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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

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Principal Investigator (PI): Carl W. Kruse, ISGS

Funded coinvestigators: S. L. Carlson, ISGS; V. L. Snoeyink and C. Feizoulof, U of I; D. N. Assanis and M. Syrimis, U of I; S. M. Fatemi, Amoco.

Other Participants: C.R. Porter, Western Res. Institute; R.C. Bourke, GM Allison Gas Turbine Div.; T. Uzkan, GM Electro-Motive Div.; J.W. Zondlo, West Virginia Univ.; J.H. Lora, Repap Technologies; E. Klavetter, Sandia Nat. Lab.; R.C. Strickland, TVA; C.L. Knudson, UNDEERC; J.A. Mahoney and R.T. Lagman, Amoco; J.M. Lytle, L. Kohlenberger, A. Lizzio, M. Rostam-Abadi, and M. Chou, ISGS.

Project Monitor: Franklin I. Honea CRSC

ABSTRACT

The first step in the envisioned integrated, multi-product approach for utilizing Illinois coal is the production of ultra low-ash coal. Subsequent steps would convert low-ash coal to high-value products through mild gasification, char activation, and oxidation reactions. Approximately eight pounds of low-ash coal has been obtained from the crude reactor slurry produced for us at the University of North Dakota Energy and Environmental Research Center (UNDEERC). After treatment to remove the remaining meta-cresol, this material will be subjected to mild gasification. Low-ash mild gasification char will be activated and a catalyst surface will be added by oxidation. Comparison of properties among chars with differing levels of mineral matter will then proceed. Although the mineral matter level will not be as low as expected based on previous material from UNDEERC, it should be low enough to assess differences in char properties due to mineral matter content.

A 20% coal:80% diesel fuel slurry was tested in cylinder two of a two-cylinder, diesel engine after the necessary modifications in the engine's fuel injection system were made. Four tests indicated that the coal successfully substitutes for diesel fuel in the slurry. The fuel burns in the cylinder, with slightly improved thermal and combustion efficiency. The tests were performed at 1800 rpm and 2200 rpm and 75% load. The fuel injection system of the engine did not maintain adequate fueling of cylinder two with slurry at the lower speed, thus causing deterioration in performance. The slurry was handled better at the high speed and performance was improved. The coal particles did not have an apparent effect on heat release profiles.

The change in the surface properties of Calgon F-400 commercial activated carbon caused by several treatments were examined by X-ray Photoelectron Spectroscopy (XPS). The treatments included washing with 1.0 M hydrochloric acid and 1.0 M nitric acid, oxidation with air at 300°C, and by oxidation with boiling nitric acid. Surface oxygen increased with oxidation as expected. Nitrogen is less abundant on the surface than in the bulk. Nitrogen binding energies suggest alkylamines, aromatic amines and pyridine derivatives. Three sulfur species were seen in all samples. Their binding energies correspond to mercaptans, disulfides and thiophenes.

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MASTER

EXECUTIVE SUMMARY

The first step in the envisioned integrated, multi-product approach for utilizing Illinois coal is the production of ultra low-ash coal. Subsequent steps would convert low-ash coal to high-value products through mild gasification, char activation, and oxidation reactions. The ultra low-ash coal is produced by solubilizing coal in a phenolic solvent under ChemCoal™ process conditions, separating the coal solution from insoluble mineral matter, and then precipitating the clean coal (CC-solids). The major products of mild gasification of low-ash coal would be liquids (higher hydrogen content than from the parent coal) and low-ash char. The low ash-char is further upgraded to activated char, and/or an oxidized activated char which has catalytic properties.

A supply of clean coal has been obtained from 12 gallons of ChemCoal slurry. TGA shows approximately 10-15% meta-cresol remains. We estimate that we will have a little more than 3600 grams when all the product has been treated in a vacuum oven at a temperature high enough to remove the remaining meta-cresol. Ash content may approach 0.9% on a cresol-free basis for the composite. This is three times higher than expected based on last year's work. Despite the higher level, it should still be possible to evaluate advantages of lowering the ash before mild gasification. Based on experience at the ISGS last year when we duplicated the procedure for precipitation and recovery of CC-solids from reactor slurry developed at UNDEERC, we did not expect problems in isolating a low-ash product. As reported last quarter, neither we nor our contractor, Applied Research and Development Laboratories of Mt. Vernon, Illinois, obtained the low ash CC-solids (< 0.3% ash) from the slurry supplied to us by UNDEERC at the end of the last contract. This slurry was made in a larger autoclave and changes accompanying the scale-up are believed responsible for the problem.

Our work plan for this year included characterization of oils produced both by the mild gasification of the CC-solids and of a low ash coal produced by acid extraction (HF) of the mineral matter. The characterization work would have been performed by the National Institute for Petroleum and Energy Research (NIPER) in Bartlesville, Oklahoma. In consultation with the project monitor, the decision was made to eliminate this task. Most of the funds for allotted to the NIPER analyses were consumed in isolating the CC-solids. The UNDEERC tests in the larger autoclave appear to be atypical. Efforts to carefully characterize liquid products appears unwarranted especially in the light of all engineering tasks related to CC-solids production. The labor that would have been spent in making careful material balances around mild gasification runs will be redirected to extend work on the oxidized char catalyst.

Tests in the two cylinder Lister Petter diesel research engine in the Automotive Systems Laboratory at the Department of Mechanical and Industrial Engineering of the University of Illinois were successful. The slurry test rig assembled to simulate injection into a diesel engine was used to modify the fuel injection system. The clearance gap between the needle of the fuel injector and the bore in the nozzle was increased by lapping the needle with fine emery paper. This reduced the resistance to flow of fuel in a fuel bypass path thus increasing the leakage flow from the injector. The increased flow prevented coal particles from sticking onto the needle which was causing plugging of the injector. Despite initial concerns, it was possible to successfully handle the slurry without having to reduce the opening pressure of the injector. Opening pressure was retained at 3000

psi, the manufacturer's specification, ensuring adequate fuel atomization. The injection test rig was also useful in settling on a recipe for the composition of the fuel which did not plug the injector.

The higher of two speeds (2200 and 1800 rpm), and higher load conditions were more favorable for coal slurry operation of the diesel engine. At these conditions the fuel injection system maintained adequate fueling of the second cylinder, thus keeping the cylinder performance high. The coal particles in the slurry burned despite the shorter residence time as evidenced by improved performance as measured by (a) the unchanged heat release profiles, (b) the higher degree of combustion completion, and (c) the increased thermal efficiency in the cylinder. Deterioration in performance of cylinder two, at the lower speed and load, is caused by the reduced fueling. The injection system is unable to maintain an adequate supply of fuel. The higher degree of combustion completion, the insignificant changes in heat release profiles, and the improved thermal efficiency all show that coal burns in the cylinder. Future work is limited by coal availability. The remaining coal is enough to run the engine for approximately thirty minutes with a coal loading of 40%. Efforts are being made to find additional low-ash coal for further testing.

Preparation of seven samples to be investigated in the adsorption phase of the project has been completed. Proximate and ultimate analyses of these seven samples have been obtained and they have also been examined by X-ray Photoelectron Spectroscopy (XPS). Surface oxygen increased with oxidation as expected. Nitrogen is less abundant on the surface than in the bulk. Nitrogen binding energies suggest alkylamines, aromatic amines and pyridine derivatives. Three sulfur species were seen in all samples. Their binding energies correspond to mercaptans, disulfides and thiophenes. A source of zinc in samples treated with nitric acid will be identified. Surface areas of these seven samples have been determined by nitrogen adsorption and application of the BET equation. The apparent densities of the samples have been obtained using ASTM methods. The adsorption capacities of the samples will be determined using aromatic and aliphatic compounds. The effect of oxygen surface groups on adsorption of these compounds will be assessed.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

OBJECTIVES

The primary objective of the envisioned Integrated Production/Use (IPU) approach is to achieve high-value, coal-derived products from Illinois coal, especially coal char derivatives. The first step of the IPU approach is the preparation of ultra low-ash coal by dissolving coal away from mineral matter with a phenolic solvent (ChemCoal process). Low-ash coal would have fuel applications as diesel fuel and as gas turbine fuel. However, higher-value products are projected by subjecting the low-ash coal to mild gasification. These products include premium liquids and a low-ash char suitable for conversion to activated carbon, carbon molecular sieves and catalysts. Current objectives include:

- extend the body of knowledge concerning the combustion properties of clean coal in a diesel engine,
- expand the knowledge of making activated carbon by making it from mild gasification, low-ash char,
- broaden the knowledge of how to selectively adsorb one class or type of compound from a mixture,
- compare properties of oxidized activated char (OAC) catalysts produced from low-ash char with those made from high-ash char examined under a previous contract,
- further define the potential for adsorbing unwanted organics (halides in particular) from dilute solutions and then converting them to readily manageable hydrocarbons and acidic or basic gases by elimination reactions catalyzed by the OAC.

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 both physical and chemical coal cleaning, and on the mild gasification of coal. The envisioned IPU approach meets many of the current goals of these organizations. Although marketing of a single product from a process is acknowledged to be less complicated than finding markets for several products, there are cases of successful multiproduct strategies for utilizing a natural resource. Petroleum refining and petrochemicals are prominent examples. Information on the technical suitability for using several products should precede assignment of a monetary value to products of a coal utilization strategy. The work proposed under this project provides portions of knowledge needed to evaluate the technical potential of coal-derived products, especially ultra clean coal and its derivatives.

The IPU approach produces a low-ash coal, a mineral rich coal fraction, and coal-derived liquids on the path to making the desired char. The marketability and price of the char are key factors for economic viability of mild gasification.

To have a significant impact on coal production in the State of Illinois, any char market should be large and have a potential price structure greater than the utility boiler fuel

value. Among the markets which could have the volume to influence the char market significantly is the activated carbon market. OAC is useful for water purification and for adsorbing components from nonaqueous solutions or suspensions. Not only is the potential volume for char-derived adsorbent attractive, but the price of a competitive high quality carbon is more than \$1000/ton.

An important advantage that OAC is projected to have over commercial activated carbon is the capacity to catalyze chemical elimination reactions. It may also catalyze desirable transformations of coal-derived liquids such as cleavage of carbon-carbon bonds. It remains to be determined what the appropriate balance between catalytic properties and adsorbent capacity will be.

When the technical benefits of taking much of the mineral matter out of coal before further processing are known, it should be possible to estimate a monetary value of this upgraded char. The technical benefits of cleaning solid coal to a level acceptable in a fuel for diesel engines and gas turbines is a major advance. There could be an economy of scale for producing an ultra low-ash coal. If it exists, it will be an important factor in assessing how much effort is justified to develop 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 catalysts [1-3]. Exploiting the properties of OAC was an objective of previous collaborative work with Amoco personnel and it is carried forward in this project. 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 decompose 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.

The overall objective of one segment of the project being carried out in the U of I Civil Engineering Department 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 [4-8]. Papirer and co-workers [6] 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 [9-11]. This is due to the presence of background organic matter in natural water which competes with the targeted compound for adsorption sites [12]. 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 [7]. 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 [13].

EXPERIMENTAL PROCEDURES

Twelve gallons of slurry from two ChemCoal runs in a large autoclave at the University of North Dakota Energy and Environmental Research Center (UNDEERC) was previously delivered to Applied Research and Development Laboratory, Inc. (ARDL) in Mt. Vernon, Illinois, for processing. The isolation procedure for the clean coal was the one developed at UNDEERC and duplicated last year at the ISGS. ARDL could not duplicate the low ash values obtained last year. ISGS tests on the slurry confirmed the problem. The scale-up to a larger autoclave at UNDEERC appears to have been accompanied by a different level of bond-breaking. More low molecular weight material may have been produced. ARDL has now completed the processing by a modified procedure and has delivered the ChemCoal solids.

Fuel assessments in a diesel engine (Syrimis, U of I)

A two cylinder Lister Petter diesel research engine and an injection test rig to test pumping and atomization characteristics of the fuel slurries have been described in previous reports. The test rig was used to modify the fuel injection system, and to find a recipe for the composition of the fuel which did not plug the injector. The clearance gap between the needle of the fuel injector and the bore in the nozzle was increased by lapping the needle with fine emery paper. This reduced the resistance in the leakage fuel path thus increasing the leakage flow from the injector. The increased flow prevented coal particles from sticking onto the needle and causing plugging of the injector. Despite initial expectations, it was possible to successfully handle the slurry without having to reduce the opening pressure of the injector. Opening pressure was retained at 3000 psi, the manufacturer's specification, ensuring adequate fuel atomization.

During the tests in the injection rig, the operation of the injector was monitored by observing the needle lift signal in an oscilloscope. Any change in the lift signal indicated that something was going wrong in the injector and the test was stopped. It was thus possible to prevent irreparable damage to the nozzle, that is to prevent plugging to the extent at which the needle could not be removed from the nozzle. In a successful run the needle lift signal stayed the same during the test. In the absence of sufficient quantities of CC-solids for engine tests, low-ash coal provided by AMAX was used. It was produced by caustic dissolution of ash. This is a small amount of coal remaining from the preparation of slurries by AMAX for contracts funded by U.S. DOE.

Adsorption studies (Feizoulof, U of I)

Surface treatment of char - 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 700 g of a 16x20 mesh size fraction (U.S. Standard Size) was separated for use in further tests. The 16x20 "as received" F-400, designated **AR000**, was used to prepare six other samples with varying surface chemistry. First, AR000 was acid-leached with 1.0 M hydrochloric acid and 1.0 M nitric acid in an attempt to remove mineral impurities which may interfere with future work. This acid-washed sample was designated **AW100**. AW100 was placed in a fluidized bed reactor, heated to 950°C at 20°C per minute and held at 950°C for 30 minutes in ultra-high purity (UHP) nitrogen gas, before allowing it to cool in UHP nitrogen. This sample, designated **FN950**, was split into five batches. One batch underwent no further treatment. One portion of FN950 was placed in a fluidized bed reactor and heated to 300°C at 20°C per minute in an atmosphere of 10% O₂/90% N₂. The sample remained fluidized at 300°C for 5 minutes before it was allowed to cool in an atmosphere of 10% O₂/90% N₂. This sample was designated **AO305**. Another sample, designated **AO330**, was prepared in a fashion identical to AO305, except it remained fluidized at 300°C for 30 minutes. One hundred grams of FN950 was placed in a round-bottomed boiling flask which was filled with 500 ml of boiling 0.5 M HNO₃. The sample was allowed to reflux for 30 minutes. This sample was designated **HN050**. A sample designated **HN100** was prepared in an identical manner, except 1.0 M nitric acid was used as opposed to 0.5 M.

All of these samples were submitted to the Coal Lab located at the Illinois State Geological Survey for proximate and ultimate analyses. Detailed descriptions of the equipment used to conduct these analyses may be found elsewhere [14]. Results of these analyses may be found in Table 1.

The surface areas of the samples were measured (see Table 1) using adsorption of N₂ at 77 K and application of the Brunauer, Emmet, and Teller (BET) equation. The sample was outgassed under vacuum at 110°C for approximately 24 hours prior to the analysis.

The apparent densities (AD) of the samples were determined according to the ASTM "Standard Test Method for Apparent Density of Activated Carbon" [15]. Its units are mass of GAC per unit volume of an unstratified, packed bed of GAC. The volume measured is that of a GAC bed packed by a free-fall of GAC into a graduated cylinder. Therefore, the volume term of this density measurement includes inter-particle and intra-particle voids. All of the samples were placed in a drying oven for 24 hours prior to AD measurements in order to drive off any moisture which may have been present.

XPS characterization treated surfaces (Fatemi, Amoco) - X-ray Photoelectron Spectroscopy (XPS) was used to study the surface compositions and chemistry of Calgon F-400 activated carbon and the six samples prepared from it by C. Feizoulof. Elemental surface composition (relative elemental weight percent) and a summary of binding energies (BE), as determined by XPS, for all samples are shown in Tables 1 and 2, respectively.

Catalyst activity - dehydrochlorination (Fatemi, Amoco)

The catalytic properties of the oxidized activated char were investigated using OST3-9 char (from last year's project) for dehydrochlorination of 3-chloro-3-methyl pentane from Aldrich Chemical. Dehydrochlorination experiments were performed by pipetting 5.0 ml of the alkyl chloride into a 25 ml micro evaporator. The sample was heated to 120°C and allowed to reflux for 5 minutes. At this time, 0.5 g activated-oxidized char (OST3-9 or OST10-14) was added to the refluxing sample and allowed to reflux for an additional 10 minutes. The mixture was allowed to cool to room temperature before filtration. The solution was then analyzed by GC/MS. In some experiments, the material boiling above about 60°C was distilled and collected. In these experiments, the distillate and the remaining solution were both used for the GC/MS analyses.

The GC/MS analyses were performed using a Varian Saturn GC/MS instrument equipped with FID (flame ionization) detector and a vitreous silica inlet splitter (VSIS). The VSIS allows dual column dual detector capability. In this system, two identical DB-5 columns, 30 m long with 0.25 mm ID and 0.25 μ m film thickness, were connected to a single injector via VSIS. This allowed a simultaneous two detector (FID and MS) analyses from a single injection. Samples were diluted with normal octane using a ratio of 1:5. An aliquot of 1.0 μ l of diluted solution was injected into the columns using the split mode. The GC column temperature was held at 37°C for 7 minutes then heated to 150°C with the heating rate of 10°C/min. The injector and detector temperatures were both set at 300°C and the transfer line temperature was set at 280°C.

RESULTS AND DISCUSSION

Low ash ChemCoal solids

Based on experience at the ISGS last year when we duplicated the procedure for precipitation and recovery of CC-solids from reactor slurry developed at UNDEERC, we did not expect our contractor, ARDL, to have difficulty isolating a low-ash product from the twelve gallons provided. As reported last quarter, neither we nor our contractor have gotten the low ash CC-solids (< 0.3% ash) from the slurry supplied to us by UNDEERC at the end of the last contract. ARDL has now finished the work-up and delivered the product (see Table 3). TGA for the last five batches appear in Figure 1. All samples have about 15% meta-cresol remaining. We estimate that we will have a little more than 3600 grams to work with when all the product we have has been treated in a vacuum oven at a temperature high enough to remove the remaining meta-cresol.

Fuel assessments in a diesel engine

The fuel composition was: 20% coal, (average particle size 5 microns), 79.5% diesel fuel, 0.5% castor oil, and 0.05% (to the coal) LP6, a surfactant made by ICI. Castor oil, a substance well known for its lubricative and adhesive properties, was added to the fuel for better lubrication of the nozzle. Photographic study of the spray pattern was postponed, and engine testing was pursued. Engine tests were performed at 75% load, at two different speeds, in the following sequence:

1. 2200 rpm, 27 lbf-ft, 10 in Hg boost, 40 minutes
2. 1800 rpm, 24 lbf-ft, 10 in Hg boost, 3 hours
3. 1800 rpm, 24 lbf-ft, 10 in Hg boost, 40 minutes
4. 2200 rpm, 27 lbf-ft, 10 in Hg boost, 40 minutes.

Ignition, and combustion of the coal particles in the cylinder are enhanced by high cylinder temperatures, produced by high engine load, and the presence of adequate amount of oxygen in the cylinder, provided by the increased intake pressure of 10 in Hg (5 p.s.i gauge).

In each test the engine was run with diesel fuel in both cylinders for about an hour and a half for engine conditions to stabilize, before the fuel of the second cylinder was changed to slurry. Data acquisition started half an hour before the change of fuel in the cylinder. Comparison of the two fuels was made by comparing performance variables, and also heat release results of the two cylinders. In the discussion to follow, zero time is the instant at which the fuel to cylinder two was changed to coal slurry. Negative time was the period in which both cylinders were burning diesel, while positive time was the period when cylinder two was burning slurry.

At each condition, the results of both tests were the same. At the low speed there was deterioration in the performance of cylinder two with the slurry, where as at the higher speed performance of cylinder two was improved with the slurry. Changes in performance were caused by changes in the fuel consumption of the cylinders. At 1800 rpm, the fuel injection system could not handle the coal slurry sufficiently. Fueling of the second cylinder was significantly reduced after the fuel was changed to slurry, resulting in reduced power output. On the other hand, at 2200 rpm the fuel system maintained adequate fueling to cylinder two, thus keeping the cylinder performance high.

At 2200 rpm, improved performance of cylinder two with slurry was realized by the increase in Net Indicated Mean Effective Pressure (IMEP_{net}), a measure of the power output of the cylinder, and exhaust temperature, see Figures 2-3. On the other hand, at 1800 rpm, deteriorated performance of the cylinder was realized by the decrease in IMEP_{net}, and exhaust temperature, see Figure 4-5. Variation of the IMEP_{net}, and exhaust temperature in each cylinder follow the same trend as the variation of fuel consumption.

When diesel fuel is used in both cylinders in the engine, the variation of fuel consumption of the two cylinders is the same. Fueling to the cylinders is controlled by the governor, a mechanical controller incorporated in the engine, so as to maintain the required load at constant speed. Upon a change in load, the governor turns by an equal amount the plunger of each fuel pump, and equally increases or decreases fueling to the cylinders so that the load is met without a change in speed. The different trends in the fueling of the cylinders in the tests was caused by the different nature of the fuels.

At the higher speed, due to the increase in the power output of cylinder two with slurry, the governor tried to reduce fueling to the cylinders, shown by the reduction in fueling of cylinder one. However, fueling of cylinder two was not reduced, it stayed the same in test 1 while it was increased in test 4. On the other hand, at 1800 rpm due to the reduced power output of cylinder two, caused by reduced fueling, the governor tried to increase fueling to the cylinders. In this case only fueling of cylinder one was increased, while fueling to cylinder two did not change. It seems that the fuel system is not very sensible

to the fuel properties when operating near its design conditions, i.e. at the maximum break torque speed, 2100 rpm in this case.

Fuel consumption changes were caused by changes in injection timing. The coal particles in the fuel caused a delay in the start of injection in cylinder two at both conditions, and non repeatable injection duration at 1800 rpm. The delay in start of injection was .25 degrees at 2200 rpm, and .75 degrees at 1800 rpm. Again the variability of injection timing at 1800 rpm proves the inability of the fuel system to handle the slurry. Delayed injection was caused by the reduced speed of sound in the slurry, due to its higher density. Pressure in the fuel line is built up by a pressure wave created when the plunger starts its stroke. The wave, which travels at the speed of sound, may have to cover the length of the fuel line more than once, before line pressure reaches the opening pressure of the injector for injection to start. In this way reduced speed of sound causes delayed injection.

Smoke numbers, a measure of the particulates in the exhaust, were consistently higher for cylinder one. When the fuel was changed in cylinder two, smoke numbers went through a transition period and stabilized at slightly higher values than their initial ones.

By comparing the contribution of each cylinder to the total load with the amount of fuel energy supplied, one may calculate the thermal efficiency in the cylinder. The contribution of each cylinder towards the load is given by the ratio of its IMEPnet to the sum of the two IMEPnets, e.g.:

$$\epsilon_{\text{cyl2}} = \frac{\text{IMEP}_{\text{net2}}}{\text{IMEP}_{\text{net1}} + \text{IMEP}_{\text{net2}}}, \text{ and } \eta_{\text{th2}} = \frac{\epsilon_{\text{cyl2}} * \text{Total Power}}{m_{\text{fuel2}} * \text{LHV}}$$

For the last two tests the thermal efficiencies of the cylinders were:

	<u>Time</u>	<u>Cylinder One</u>	<u>Cylinder Two</u>
Test Three	-10 minutes	33.8%	31.9%
	60 minutes	32.9%	33.6%
Test Four	- 10 minutes	32.5%	30.4%
	40 minutes	31.7%	33.5%

Slurry combustion results in higher thermal efficiency in cylinder two, at both testing conditions.

Heat release analysis of the results gave more insight to the combustion characteristics of the coal slurry. At the high speed tests the heat release profiles obtained with the slurry were almost identical to the ones obtained in cylinder two with diesel. At the lower speed the differences between the heat release profiles were caused by injection timing, and fuel consumption differences. Heat release results from the third and fourth test are presented.

TEST 3: Heat release profiles for the cylinders at 60 minutes slurry time are shown in Figure 6. Delayed start of injection causes ignition to start later in cylinder two, and the

initial combustion rate to be lower. Cylinder two reaches a higher peak heat release during premixed combustion, while increased fueling maintains heat release higher in cylinder two during mixing controlled combustion. Combustion is completed faster in cylinder two, since less fuel is supplied. Relative heat release rate reaches a higher value in cylinder two. Cylinder temperature is higher in cylinder one.

Comparison of the heat release profiles in the same cylinder at different times is shown in Figure 7. The heat release profiles in the cylinders at 25 and 60 minutes are identical. Cylinder one reaches a higher heat release during diffusion combustion, at 25 minutes, due to the higher loading, and fueling rate. Combustion of diesel fuel in cylinder two reaches a higher peak heat release than combustion of slurry, while heat release during diffusion controlled combustion is the same. The higher peak heat release was caused by the earlier injection in cylinder one. The difference in start of injection was .75 degrees. Combustion of the slurry ends faster due to reduced fueling.

Burn of coal particles does not have an obvious effect in the heat release profile. However, the fact that only timing related differences exist between the heat release profiles of diesel and coal-diesel slurry, the improved thermal efficiency of cylinder two, and the higher degree of combustion completion show that coal burns in the cylinder. The deterioration in performance upon change of fuel to slurry is caused by the reduction in the fueling rate of the cylinder.

TEST 4: The heat release profiles in the two cylinders at forty minutes of slurry operation are shown in Figure 8. Cylinder two reaches a higher peak heat release, and has a faster initial burning rate, indicated by the steeper slope of the curve. Relative heat release results show that combustion reaches a higher degree of completion in cylinder two. Finally, cylinder temperature is higher in cylinder two.

Comparison of the net heat release profiles for the two cylinders at different times in the test are shown in Figure 9. There are not any significant differences in the profiles for cylinder two due to the slurry. Fifteen minutes in slurry operation the profile is almost identical to the diesel profile, it is only shifted to the left by .5 degree due to earlier ignition. At forty minutes, the profile becomes slightly smoother in the diffusion control region. The relatively small change in fuel consumption of the cylinder, about 4%, keeps the duration of combustion for diesel and coal slurry practically the same. Similarly, the heat release profiles for cylinder one do not change through the test.

The improved performance, the higher thermal efficiency, the unchanged heat release profiles, and the higher degree of combustion completion in cylinder two, all show that the coal burns in the cylinder. The coal burns fast enough so that its contribution to the cylinder performance is not affected by the shorter residence time.

Adsorption studies - properties of treated chars

Acquisition, preparation, and characterization of a commercial granular activated carbon (GAC) (Feizoulof, U of I) - AW100 was heated in nitrogen to an extreme temperature in order to effect removal of oxygen functional groups on the surface of the carbon. Heating of carbon to high temperatures causes oxygen on the surface to come off as CO and CO₂ [16]. This sample was allowed to cool in nitrogen to room

temperature and then exposed to the atmosphere. Basic surface oxides are formed when surface oxygen functionalities are freed from the carbon surface by heating in an inert atmosphere and then allowing the carbon to come into contact with oxygen only after cooling to low temperatures in an inert atmosphere [16]. Therefore, sample FN950 will possess a basic surface nature.

Acidic surface oxides are formed when carbon is treated with oxygen at temperatures near its ignition point and also on reaction with oxidizing solutions [16]. Thus, samples AO305, AO330, HN050, and HN100 will behave as acidic carbons. The purpose of the different residence times used in preparation of the AO carbons and the different concentrations of HNO_3 used in preparation of the HN carbons was to put differing amounts of oxygen on the surface of the carbon. Examination of Table 1 reveals that the AO carbons have less oxygen (obtained by difference) than the FN950 from which they were prepared. This is not expected; however, this phenomenon has been previously observed by Kruse and co-workers [17]. Kruse's work found that oxygen values obtained by difference were lower for air oxidized samples than for their precursors, while oxygen values obtained by direct measurement for the same air oxidized samples were higher than those of their precursors. Other methods, including CO/CO_2 temperature-programmed desorption and X-ray photoelectron spectroscopy, will be used to better quantify the amount of oxygen present on the oxidized samples.

Determination of surface areas using nitrogen adsorption at 77K and application of the BET equation revealed that the surface areas of the carbons were not changed significantly by the various treatments. This is a good indication that the physical characteristics of the carbons were not altered drastically by the treatments. Further work characterizing the micropore and mesopore volumes of the carbons is currently underway.

Inspection of Table 1 shows that the carbons treated with nitric acid have higher apparent densities than the other carbons. This is expected since treatment with nitric acid adds significant amounts of oxygen to the surface of carbons. Puri and co-workers [18] found that the oxygen content of an outgassed charcoal could be increased to greater than 20% by oxidation with nitric acid.

XPS surface characterization - (Fatemi, Amoco) - Based on elemental surface composition (relative elemental weight percent) and a summary of binding energies (BE), as determined by XPS, for all samples (Tables 1 and 2, respectively), it appears that acid washing with 1.0 M HCl and 1.0 M HNO_3 increased the concentration of oxygen on the surface of the activated carbon (AR000) by more than 2 weight percent (AW100). However, the pyrolysis step removed the oxygen from this sample (FN950) and both air oxidation steps which followed the pyrolysis step did not have any significant effect on the surface oxygen (AO305 and AO330). It appears that the most effective oxidation procedure used is the HNO_3 acid washing. The HNO_3 oxidation increased the concentration of oxygen in the surface of the activated carbon by 4-5 weight percent (HN100).

The most surprising data in Table 1 is the presence of zinc in all three acid washed samples, especially in a very high concentration in sample HN100. The data suggest that the appearance of Zn is related to the use of nitric acid. The concentration of the Zn is, however, not related directly to the amount of nitric acid used. The highest concentration

occurs for the most severe treatment. The zinc does not appear to be on the surface of either the original activated carbon nor the pyrolyzed and air oxidized samples. One hypothesis that will be examined starts with a possibility that there is zinc in the mineral matter of the activated carbon. If this is found to be so, it may be that the nitric acid oxidation dissolves zinc from ash components and then allows it to be adsorbed on the surface of the activated carbon.

The elemental binding energies shown in Table 2 indicate significant differences in the chemical species concentrated on the surface of the samples. Several different species of the elements carbon, oxygen, nitrogen, and sulfur were identifiable in the surfaces of the samples from the binding energy information presented in Table 2. Carbon type species such as hydrocarbon (C-C and C-H at 284.6 ± 0.2 eV), oxidized carbon (C-O and C=O at 286 ± 0.2 eV) and carbonate/carboxylic carbon ($\text{CO}_3^{2-}/\text{CO}_2^-$ at 289.0 ± 0.6 eV) are present in all samples. It appears, however, there is no significant change in the concentration of the carbon species with any of the oxidation procedures.

The nitrogen binding energies suggest the presence of amines (RNH_2) including alkylamines, aromatic (phenyl) amines and pyridine derivatives at 399.0 ± 0.6 eV, pyrrolic nitrogen species at 399.7 ± 0.2 eV, ammonium derivatives (RNH_3^+) at 401.6 ± 0.4 eV, pyridines at 405.8 ± 0.7 eV, and two unidentifiable species at 402.7 and 403.0 eV. The surface binding energy data in Table 2 clearly indicate that species of ammonium derivatives are present in all samples. However, the concentration of these species is different for each sample. It is about 67% in the original activated carbon sample (AR000), reaches the maximum of 82% in the pyrolyzed sample (FN950), and the minimum of about 50% for the two acid washed samples (HN050 and HN100). It appears that amines are formed during the pyrolysis step and are increased by both air oxidation and nitric acid washing procedures. Pyridines are also present in most samples. Their concentrations, however, are not changed significantly by the oxidation processes.

Three types of sulfur species were seen in all samples. The sulfur species observed were at binding energies of 163.7 ± 0.2 eV (alkyl sulfide), 164.9 ± 0.2 eV (elemental and/or organic sulfur species such as mercaptans, disulfides, and thiophenes), and 168.6 ± 0.4 eV (sulfates and sulfonates sulfur), respectively. While no significant changes were observed in the concentration of sulfur species at binding energy of 163.6 ± 0.6 eV, there were some changes in the concentrations of the other two types of sulfur species.

Baseline chloride for catalyst activity determinations (Fatemi, Amoco)

The results of the study indicated that the concentration of cis and trans isomers of 3-methyl-2-pentene vary according to the way the experiment is performed. As expected, the distillates collected from the distillation experiments yielded the highest concentration of olefinic products. The concentration of 3-methyl-2-pentene (cis/trans) in these samples was as high as 40% of the total distillate.

CONCLUSIONS AND FUTURE WORK

- Approximately 8 pounds (3600 grams) of clean coal has been isolated from 12 gallons of ChemCoal slurry and delivered to the ISGS by Applied Research and Development Laboratories. Ash content may approach 0.8% on a cresol-free basis for the

composite. This is almost three times higher than expected based on last years work. Despite the higher level, it should still be possible to evaluate advantages of lowering the ash before mild gasification.

- The higher of the two speeds (2200 and 1800 rpm), higher load conditions are more favorable for coal slurry operation of the diesel engine. At these condition the fuel injection system maintained adequate fueling of the second cylinder, thus keeping the cylinder performance high. The coal particles in the slurry burned despite the shorter residence time as evidenced by improved performance: the unchanged heat release profiles, the higher degree of combustion completion, and the increased thermal efficiency in the cylinder. Deterioration in performance of cylinder two, at the lower speed and load, is caused by the reduced fueling. The injection system is unable to maintain an adequate supply of fuel. The higher degree of combustion completion, the insignificant changes in heat release profiles, and the improved thermal efficiency all show that coal burns in the cylinder. Future work is limited by coal availability. The remaining coal is enough to run the engine for approximately thirty minutes with a coal loading of 40%. Efforts are being made to find additional low-ash coal for further testing.
- Preparation of seven samples to be investigated in the adsorption phase of the project has been completed. Proximate and ultimate analyses of these seven samples have been obtained and they have also been examined by λ -ray Photoelectron Spectroscopy (XPS). Surface oxygen increased with oxidation as expected. Nitrogen is less abundant on the surface than in the bulk. Nitrogen binding energies suggest alkylamines, aromatic amines and pyridine derivatives. Three sulfur species were seen in all samples. Their binding energies correspond to mercaptans, disulfides and thiophenes. A source of zinc in samples treated with nitric acid will be identified. Surface areas of these seven samples have been determined by nitrogen adsorption and application of the BET equation. The apparent densities of the samples have been obtained using ASTM methods. The adsorption capacities of the samples will be determined using aromatic and aliphatic compounds. The effect of oxygen surface groups on adsorption of these compounds will be assessed.

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Table 1.
Sample Characterization (Proximate & Ultimate Analyses, Nitrogen Surface Areas,
Apparent Densities) and Surface Composition (wt.%, Relative) Data from XPS
Analyses

	AR000	AW100	FN950	AO305	AO330	HN050	HN100
Volatile Matter ¹	6.5	12.0	10.5	10.6	10.8	15.0	15.1
Fixed Carbon ¹	87.3	82.2	81.8	83.0	82.9	78.5	77.4
H-T Ash ¹	6.3	5.7	7.7	6.4	6.3	6.5	7.6
Hydrogen ¹	0.26	0.22	0.43	0.25	0.32	0.26	0.21
Carbon ¹	90.55	87.55	88.46	90.71	90.37	87.54	85.27
XPS Carbon	91.8	89.2	91.1	91.6	91.6	87.4	84.1
Nitrogen ¹	0.95	1.02	0.89	0.95	0.85	1.15	1.48
XPS Nitrogen	0.3	0.3	0.6	0.6	0.5	0.6	0.5
Oxygen ¹	1.27	4.66	1.94	0.87	1.37	3.82	4.79
XPS Oxygen	7.0	9.2	7.5	7.0	7.2	10.2	11.3
Sulfur ¹	0.72	0.83	0.62	0.82	0.82	0.74	0.69
XPS Sulfur	0.8	0.8	0.8	0.8	0.8	0.8	0.5
Zn by XPS	---	0.5	---	---	---	0.5	3.1
Cu by XPS	---	Trc.	Trc.	Trc.	Trc.	0.5	0.5
Surface Area ² (m ² /g)	1061	1073	1124	1058	1121	1012	986
Apparent Density (g/cc)	0.443	0.452	0.445	0.438	0.442	0.459	0.469

1 - Values given on a moisture-free basis

2 - Values given on an ash-free basis

Sample Key

AR000 Calgon F-400 commercial active carbon (as-received).
 AW100 AR000 acid washed in 1.0 M HCl and 1.0 M HNO₃.
 FN950 AW100 fluidized at 950°C in N₂ for 30 minutes.
 AO305 FN950 air oxidized at 300°C in 10% O₂/90% N₂ atmosphere for 5 minutes.
 AO335 FN950 air oxidized at 300°C in 10% O₂/90% N₂ atmosphere for 30 minutes.
 HN050 FN950 oxidized with 0.5 M HNO₃.
 HN100 FN950 oxidized with 1.0 M HNO₃.

Table 2.
Binding Energies (eV) Data from XPS Analyses of the Original and
Treated Calgon F-400 Activated Carbon Samples

Sample	C 1s %		O 1s %		N 1s %		S 2p %	
AR000	284.5	73	533.4	76	401.3	67	163.6	49
	286.4	13	536.8	24	403.0	23	164.9	36
	289.3	14			405.1	10	169.0	16
AW100	284.7	71	533.4	80	401.4	73	163.7	45
	286.6	13	537.0	20	402.7	13	165.0	29
	289.5	16			405.8	14	168.3	26
FN950	284.8	72	533.5	77	399.6	8	163.7	50
	286.7	13	537.0	23	401.7	82	165.0	34
	289.6	15			406.3	10	168.6	16
AO305	284.7	72	533.6	77	399.2	16	163.8	47
	286.5	12	537.0	23	401.9	71	165.1	32
	289.1	16			406.5	13	168.7	21
AO330	284.7	72	533.6	74	398.7	19	163.8	51
	286.5	12	537.0	26	401.5	64	165.1	36
	289.3	16			406.1	17	168.5	13
HN050	284.6	69	533.3	79	399.9	30	163.6	46
	286.4	13	536.8	21	401.8	50	165.0	28
	289.3	18			406.0	20	168.3	26
HN100	284.6	70	533.2	81	399.6	26	163.5	44
	286.4	13	536.6	19	401.6	51	164.8	31
	289.0	17			405.9	23	168.4	25

Table 3.
Material Inventory for Work-up at ARDL

BATCH	RAW PRODUCT USED (L)	RAW PRODUCT REMAINING (L)	PRODUCT DELIVERED BY ARDL (g)	PROJECTED CRESOL-FREE PRODUCT (g)
1	1.6	37	207	176
2	8	29	392	353
3	4	25	250	232
4	4	21	439	360
5	4	17	427	371
6	4	13	missing	
7	1	12	54	100
			35	
			48	
8 (4/92)	1	10	240	221
9 (A)	2	8	434	378
10 (B)	2	6	411	353
11 (C)	2	4	376	330
12 (D)	2	2	443	372
13 (E)	2	0	455	387

Figure 1. TGA of Last Five Batches of CC-solids from ARDL

Note: Malfunctioning of transducer in cylinder two was partly responsible for the difference in IMEP net of the cylinders.

Figure 2. Test One, Performance Data (2200 rpm, 27 lbf-ft, 10 in Hg boost).

Figure 3. Test Four, Performance Data (2200 rpm, 27 lbf-ft, 10 in Hg boost).

Figure 4. Test Two, Performance Data (1800 rpm, 24 lbf-ft, 10 in Hg boost).

Figure 5. Test Three, Performance Data (1800 rpm, 24 lbf-ft, 10 in Hg boost).

Figure 6. Test Three, Heat Release Data at 60 minutes (Cylinder one Diesel, Cylinder Two Coal Slurry).

Figure 7. Test Three, Net Heat Release Comparison.

Figure 8. Test Four, Heat Release Data at 40 minutes (Cylinder One Diesel, Cylinder Two Coal Slurry).

Figure 9. Test Four, Net Heat Release Comparison.

Figure 9. Test Four, Net Heat Release Comparison. (continued)

PROJECT MANAGEMENT REPORT

March 1, 1992 through May 31, 1992

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

Principal Investigator: Carl W. Kruse, ISGS
615 East Peabody Drive Phone (217) 333-5161
Champaign, IL 61820 FAX (217)-333-8566

Funded coinvestigators:

V. L. Snoeyink	U of I	M. Syrimis	U of I
C. Feizoulof	U of I	S. M. Fatemi	Amoco
D. N. Assanis	U of I		

Other Participants

*C. L. Knudson	UNDEERC	J. Mahoney	Amoco
C. R. Porter,	Western Research Institute	J. M. Lytle	ISGS
R. C. Bourke,	GM Allison Gas Turbine Div.	L. Kohlenberger	ISGS
R. C. Strickland	TVA	A. Lizzio	ISGS
T. Uzkan	GM Electro-Motive Div.	M. Rostam-Abadi	ISGS
J. W. Zondlo	West Virginia Univ.	M. Chou	ISGS
J. H. Lora	Repap Technologies		
E. Klavetter	Sandia National Lab		

Project Monitor: Franklin I. Honea CRSC

COMMENTS

* Curt Knudson is moved on this report from the Funded Participant category to the Other Participants category. He was carried forward into the down-scaled proposal (down-scaled from \$252,671 to \$148,959) as a subcontractor to be paid \$3,000. It was the PI's desire to maintain at least a token involvement by UNDEERC (matched by DoE funds) for the first year, thinking that the CRSC request for proposals in 1992 might request projects which would take advantage of the interest the participants named above had in researching engineering aspects of producing an ultra clean coal. That request did not materialize. When Curt Knudson was became aware that the cost for separation of the clean coal would be more than budgeted, and he also knew there would be no engineering work in 1992-93, he suggested the change in his relationship to the project recorded above. He has continued to be available to answer questions at no cost to the project, for which the PI is most grateful.

The hiring of a technical person to work on this contract at the ISGS was delayed until February 1992. Amoco received its subcontract from the University of Illinois in late February 1992. The two university professors will draw from the direct labor line this summer, not prorated through the year as projected. The late starts and saving of funds until summer account for most of the \$27,000 that expenditures lag projections.

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.

Schedule

SCHEDULE OF PROJECT MILESTONES

Milestones:

- Task 1 Production of low ash coal
 - Task 1a Low ash ChemCoal solids - UNDEERC/ARDL
 - Task 1b Low ash coal control - ISGS
- Task 2 Mild gasification of low-ash coals - ISGS
 - Task 2a Characterization of oils - ISGS (deleted)
 - Task 2b Low ash chars - ISGS
- Task 3 Fuel assessments in a diesel engine - UIUC - Assanis/Syrimis
- Task 4 Activated and oxidized/activated low ash char
 - Task 4a Preparation of chars - ISGS
 - Task 4b Characterization and use - Amoco
 - Task 4c Adsorption studies - UIUC - Snoeyink/Feizoulouf
- Task 5 Catalytic Hydrolysis and Liquefaction
- Technical reports
- Financial reports

**DATE
FILMED**
12/21/92