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TECHNICAL REPORT

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Project Title: INTEGRATED PRODUCTION/USE OF ULTRA LOW-ASH COAL, PREMIUM LIQUIDS AND CLEAN CHAR DE-FG22-91PC91334

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ABSTRACT

This integrated, multi-product approach for utilizing Illinois coal starts with the production of ultra low-ash coal and then converts it to high-value, coal-derived, products. The ultra low-ash coal is produced by solubilizing coal in a phenolic solvent under ChemCoal™ process conditions, separating the coal solution from insoluble ash, and then precipitating the clean coal by dilution of the solvent with methanol. Two major products, liquids and low-ash char, are then produced by mild gasification of the low-ash coal. The low ash-char is further upgraded to activated char, and/or an oxidized activated char which has catalytic properties. Characterization of products at each stage is part of this project.

Fourteen gallons of reactor product from two ChemCoal runs in large autoclaves at the University of North Dakota Energy and Environmental Research Center has been delivered for processing to a subcontractor, Applied Research and Development Laboratory, Inc. (ARDL) in Mt. Vernon, Illinois. The ChemCoal solids (CC-solids) to separated by ARDL will be used for 1) diesel engine tests and 2) for mild gasification runs to produce coal-derived liquids and low-ash char. The CC-solids will be fed in the engine in slurry form. Producing a reasonably stable slurry has become the first priority. Testing of slurries in an injection test rig under construction in the Automotive Systems Laboratory at the Department of Mechanical and Industrial Engineering of the University of Illinois will precede tests in the engine. The properties of the mild gasification liquids will be compared to those of liquids produced from the coal without ash removal. Work on developing the procedures for the study of selective adsorption on activated carbon has begun. In the absence of carbon produced in this project, commercial activated carbon is being used for methods development.

This project is funded by the U. S. Department of Energy (METC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

EXECUTIVE SUMMARY

Char is more often than not an undesired product of coal utilization processes. Because char's mineral matter content is generally higher than that of the coal from which it is produced, char's heat content is usually lower than that of the coal from which it is derived. Additionally, volatile components initially in the coal have been removed, and for this reason, most char does not have the combustion properties expected of a good solid fuel. The market for char is very limited. Char's low value is often a restraint on economics of a coal utilization approach if it produces significant amounts of char.

It is the objective of this research to invert the normal scale of product values, i.e. make chars that, because of their unique properties, are the most valuable material in the product slate. This approach lets other products reach their highest value under the "high quality char" constraint. In this approach, "ultra low-ash" is an essential criterion for quality char. Without doubt, a barrier to use of coal in internal combustion engines or gas turbines will have been removed by taking out all of the abrasive minerals! Setting our sights on clean char does not necessarily lower the quality of other products if we remove all the mineral matter as the first step. We will not be surprised if we find that the properties and yields of the liquids produced as a byproduct of making char from ultra low-ash coal are enhanced, especially if the initial ash removal process increases the coal's volatile matter.

Traditional coal cleaning, which involves physical separation of solid components, seldom decreases the mineral matter content below 2% for Illinois coals. The reason is that much of the pyrite and other ash-forming minerals occur in occluded grains measured in microns. They are so finely disseminated that their liberation requires grinding to extremely small particle sizes.

There are two approaches to making the separation of mineral matter from coal essentially complete. One is a preferential dissolution (or leaching) of the mineral components leaving the coal essentially untouched. A second approach, the primary one for this project, is to dissolve the coal macerals leaving the mineral matter in the solid state. This latter approach does not leave the coal's structure completely unaltered because the coal's molecular weight must be reduced to get the coal macerals into solution. However, if the proportion of bonds broken is kept low, the properties of the solid recovered are not unlike those of the initial coal with two exceptions: the low-ash product has more volatile matter and this variety of low-ash coal can be expected to melt at a temperature lower than the coal before processing.

The phenolic solvent alone is insufficient to promote solubilization. Either acid or base is added and also carbon monoxide and water which react in situ to produce a reducing atmosphere under reaction conditions. Very little gas is produced. The coal's hydrogen is conserved in the liquid and solid products in the ChemCoal process. ChemCoal solids are low-ash, coal-like solids after precipitation from the phenolic solvent. A Continuous Process Unit (CPU) was built in 1985 at the University of North Dakota Energy and Environmental Research Center (UNDEERC). Western low rank coals received most of the attention in earlier studies. The western coal has a relatively high proportion of phenolic oxygen atoms and it provides sufficient phenols and cresols for a recycle process solvent. Previous ISGS contracts with CRSC supplemented by funds from the U.S. Department of Energy explored the addition of lignin when processing bituminous coal that has a deficiency of phenolic precursors. The source of lignin was 1) residue from TVA's acid hydrolysis processing of hard wood or municipal waste for alcohol production, or 2) a residue, called ALCELL®, produced as a byproduct of chemical pulping of hard wood by Repap Technologies' chemical pulping at its facility in Newcastle, New Brunswick.

Using the lignin-augmented depolymerization variation of the ChemCoal process, solids have been produced from Herrin (Illinois No. 6) coal (Illinois Basin Coal Sample Program IBC-109) having only 0.2-0.3 wt% ash and 0.6 wt% sulfur. Yields have been 60-70 wt% (based on maf coal). Essentially all the pyritic sulfur and about 10% of the organic sulfur was removed. The ChemCoal solid had a high volatile matter content, more than 50%, but is was not sticky. It passed preliminary screening tests for suitability as a gas turbine fuel at Allison Division of General Motors. The Electro-Motive Division of General Motors provided advice for assessing the potential of ultra low-ash coal as a diesel fuel. Under this project the evaluation of low-ash coal as a fuel for diesel engines will continue at the University of Illinois in a two cylinder Lister Petter diesel research engine.

A variation of the coal solubilization approach to separate coal from ash-forming minerals is one developed at West Virginia University. Significant portions of some coals can be extracted with N-methylpyrrolidone (NMP). Samples of this variety of ultra low-ash coal have been, and will continue to be, made available to us for comparative purposes. Material obtained by NMP extraction is believe to be a chemically unaltered fraction of the coal whereas portions of the material produced by the modified ChemCoal™ process have been brought into solution by lowering their molecular weights.

To have a reasonable impact on economics, any market considered for char must be a large one and must have a potential price structure greater than fuel value. This proposal addresses both the need for a volume outlet and the need for a potential price higher than that of fuel. Among the markets which could have the volume to influence the char market significantly is the activated carbon market. Activated carbon is used for water purification and also for adsorbing waste compounds from nonaqueous solutions or suspensions. Not only is the potential sales volume for an adsorbent made from char attractive, but the current price of activated carbons against which it will compete is more than $1000/ton for a high quality product.

More than 300 chlorinated organic compounds have been identified in chlorinated potable waters, cooling waters, and sanitary effluents. Systems are needed which will trap and destroy unwanted organic compounds that are introduced into drinking water when the water is purified by chlorination. Additionally, chemical processes often produce environmentally objectionable waste compounds in aqueous solutions or organic solvents. The principal investigator for this proposal discovered in the 1960s that activated carbon and other carbonaceous materials can be converted to an effective dehydrochlorination catalysts by heating the carbonaceous materials to 500°C to 700°C in air. Oxidized char is projected to have the capacity to not only adsorb waste molecules from a variety of streams but also to catalyze chemical transformations of the unwanted adsorbed compounds into harmless or even useful chemicals. Oxidized char is potentially potential catalyst for other desirable transformations. Work under our previous CRSC contract demonstrated that oxidized/activated carbon (OAC) made from coal char catalyzes not only the dehydrochlorination of alkyl halides but also the dehydration of aliphatic alcohols, the deamination of aliphatic amines, and the dehydrosulfurization of mercaptans. Under this contract, these studies will be extended to OAC made from ultra clean char and expanded to begin obtaining detailed information on the selectivity of OAC for adsorption of organic compounds. The trade-off of catalytic properties against premium adsorptive properties must be evaluated.

The liquids produced which accompany the mild gasification of the ultra low-ash coal will be characterized and evaluated by the methods developed in previous CRSC projects which had premium quality liquids as their objective.

A Sandia collaborator will process our coal and selected treated products in a catalytic hydropyrolysis regime. Information gained by this approach was initially intended to supplement engineering studies of the ChemCoal process at the ISGS, engineering studies that were not funded under the current contract. We expect to use the Sandia results as background information to improve a future proposal for engineering data on lignin-augmented ChemCoal processing of Illinois coal. The most important of the engineering questions not answered by previous UNDEERC studies is one that relates to the rate at which heat can be supplied to initiate the solubilization reactions.

The low-ash char produced under the integrated approach studied in this contract will be produced under mild gasification conditions that have been shown to achieve the highest value tar byproduct starting with coal.

Work this reporting period

Fourteen gallons of reactor product, supplied to us in September from two ChemCoal runs in large autoclaves at the University of North Dakota Energy and Environmental Research Center, has been delivered for processing to a subcontractor, Applied Research and Development Laboratory, Inc. (ARDL) in Mt. Vernon, Illinois. ARDL is carrying out two centrifugation and separation steps, on a crude reaction product. The work involves an intermediate dilution step with methanol. Based on the knowledge of one of our consultants who has worked with ARDL on other types of chemical processing, and our own conversations with Mr. Richard Curtain, laboratory manager at ARDL, we find ARDL to be not only qualified but it has the centrifugation equipment required to carry out the needed product isolation. The ChemCoal solids (CC-solids) to separated by ARDL will be used for 1) diesel engine tests and 2) for mild gasification runs to produce coal-derived liquids and low-ash char.

The CC-solids will be fed in the engine in slurry form. Producing a reasonably stable slurry has become the first priority. Testing of the suitability of the slurries for the injection system in a separate system has been advised. Testing of slurries in an injection test rig under construction in the Automotive Systems Laboratory at the Department of Mechanical and Industrial Engineering of the University of Illinois will precede tests in the engine.

Work on developing the procedures for the study of selective adsorption on activated carbon has begun. In the absence of activated carbon produced in this project, commercial activated carbon is being used for methods development.

GOALS AND OBJECTIVES

The principal objective of this Integrated Production/Use (IPU) approach is to achieve high-value, coal-derived products from Illinois coal, especially types of char that will be marketable. This approach to coal utilization uses ultra low-ash coal to produce premium liquids and low-ash char. The first goal is to remove essentially all the ash-forming minerals, including pyrite, from coal by two methods, 1) the ChemCoal [1] process and 2) leaching with acids. A second goal is to produce low-ash char through mild gasification. We anticipate that agglomeration may be a problem and may consider one or more of three approaches to solving this problem if it occurs. The three approaches are 1) slow heating rate, 2) preoxidation or 3) extrusion of the coal into the hot zone.

A third goal is to make even higher value derivatives of the ultra low-ash char. Converting it to an activated carbon is the first approach. Some activated carbons are marketed today for hundreds of dollars per ton. A second approach is to produce oxidized/activated carbon (OAC) having catalytic properties. OAC is potentially another high value product. We have developed procedures for characterizing these materials in a previous project, and one goal is to extend our expertise and fundamental knowledge in this area.

Evaluation of the fuel value of intermediates and products on the production pathway, especially of ultra low-ash coal, is a fourth goal. Combustion characteristics of the ultra low-ash coal in a diesel engine will be evaluated in a unique engine located in the University of Illinois automotive testing facilities. The objective is to determine where our fuel ranks with respect to other coal-derived fuels through comparisons of diesel engine data and data obtained on a wide range of fuels in a combustion bomb apparatus located at the Morgantown Energy Technology Center (METC).

Because the modified ChemCoal^{TM} process produces a clean coal-like solid with significantly higher volatile matter than the feed coal, a fifth goal is to determine how this increase affects the properties of mild gasification liquids produced during the production of ultra low-ash char. The goal is to learn how much additional energy-producing material reaches the liquid phase by this route. The objective is to characterize the tars by the procedures used in previous mild gasification work at the ISGS. Additionally, IBC-109 coal, and the two low-ash samples produced from it, will be subjected to hydropyrolysis under conditions found in tests at Sandia National Laboratories to be effective with Illinois Herrin coal; the goal is to provide additional comparisons of yields and energy balances.

Tasks

Task 1 Production of low ash coal

Task 1a Low ash ChemCoal solids - UNDEERC/ARDL UNDEERC produced as much crude reactor product as time permitted with matching funds from the last year's contract (estimate 14 gallons containing as much as 9 pounds of CC-ultra low-ash solids). The conditions were those shown in last year's research to give desired low-ash CC-solids in the highest per batch yield. Workup of the reaction product will be carried out on a subcontract to Applied Research and Development Laboratory, Inc. in Mt. Vernon, Illinois. This material will be designated Type CC.

Task 1b Low ash coal control - ISGS - Two to four pounds of a second low-ash coal for use as a control will be that produced by dissolution of coal's mineral matter with acids (HF, HCl and HNO_3). Because this sample, designated Type AE (acid extracted), contains all the carbonaceous material (coal macerals) not extracted (dissolved) by the acids, and no chemical transformation of the coal itself has taken place, AE coal's volatile content should be that of the parent coal. Use of this sample along side the CC-solid in key reactions should make possible a preliminary assessment of benefits attributable to the extra volatile matter in the CC-solid. Caustic leaching of the type practiced by Amax Coal Company is an alternate to acid leaching. If preliminary tests should show that this method reduces the ash to levels acceptable in the diesel engine, upon approval of the CRSC monitor, a caustic leached (CL) coal may be substituted as the control.

Task 2 Mild gasification of low-ash coals - ISGS - The CC-solids and the control (AE-coal) will be subjected to mild gasification in the apparatus developed initially under funding for a project entitled PRETREATMENT OF COAL TO IMPROVE PYROLYSIS PERFORMANCE directed by C. W. Kruse and funded by the Electric Power Research Institute (EPRI) and subsequently modified under CRSC research contracts on mild gasification at the ISGS directed by M. D. Stephenson, A. D. Williams and C. W. Kruse.

Task 2a Characterization of oils -ISGS - Oils from both CC-solids and the AE-coal control will be characterized at the National Institute for Petroleum and Energy Research (NIPER) in Bartlesville. Analyses and the methods used are:

	Method
Carbon	PE 240C
Hydrogen	PE 240C
Nitrogen	ASTM D 4629, chemiluminescence
Sulfur	ASTM D 1552
Ash	ASTM D 482
Specific Gravity	ASTM D 4052, Mettler Digital Density Meter
Viscosity	ASTM D 445, Kinematic at 100°F
Simulated Distillation[*]	Proposed ASTM Crude Oil Method
Pour Point	ASTM D 97

[*] The simulated distillation has not been formally adopted by ASTM but is routinely used in NIPER's laboratory. It provides good relative information.

Task 2b Low ash chars - ISGS - In addition to the chars produced by the mild gasification runs to collect all the oil using the electrostatic precipitator, additional char will be made without attempting to obtain the highest recovery of tar possible. This latter production running will provide the bulk of the low-ash char used for subsequent tests.

Task 3 Fuel assessments in a diesel engine - UIUC - This work is carried out by an MS graduate student, Michalis Syrimis, under the direction of Dennis N. Assanis, Associate Professor, Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, 1206 West Green Street, Urbana, IL 61801. Mr. Syrimis has set up the engine in the Automotive Systems Laboratory at the Department of Mechanical and Industrial Engineering of the University of Illinois. Engine performance and emission variables are monitored during the engine cycle. These experimental measurements, supplemented by analytical models of combustion heat release, are used to study a fuel's combustion characteristics such as ignition delay, combustion duration and combustion completeness. Furthermore, from this type of testing it is possible to determine the effects of burning the new fuels on engine components.

Feeding the solid fuel to the engine remains a problem. Reasonably stable slurries are needed and the initial effort is directed toward identifying chemical additives that will solve this problem.

Task 4 Activated and oxidized/activated low ash char - Methods have been developed to achieve reproducible burning to obtain a desired percent burnoff. A close relationship exists between the percent weight loss and the nitrogen surface area. The catalyst is produced by subsequent oxidation at a lower temperature.

Task 4a Preparation of chars - ISGS - In this task, relatively small quantities (less than 100-grams per type) of activated/oxidized low-ash char will be produced. Low-ash char, produced in Task 2b, will be activated to create a porous carbon structure. Coal chars will be gasified with 50% steam/50% nitrogen at 870°C in a fluidized bed reactor to produce activated chars with N_2-BET surface areas of 500 m^2/g-600 m^2/g. Following activation, the chars are oxidized in a fluidized bed reactor to produce catalysts. The temperature of oxidation is sufficiently low so that the reaction conditions are in the chemical kinetic controlled regime for carbon-oxygen reactions. Increasing temperatures lead to a diffusion controlled reaction involving a shrinking-core type of burn-off and thus destruction of porosity. The planned work will attempt to further quantify the effects of oxygen content vs. catalytic activity. OAC from this task supplies Amoco Corporation and two Departments of the University of Illinois with needed materials.

Task 4b Characterization and use - Amoco - A combination of experimental procedures will be used to further investigate the use of OAC for sorption and destruction of possible pollutants and environmentally toxic components. A combination of thermogravimetric analyzer (TGA) on-line with a GC/MS and FTIR will be used to study the thermal characteristics and chemical behavior of the chars before and after treatment with possible pollutants and environmentally toxic components.

Task 4c Adsorption studies - UIUC - This work will be carried out by a graduate student, Cuneyt Feizoulof, under the direction of Vernon L. Snoeyink, Professor, Department of Civil Engineering, University of Illinois at Urbana-Champaign, 205 N. Mathews, Urbana, IL 61801. In this task, the adsorptive capabilities of OAC will be further investigated.

In order to evaluate the adsorptive properties of an activated carbon, its equilibrium capacity must be determined. It has been found that the ability of an activated carbon to adsorb a targeted compound is substantially less in natural water than in distilled-deionized water. This is due to the presence of background organic matter in natural water which competes with the targeted compound for adsorption sites. Any carbon which can be made to selectively adsorb a contaminant will be considered quite valuable.

It is known that, depending on the oxidative treatment, the carbon's surface may have an acidic or basic nature. This research task addresses the selective adsorption of organics from solutions as it relates to the surface characteristics of an activated carbon. It may be possible to tailor-make oxygenated surfaces which preferentially adsorb undesirable organic compounds. It has been shown in the literature that carbon surfaces can be varied to cause selective adsorption of a compound from a binary solution. However, little is known about how this surface chemistry will affect the activated carbon's adsorption of targeted compounds from solutions containing a myriad of background matter which can potentially compete for adsorption sites. Therefore, it is proposed that a fundamental study exploring the selective adsorption of organic compounds from competitive media be initiated.

The upcoming work will examine whether or not the acidic or basic surface nature of an activated carbon affects its ability to preferentially adsorb the compounds trichlorophenol and trichloroethylene. Initial testing will be done with a commercial granular activated carbon (GAC) manufactured from bituminous coal. This will provide an effective basis for comparison to an activated char produced from CC char and/or AE char. The GAC and activated char will be characterized in methods consistent with those used in evaluating activated carbon. This will include analyses to obtain data such as surface area, pore size distribution, ash content, and iodine number. In addition, carbons with oxygenated surfaces of acidic and basic nature will be supplied to be tested as catalysts. This testing may provide insight as to what type of functionalities catalyze the elimination reactions, i.e. dehydrochlorination and dehydration, observed in the current contract.

The Environmental Engineering and Science Laboratories of the Department of Civil Engineering at the University of Illinois will be made available for this task. The labs are well equipped for research in the chemical, physical, and biological aspects of water treatment.

<u>Task 5 Catalytic Hydropyrolysis and Liquefaction - Sandia</u> - This work will be carried out by Dr. Klavetter. Dr. Klavetter proposes to perform noncatalytic and catalytic fixed-bed hydropyrolysis tests on the IBC-109 coal we are using in this project to determine tar yields, conversion yields, and gas yields. Results will be compared with results of tests on other selected coals, including other untreated Illinois coals. A further extension of the work is the upgrading of the resulting tars using two-stage catalytic hydropyrolysis and comparison of the resulting liquids with the ones produced by mild gasification at the ISGS.

INTRODUCTION AND BACKGROUND

The CRSC and the U.S. Department of Energy through its technology centers, Pittsburgh Energy Technology Center and Morgantown Energy Technology Center, continue to support research on coal cleaning, both physical and chemical, and the mild gasification of coal. The research described fits many of the current goals of these organizations. Marketing of a single product from a process is acknowledged to be less complicated than finding markets for several products. Nevertheless, there are examples of successful multiproduct strategies for a natural resource, petroleum refining for example. The work proposed herein will provide portions of knowledge needed to evaluate the technical potential of coal-derived products, especially ultra clean coal and chars made from it. In such cases, where the sales potential of several products must be factored in and values assigned, technical information on suitability for various uses must precede assignment of a value.

The IPU approach, described herein, produces a low-ash coal, a mineral rich coal fraction, and coal-derived liquids on the way to char. The value and marketability of the char is a key factor for economic viability of mild gasification. This proposal addresses both the need for a volume outlet and the need for a price higher than that of coal as a utility fuel. In addition to a potentially high price for the char, the intermediates and byproducts may be at the top of value indexes for similar coal-derived products.

To have a reasonable impact on the economy of the State of Illinois and other coal producing states, any market considered for char must be a large one and must have a potential price structure greater than utility boiler fuel value. Among the markets which could have the volume to influence the char market significantly is the activated carbon market for water purification and for similar uses such as adsorbing components from nonaqueous solutions or suspensions. Not only is the volume potential for an adsorbent made from char attractive, but the price of the activated carbon against which it will compete is more than $1000/ton for a high quality product.

An important advantage that oxidized activated carbon is projected to have is the capacity to catalyze chemical transformations of the unwanted adsorbed compounds into useful compounds. It may also catalyze desirable transformations of coal-derived liquids. It remains to be determined what the appropriate balance between catalytic properties and adsorbent capacity will be. The capacity of a material containing substantial mineral matter (relatively high ash content) produced by air activation in the 600°C range will be lower than values obtained for commercial activated carbon. The trade-offs both technically and economically in achieving a balance of catalytic properties and adsorptive properties must be evaluated and this project develops technical data for decision making.

When the technical benefits of taking practically all of the mineral matter out of coal before further processing are known, it should be possible to assign a monetary value to this upgrade. The technical benefits of making solid coal an acceptable fuel for diesel engines and gas turbines is a major advance. The economy of scale for producing an ultra low-ash coal, if it exists, will then be an important factor for assessing how much effort is justified in developing the modified ChemCoal process or its equivalent for a premium coal-based, solid-fuel industry.

The Principal Investigator is an inventor of record on three United States patents on oxidized carbonaceous materials as catalyts [2-4]. Exploiting the properties of OAC oxidized/activated carbon was an objective of previous collaborative work with Amoco personnel and it is carried forward in this project, in a subcontract to Amoco Research Corporation. More than 300 chlorinated organic compounds have been identified in chlorinated potable waters, cooling waters, and sanitary effluents. Systems are needed which will remove and destroy unwanted organic compounds that are introduced into drinking water during purification by chlorination. Additionally, chemical processes often produce environmentally objectionable compounds in aqueous solutions or organic solvents. Filtration through activated carbon is the conventional technology for ridding water of objectionable organics.

We wish to determine the potential for using oxidized char to adsorb undesired organic compounds, like those found in ground water, drinking water, or industrial waste streams, and then destroy the adsorbed material by elevating the temperature to the range where the oxidized carbon catalyzes elimination or oxidation reactions that transform the organics into readily manageable compounds.

Fuel assessments in a diesel engine

Dr. Assanis, Associate Professor in the Department of Mechanical and Industrial Engineering at the University of Illinois at Urbana-Champaign, joined a previous CRSC project (Lignin Augmented Depolymerization) in its second year and participated in a review and planning meeting June 4, 1990, at the Allison Plant 8 site in Indianapolis. Dr. Uzkan, one of our advisors, (GM's Electromotive Division) emphasized at that meeting the importance of combustion rates and ignition delay times relative to standard fuels. Preliminary knowledge on combustion rate and ignition delay times for CC-solids was developed in the previous CRSC contract using a combustion bomb at Morgantown Energy Technology Center (METC).

Because the maximum amount of CC-solid which can be made available in the next year or two for the proposed engine studies is in the order of a few pounds, a small two cylinder Lister Petter diesel research engine is being used. The advantages of this engine are that it requires small amounts of fuel and both of the identical cylinders are fully instrumented and supplied with two separate fuel supply systems. The engine can be run on standard fuel in one cylinder and a coal slurry in the other. This permits collection of pressure data under identical conditions. Using this approach, heat release analysis of the engine combustion using each of the fuels under identical operating conditions can be carried out. We will be able to compare combustion characteristics of the coal-derived slurry fuel(s) and obtain the baseline fuel data. Furthermore, this approach permits considerable data acquisition on small quantities of the experimental fuels. Less of the solid fuel may be required if the slurry medium is an organic which has reasonably good fuel characteristics.

Adsorption studies

The overall objective of this segment of the project is to evaluate the effects of an activated carbon's surface chemistry on aqueous adsorptive properties. For several years, considerable work on the study of surface groups on carbons has been conducted [5-9]. Papirer and co-workers [7] state that the existence of surface groups on carbons largely determines their specific interaction capacity; a property which besides texture, is of great importance for the use of active carbons. It is known that the surface of a carbon may have an acidic or basic nature. Recently, new opportunities employing the acidic or basic nature of the carbon surface have been realized.

In order to evaluate the adsorptive performance of an activated carbon, its equilibrium capacity must be determined. Several investigators have found that the ability of an activated carbon to adsorb a targeted compound is substantially less in natural water than in distilled-deionized water [10-12]. This is due to the presence of background organic matter in natural water which competes with the targeted compound for adsorption sites [13]. Therefore, any carbon which can be made to selectively adsorb a contaminant will be considered quite valuable.

This work will examine whether or not the acidic or basic surface nature of an activated carbon affects its ability to preferentially adsorb the compounds trichlorophenol and trichloroethylene. Puri found that when placed in a benzene-methanol mixture, charcoals could be made selective for either benzene or methanol adsorption [8]. Carbons with an acidic nature tend to be hydrophilic and preferentially adsorb polar compounds, while those with a basic nature tend to be more hydrophobic and preferentially adsorb non-polar compounds. Davini found that activated carbon with a basic nature preferentially adsorbed benzoic acid, while activated carbon with an acidic nature adsorbed diphenylguanidine [14].

EXPERIMENTAL PROCEDURES

Product from two ChemCoal runs in large autoclaves at University of North Dakota Energy and Environmental Research Center (UNDEERC) totaling 14 gallons has been delivered to a subcontractor, Applied Research and Development Laboratory, Inc. (ARDL) in Mt. Vernon, Illinois, for processing. The procedures for isolation are those developed at UNDEERC and duplicated at the ISGS with excellent reproducibility on material after several months standing. They are described in detail in the Final Technical Report for September 1, 1989, through August 31, 1991, for the CRSC project entitled LIGNIN-AUGMENTED BITUMINOUS COAL DEPOLYMERIZATION: A ROUTE TO CLEAN FUELS.

Fuel assessments in a diesel engine

In addition to the two cylinder Lister Petter diesel research engine which was readied for testing under the previous CRSC contract, we have started building an injection test rig for testing pumping and atomization characteristics of the fuel slurries we are developing. The rig will be made with components identical to those used in the engine, i.e. injection pump, fuel line, and fuel injector. A fuel (carrier liquid, coal, and additives) will not be used in the engine unless it can pass through the test rig for a certain time. The rig will allow us to make necessary adjustments to the mechanical components and to the fuel.

We expect to have to reduce the opening pressure of the injector, for diesel fuel operation is 3000 psi, in order to get good fuel atomization. Also, plugging of the rig will indicate that the fuel is 'unstable', shearing of the fuel causes coal to separate, and so the additives concentration, surfactant and stabilizer, must be changed. The rig will allow the recovery of the fuel, and also the use of regular, and high speed photography for the study of the spray. Visualization of the spray will enlighten our understanding of the combustion of the slurry.

Listing of source and type of chemical additives used:

Air Products: CT141: anionic dispersant
GA: blend of nonionic surfactants
Surfynol 485: non-ionic surfactant.

Henkel: Nopcosperse 092 : Cationic fatty derivative, surfactant
Stabilizer CW-11: Mixture of natural gums, dispersant.

Witco: Sodium Petronate L: oil-soluble petroleum sulfonate, surfactant.

Adsorption studies

Acquisition, preparation, and characterization of a commercial granular activated carbon (GAC) - A commercial granular activated carbon (GAC), Filtrasorb-400 (F-400), manufactured from a bituminous coal, was obtained from the Calgon Corporation. To insure sample uniformity, approximately 500 g of a 16x20 mesh size fraction (U.S. Standard Size) was separated for use in adsorption tests. A portion of this 500 g sample was submitted to the Coal Lab located at the Illinois State Geological Survey for proximate and ultimate analyses.

Adsorption capabilities of granular activated carbon in distilled-deionized water - Initial adsorption tests were conducted with a GAC which was present and for which adsorption data was available. Adsorption isotherms of para-nitrophenol (PNP) on a GAC were obtained. The following procedures were used in obtaining the adsorption isotherms.

1. A 0.01 M stock solution of PNP was prepared.
2. A small sample (about 2 g) of GAC was dried and pulverized in a SPEX 8000 Mixer/Mill for 5 minutes.
3. The pulverized carbon was weighed into ten 125 ml serum bottles in the following quantities: 0, 0, 2, 4, 5, 6, 7, 8, 10, and 12 mg.
4. Ten ml of 0.01 M PNP was pipetted into a 1.0 liter volumetric flask and diluted to 1.0 liter, giving a 0.0001 M PNP solution. Three drops of hydrochloric acid were added to this solution.
5. One hundred ml of 0.0001 M PNP solution was pipetted into each of the ten serum bottles.
6. The bottles were sealed with teflon-lined rubber septa, placed on an end-over-end tumbler, and allowed to equilibrate.
7. The bottles were removed from the tumbler and the carbon was removed from the solution by vacuum filtration.
8. The pH of each solution was adjusted to 11+ units using concentrated sodium hydroxide.
9. The concentration of PNP remaining in the solutions were determined using a spectrophotometer.

This test was run in duplicate in order to check the results and insure data reproducibility. The adsorption curves are given in Figure 1.

RESULTS AND DISCUSSION

Low ash ChemCoal solids

Based on our experience in Champaign of duplicating the separation procedure developed at UNDEERC, we do not expect ARDL to have difficulty isolating the CC-solids. We expect to have the material in December.

Product from two ChemCoal runs in large autoclaves at University of North Dakota Energy and Environmental Research Center (UNDEERC) totaling 14 gallons has been delivered to a subcontractor, Applied Research and Development Laboratory, Inc. (ARDL) in Mt. Vernon, Illinois, for processing.

Fuel assessments in a diesel engine

Work during this first quarter at the Automotive lab has been concentrated on the preparation of the coal slurry fuel. The available coal is a low-ash caustic/acid-leached coal provided by AMAX Research and Development, and it was ground in a fluid energy mill to an average size of 5mm.

Dispersing coal into liquids usually requires the use of chemical additives, surfactants (wetting agents) and/or dispersants (stabilizers). The nature and the amount of the additives to use are very coal specific, depending on the surface properties of the coal particles. The surface properties depend on the type of coal, e.g. amount of ash, and the type of the size reduction process used, chemical groups on the surface, and surface tension. As a result, there is no recipe giving the type and the amount of additives to use, and the only way to find them is experimentation. It must be mentioned here, that as the effect of the additives on the combustion characteristics of the slurry are unknown, it is desirable to use small concentrations, and if possible not use them at all.
We made samples with four different carrier liquids, diesel fuel, ethanol, n-butanol, and the methyl-soyate ester, and 10% coal (5g coal, 45g liquid). The samples were agitated by hand. The diesel, the ester, and the ethanol samples started separating after one hour, a clear liquid layer started forming at the top of the solution. The three solutions were finally completely separated, a coal layer formed at the bottom with clear liquid above it. The butanol sample however did not separate completely in six hours. A coal layer formed again at the bottom but the liquid above it was not clear indicating that the smaller particles in the coal were kept in suspension. Stirring the solution with an ultrasonic agitator increased the suspension time for all the samples without changing the end result. Looking at a sonicated and a hand shaken sample under a microscope, we realize that the sonicator did not change the size of the particles, i.e. it did not cause breaking down of particles, however it did cause agglomeration of particles to break down to the individual particles. A scanning electron microscope photograph of the sonicated sample show the particles to be irregular shaped pieces with sharp edges having a wide variety of sizes well below 10 microns.

Having observed that the carrier fuels alone did not suspend the coal we started looking into additives. We obtained samples of the additives reported by M.D Gurney et al. (1984), as well as of several others suggested by manufacturers, see listing. We made ladder studies with the chemicals Surfynol 485, GA , and CT141 using ethanol, and butanol but we could not get stable suspensions. Then we did the same with diesel fuel and the surfactants Nopcosperse 092, Surfynol 485, and Sodium Petronate. Even though we did not get stable suspensions we were able to identify a potential concentration range for each of the surfactants: These ranges are:

Nopcosperse 092 .4-.6%
Surfynol 485 .8-1.%
Sodium Petronate .6-.8%.

Subsequently, we tried using the surfactants with the stabilizer CW-11, a mixture of natural gums, which is again reported by M.D. Gurney [15]. However, the suspension was again not stable.

Although a stable suspension is desirable it is not absolutely required. If the fuel can be formulated so as to stay in suspension while being pumped through the fuel injection system, without plugging it, it does not really matter if it is slowly separating while sitting in a tank. The tank can be stirred to maintain the suspension. The real issue is whether or not it can withstand the severe shearing stresses in the injection pump and the injector without separating from the solution.

The steps in our work will be:

- Finish the construction of the injection test rig and proceed with the formulation testing of the diesel-coal slurry, using the three surfactants mentioned above.
- Try to get more fuel by wet grinding AMAX coal in diesel fuel, using a ball mill. Wet-milling has the advantage of preventing oxidation of the coal surface. The oxides, which are formed on the surface of coal particles soon after grinding, give to the coal water-loving characteristics thus making suspending it in oil difficult.

Adsorption studies

Acquisition, preparation, and characterization of a commercial granular activated carbon (GAC) - In order to obtain a representative GAC sample, a narrow size fraction of particles in the dominant size range (16x20 mesh) was obtained. According to Randtke and Snoeyink [16], there may be significant variation in adsorptive capacity with particle size. Activation conditions may be such that the inner cores of the larger particles are not completely activated, resulting in a decrease in adsorptive capacity with increasing particle size. Therefore, a relatively narrow size fraction is obtained to insure sample uniformity.

Adsorption capabilities of granular activated carbon in distilled-deionized water - Initial adsorption tests were conducted with a readily available GAC for which previous adsorption data were present. Adsorption of PNP by the GAC was examined and the adsorption curves are seen in Figure 1. One can see that the two curves are relatively consistent, an indication of good data reproducibility. Data obtained by the current investigator on this GAC found its adsorption capacity to be lower than that found by a previous investigator. This difference can probably be attributed to the fact that the carbon lost some of its adsorptive capacity as time went by and the carbon was periodically exposed to the atmosphere. The carbon may have adsorbed impurities from the air, leading to a decrease in its adsorptive capacity. However, this should not effect the data reproducibility if the tests are run relatively recently to one another. This is observed in Figure 1.

CONCLUSIONS AND FUTURE WORK

- The pound quantities of ChemCoal solids which will supplement the small amount of material carried forward from the previous project should be available in December from our subcontractor, ARDL.
- A final additive package for a slurry to be fed to the diesel engine has not been selected, however, three surfactants with promising behavior were identified.
- An injection test rig for testing the slurry before using it in the diesel engine will be build. The rig will help us find the additive concentrations to use.
- A commercial GAC manufactured from a bituminous coal (F-400) was obtained from the Calgon Corporation.

- A representative sample of the F-400 was obtained by sieving for the 16x20 mesh particle size fraction.
- The F-400 was submitted for proximate and ultimate characterization.
- It was found that good reproducibility could be obtained for PNP adsorption tests.
- Future adsorption work will focus on further characterization of F-400 so that it may be compared to activated carbons manufactured from Illinois bituminous coals. In addition, the effects of the carbon's surface chemistry on adsorptive capacity will be examined. Carbon's of varying surface chemistry will be supplied to the principal investigator of this project so that their catalytic properties may be determined.
- Work at Amoco should commence in the next quarter when a subcontract can replace the letter of intent sent by the University of Illinois.

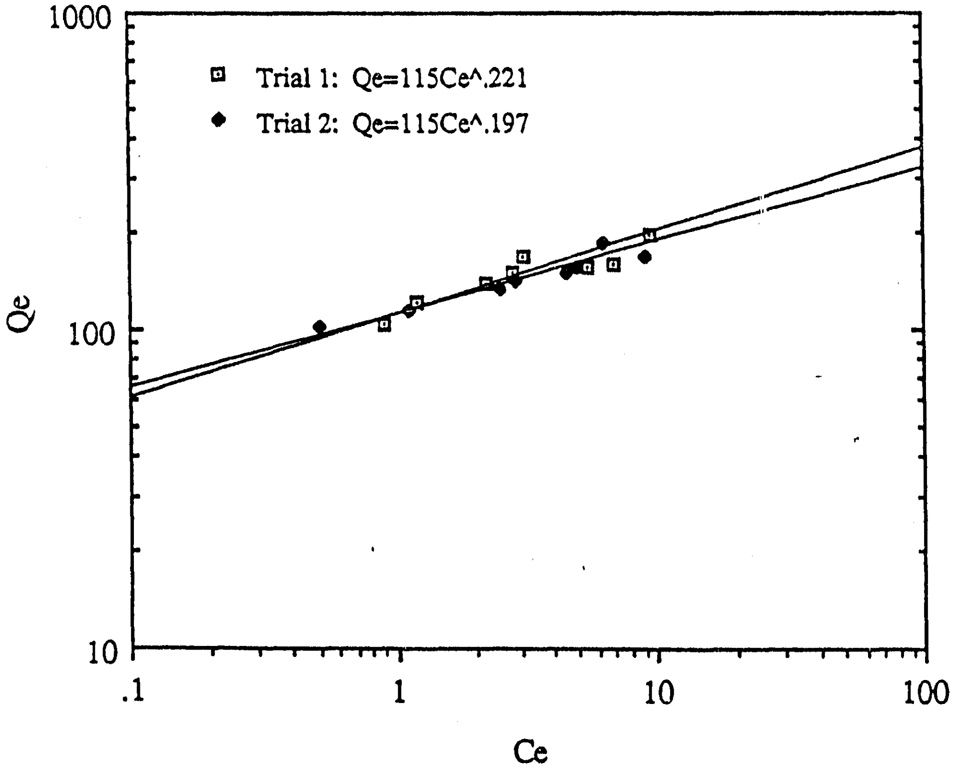

Figure 1, PNP adsorption isotherms

REFERENCES

1. Knudson, C.L. "Wyodak Coal: Composition, Reactions, and Products" Research Project 2655-3 1986 A Final Report prepared for the Electric Power Research Institute
2. Kruse, C.W.; Ray, G.C., 1966, "Dehydrohalogenation of hydrocarbon halides" US Patent 3,240,834, March 15.
3. Kruse, C.W., 1969, "Polymerization" US Patent 3,437,695, April 8
4. Mahan, J. E., Reusser, R. E., Kruse, C. W. "Dehydrohalogenation process," US 3,352,935, November 14. 1967.
5. Donnet, J. B. **Carbon**, 6, p. 161 (1968).
6. Arico', A. S., V. Antonucci, M. Minutoli, and N. Giordano. **Carbon**, 27, p. 337 (1989).
7. Papirer, E., J. Dentzer, S. Li, and J. B. Donnet. **Carbon**, 29(1), p. 69 (1991).
8. Puri, B. R. **Carbon**, 4, p. 391 (1966).
9. Boehm, H. P. and G. Bewer. The Role of Surface Oxides in the Gasification of Carbon and the Thermal Stability of Functional Groups. University of Munich, W. Germany (1974).
10. Sontheimer, H., J. C. Crittenden, and R. S. Summers. Activated Carbon for Water Treatment. Second Edition in English. DVGW-Forschungstelle, Engler-Bunte-Institut. University of Karlsruhe, Karlsruhe, FRG (1988).
11. Miltner, R. J., D. B. Baker, T. F. Speth, and C. A. Fronk. **JAWWA**, 81(1), p. 43 (1989).
12. Najm, I. N., V. L. Snoeyink, M. T. Suidan, C. H. Lee, and Y. Richard. **JAWWA**, 82(1), p.65 (1990).
13. Najm, I. N., V. L. Snoeyink, and Y. Richard. Effect of Initial SOC Concentrations on its Activated Carbon Adsorption Capacity in Natural Water. JAWWA (1991).
14. Davini, P. **Fuel**, 68, p. 145 (1989).
15. Gurney, M. D., Clingenpeel, J. M. And Ecceleston, D. B., " A program to Examine the Use of Coal Slurry Fuels", ASME Paper 84-DGP-8, 1984.
16. Randtke, S. J. and Snoeyink, V. L. **Research and Technology: JAWWA**, August 1983, p. 408.

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