molecules to the coal surface via hydrogen bonding. In addition, the double bonds associated with the carbonyl groups have a strong polar character, and they can attract polar water molecules to the coal surface, rendering it hydrophilic. A coal beneficiation process has been developed which enhances its surface hydrophobicity. Oxidized coal, containing various oxygen functional groups which are hydrophilic in nature has been alkylated. This process enhanced coal surface hydrophobicity. The added surface alkyl groups improved flotation kinetics through film thinning phenomena and control of the hydrophobic/hydrophilic distribution of surface sites as the coal deashed more efficiently.

RESEARCH TITLE: Characterization studies of coal-derived liquids

PRINCIPAL INVESTIGATOR: Vinayak N. Kabadi

STUDENT/DEGREE PROGRAM: Collins R. Geter

INSTITUTION: North Carolina A&T State University

OBJECTIVES:

The broad objective of the DOE grant is to involve undergraduate students at HBCU's fossil energy research activities. The other objective of this project is to

characterize coal derived liquids for distribution of oxygen, nitrogen and sulfur heteroatoms relative to the average molecular weight distribution of the coal liquid. The technique of size exclusion chromatography will be used. Our recent work on thermodynamics of coal liquids (to be published in FUEL) showed that the distribution of heteroatoms in coal liquids should be known for accurate predictions of the thermodynamic properties of the liquid. This motivated us to undertake this project. The chromatographic separations and analysis work will be done by the undergraduate research assistants.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS:

The Perkin-Elmer PLGel 100 A 5 micron column together with guard column and accessories have been calibrated using PL-polymer standards with o-dichlorobenzene as an internal standard. The hardware configuration consists of Perkin-Elmer LC-401 pump, LCI 100 integrator, PLGel 100 A 5 micron column and Varex light scattering detector. For each sample, two sets of LC runs will be carried out. The first run will be to determine the molecular weight distribution and the number and weight averaged molecular weights. This will be done by comparing the chromatogram with the calibration runs. A sample size of 20-50 ul, and solvent flow rate of about 2 ml/min. will be used.

In the second run, the Varex detector will be taken out of the curcuit and replaced by the fraction collector. Much larger sample sizes and solvent flow rates will be used. We have determined sample size of 500 ul and the solvent flow rate of 10 ml/min. as reasonable starting values. We have 200 ul, 500 ul and 2 ml sample loops available to vary the sample size over a wide range. The fraction collector will be set to collect 10-15 samples, each containing about 10-20mg of the original coal liquid sample. The average molecular weight of each of the fractions will be determined from the previous run. The purpose of this run is to provide

fractions of different molecular weights for analysis of atomic and molecular types. In particular, we are interested in knowing the composition of nitrogen, oxygen and sulfur compounds in these fractions. The fractions from the fraction collector will be processed to strip most of the tetrahydrofuran solvent before they are analyzed for specific chemical compositions. Two analytical methods have been identified for specific analysis of the fractions. The main technique will be elemental analysis. A Perkin Elmer elemental analyzer is available in the Chemistry Department at A&T. This way, the nitrogen, oxygen, sulfur, carbon and hydrogen content of the sample will be determined. In addition, we will determine the functional groups and their composition in the sample using the Mattson Polaris FTIR spectrometer with a horizontal ATR sampler. This will help us detect specific functional groups such as amine, hydroxyl, pyridinic nitrogen, thiophenic sulfur groups.

RESEARCH TITLE: Study of coal liquefaction catalysts

PRINCIPAL INVESTIGATOR: Bobby Wilson

STUDENT/DEGREE PROGRAM: Sylvia James

INSTITUTION: Texas Southern University

OBJECTIVES:

The specific objectives for student involvement may be summarized as follows:

1. To investigate the possible formation and characterization of partially and fully substituted diamagnetic complexes of titanium, zirconium and hafnium in the plus four oxidation state using various forms and substituted forms of the poly(pyrazolyl)borate anions.

2. To determine the molecular weight, molecular structure, mode of bonding, and magnetic and electronic properties of these complexes by use of nuclear magnetic resonance, infrared, ultraviolet-visible, and mass spectrometry.

3. To examine the physical properties such as melting point, decomposition point, solubility, of each complex.

4. To evaluate the catalytic activity of each complex in direct coal liquefaction.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS:

Current work involves the preparation and characterization of transition metal complexes; the investigation of the fundamental chemistry of these complexes (especially the poly(pyrazoly)borate and thios); and the evaluation of these and other complexes as coal liquefaction and process catalysts. The primary purpose of our research is to gain a better understanding of the molecular structure and mode of bonding in these transition metal (Ti^{4+}, Zr^{4+}, Hf^{4+}, Nb^{4+} and Mo^{5+}) complexes that are formed by reaction with the poly(pyrazolyl)borate and dithiocarbamate anions.

The student was able to characterize a hafnium (IV) complex formed by the reaction of 1:4 stoichiometric portions of hafnium tetrachloride and potassium hydrotris(pyrazolyl)borate. The synthesis of $HfBr_4$ and $[HB(Pz)_3]_2$ was achieved by reacting hafnium tetrabromide with potassium hydrotris(pyrazolyl)borate in a 1:2 stoichiometric ratio according to the following reaction:

$$HfBr_4 + 2K[HB(Pz_3] \rightarrow HfBr_2[HB(Pz_3]_2 + 2KBr$$

The complex obtained was a white crystalline powder that was found to be quite insoluble in benzene but readily soluble in halocarbons. The infrared spectrum revealed a band that is characteristic of the C-H stretch on the aromatic pyrazole ring at 3100 cm^{-1} and a transmission band due to the B-H stretch was observed at 2480 cm^{-1}. The proton n.m.r. spectrum showed two triplets at d6.40 and d6.53 that were easily assigned to the coordinated and uncoordinated 4-H proton on the pyrazole group. The 3-H and 5-H also appeared in doublets at d7.52 and d7.65 for the coordinated 3-H and 5-H, respectively. On the basis of the n.m.r.

spectrum an octahedral geometry was predicted for the $HfCl_2[HB(Pz)_3]_2$ compound with the uncoordinated pyrazolyl rings occupying trans position from one another.

RESEARCH TITLE: Removal of certain toxic heavy metal ions from coal conversion process wastewaters

PRINCIPAL INVESTIGATOR: Ray F. Wilson

STUDENT/DEGREE PROGRAM: Eika U. Johnson

INSTITUTION: Texas Southern University

OBJECTIVES:

(1) To procure and prepare synthetic solutions of coal tar phenols, namely, resorcinol, catechol, phenol, meta, ortho, and para cresols, xylenols, indanols, etc., for future studies.

(2) Prepare known and new metal complexes and coordination compounds of the aforementioned coal tar compounds with toxic and nontoxic metal ions such as iron, zinc, calcium.

(3) Determine the extraction efficiency or extraction coefficients of the complexes in various solvents from wastewater sample.

(4) Determine the formation constants for these complexes where possible, in both the wastewater samples and in the extraction solvents to see if the species of a given complex and its stability varies from the wastewater sample to the extraction solvent.

(5) Where possible the complex ions will be precipitated out of solution as solid coordination compounds and analyzed for bonding characteristics.

(6) Present data using tabular, graphical, and word description for the purpose of comparison and evaluation.

(7) Formulate a schematic diagram and procedure for the systematic separation and removal of phenols and other toxic materials from coal tar conversion wastewater samples based upon their extractability, formation constants and desirable or acceptable toxic levels.

WORK DONE, CONCLUSIONS AND ACCOMPLISHMENTS

Synthetic solutions of phenols and different toxic and non-toxic metals such as copper, zinc, cadmium, mercury, and nickel to simulate wastewater resulting from coal liquefaction processes have been prepared and analyzed. Analysis of the complexes formed between phenols and the metal ions have been carried out to determine their coordination numbers, formation constants and other polarographic and electrochemical parameters. The extraction efficiency of the aforementioned complexes from wastewater into removing solvents has been studied.

Attempts have been made to provide a procedure for the systematic separation and removal of resorcinol complexions from coal-conversion wastewaters based upon their extractability, formation constants, and acceptable toxic levels. The concentrations of resorcinol before, after one extraction and after two extractions have been measured from amperometric peak currents. It was observed that two extractions were enough to obtain quantitative separation of resorcinol into the organic phase. In general, in the presence of copper, the peak current increases after each extraction indicating some interaction between resorcinol and copper ions in aqueous solution. No evidence of extraction of copper into the organic phase was observed.

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