

**TECHNICAL REPORT**

December 1, 1991, through February 29, 1992

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

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**ABSTRACT**

The first step in the integrated, multi-product approach for utilizing Illinois coal is the production of ultra low-ash coal. Subsequent steps convert low-ash coal 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.

Isolation by our subcontractor, Applied Research and Development Laboratory, Inc. (ARDL) in Mt. Vernon, Illinois, of ChemCoal solids (CC-solids) from twelve gallons of reactor product produced at the University of North Dakota Energy and Environmental Research Center was suspended when product quality did not match previous experience. ISGS tests confirm that ash levels cannot be reduced below 0.6 wt %. The scaleup to a larger autoclave may have been accompanied by more bond-breaking and more low molecular weight material. A slurry test rig simulating injection into a diesel engine has been assembled and preliminary tests were made. A purity problem with 3-chloro-3-methyl pentane, the primary chemical used to measure catalyst activity of oxidized activated char, has been resolved by selection of a new source. A commercial granular activated carbon (GAC), Filtrasorb-400 (F-400), manufactured from a bituminous coal, was obtained from the Calgon Corporation. An acid washed variety of this carbon was prepared and characterization (including elemental analyses and adsorption isotherms) of both the acid-washed product and its precursor is underway.

**MASTER**

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## EXECUTIVE SUMMARY

Char is more often than not an undesired product of coal utilization processes because of high ash content and low calorific value. Additionally, volatile components initially in the coal have been removed, and most char does not have the combustion characteristics expected of a good solid fuel. The market for coal char is very limited. Char's low value is often a restraint on economics of a coal utilization approach, especially 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 among 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. One barrier to the 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 to 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 of the mineral components leaving the coal essentially untouched. A second approach, the primary one for this project, is to dissolve the carbonaceous components in a solvent coal leaving the mineral matter in the solid state. This latter approach does not leave the coal's structure completely unaltered. 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. There are 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.

A phenolic solvent alone does not solubilize much coal. Either acid or base is added and also carbon monoxide and water which react in situ to provide a reducing atmosphere. Very little gas need be produced. The coal's hydrogen can be conserved in the liquid and solid products when operating under one solubilization approach, 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 were produced having only 0.2-0.3 wt% ash and 0.6 wt% sulfur. The coal used was Herrin (Illinois No. 6) from lot IBC-109 in the Illinois Basin Coal Sample Program IBC-109. Yields were 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 it 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.

Another variation of the coal solubilization approach to separate coal from ash-forming minerals is employed 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 believed to be a chemically unaltered fraction of the coal whereas portions of the material produced by the modified ChemCoal™ process are higher molecular weight components that have been brought into solution by bond breaking reactions.

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 a catalyst for other desirable transformations. Work under a 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. Any trade-off of catalytic properties against premium adsorptive properties must be evaluated.

The mild gasification conditions that have been shown to achieve the highest value tar byproduct will be used for producing char from the low-ash coal. The liquids which

accompany the mild gasification 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 hydrolysis 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. One of the most important of the engineering questions not answered by previous UNDEERC studies is the rate at which heat can be supplied to initiate the solubilization reactions.

#### **Progress: this reporting period**

Isolation by our subcontractor, Applied Research and Development Laboratory, Inc. (ARDL) in Mt. Vernon, Illinois, of ChemCoal solids (CC-solids) from twelve gallons of reactor product produced at the University of North Dakota Energy and Environmental Research Center was suspended when product quality did not match previous experience. ISGS tests now confirm that ash levels cannot be reduced below 0.6 wt %. The scaleup to a larger autoclave at UNDEERC may have been accompanied by more bond-breaking and more low molecular weight material. We were able to separate CC-solids by filtration and various washing steps in previous work, but materials which plug filter paper and prevent filtration occur frequently with this material. We believe this is because lower molecular weight components lower the softening temperature of the CC-solids. There appears to be a constant amount of ash which is not taken to the bottom during centrifugation. We speculate that metals held in coordination complexes may exist. If these exist, they may be inherent in the coal and it could be complexes of metal ions that are also extracted with coal fractions by the N-methylpyrrolidone method. In any event, it appears we must accept 0.6 to 0.8% ash in the CC-solids that will be available from the 12 gallons of product produced for this project at UNDEERC. We are assessing the cost and advisability of making more that initially projected of the low-ash coal by an HCl/HF/LiAlH<sub>4</sub> treatment.

The injection of CC-solids into the diesel engine has been deferred until problems with plugging of injectors can be solved. Producing a reasonably stable, pumpable slurry has become the first priority at the Automotive Systems Laboratory at the Department of Mechanical and Industrial Engineering of the University of Illinois. A slurry test rig simulating injection into a diesel engine has been assembled and preliminary tests were made. The injection test rig is now operational. The apparatus was assembled from actual components used in the injection system of the engine, i.e. camshaft, follower, and injection pump, and is driven by an a.c. motor. The camshaft rotates at 870 rev/min, which corresponds to an engine speed of 1740 rev/min. The rig allows testing of the slurry fuel before using it in the engine, and also the photographic study of the spray. A FASTAX 16 mm, high-speed, motion camera will be used to take motion pictures of the spray at approximately 1000 frames/second.

Initial work on developing the procedures for the study of selective adsorption on activated carbon has begun in the Department of Civil Engineering of the University of Illinois. Making carbon forms which selectively adsorb a contaminant is a goal of this work. Whether or not the acidic or basic surface nature of an activated carbon affects its ability to preferentially adsorb the compounds trichlorophenol and trichloroethylene will be determined. A commercial granular activated carbon (GAC), Filtrasorb-400 (F-400), manufactured from a bituminous coal, was obtained from the Calgon Corporation for use

as a control. A portion of this activated carbon was acid washed with hydrochloric and nitric acid. Both the "as received" carbon and the material modified by acid washing are being characterized initially by proximate and ultimate analyses, BET surface area, micropore volume, and mesopore volume. They will also be characterized by the spectroscopic methods used previously by Amoco researchers on our catalytic oxidized char samples.

Amoco analyzed 3-chloro-3-methyl pentane from Wiley Organics by gas chromatograph/mass spectrometer (GC/MS) to establish a baseline for the dehydrochlorination work using activated-oxidized char from mild gasification. This material, from bottles of this chemical provided to Amoco by the PI, did not appear pure. Amoco obtained what appeared to be good chromatograms from both the GC/FID and the GC/MS analyses. However, when Amoco personnel attempted to identify the spectrum from the GC/MS, for the chemical identification, they could not get a 3-chloro-3-methyl pentane match for this sample, regardless of which library search mode we used. The analysis was repeated using a more diluted sample. While the spectrum improved dramatically, we still could not find a 3-chloro-3-methyl pentane match from the National Institute of Standards and Technology (NIST) library for the sample. The chromatograms of the sample, both from the FID and MS, suggested that there are significant amounts of impurities, at high concentrations, in this sample.

A simple distillation was used to remove the impurities from the 3-chloro-3-methyl pentane chemical provided by Wiley Organics. The distillate from the distillation was colorless while the residue was dark brown. The purity of the 3-chloro-3-methyl pentane from Wiley Organics was enhanced significantly by this simple distillation. The data suggest that while most of the high boiling impurities were removed from the original sample, the resulting distillate is still only about 88 % pure because of the low boiling impurities that were not removed by the distillation. The mass spectrum of the purified 3-chloro-3-methyl pentane was identified by a match from the NIST libraries of spectra. However, the match was very low. A new sample of 3-chloro-3-methyl pentane was obtained from Aldrich chemical. This new 3-chloro-3-methyl pentane sample was prepared and analyzed in the same way as the sample from Wiley Organics. Analysis of the neat sample suggested that 3-chloro-3-methyl pentane from Aldrich has a higher purity (97.3%) than that of the one from Wiley Organics (88.0%). Based on the data reported here, a decision was made to discard the 3-chloro-3-methyl pentane from Wiley Organics and to use the Aldrich product for the continuation of the work.

## GOALS, OBJECTIVES AND TASKS

The overall goal of the 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. Goals are:

- remove essentially all the ash-forming minerals from coal by two methods, 1) the ChemCoal [1] process and 2) dissolution of minerals with acids and lithium aluminum hydride ( $\text{LiAlH}_4$ )
- produce low-ash char through mild gasification of low-ash coal
- make higher value derivatives of the ultra low-ash char, including activated carbons and oxidized/activated carbon (OAC) having catalytic properties
- evaluate the fuel value of intermediates on the pathway to OAC, especially of ultra low-ash coal as a diesel fuel and of mild gasification tar for hydrocarbon liquids for fuel or chemicals
- provide an estimate of increased yields and energy balances of liquid phase materials produced when a ChemCoal step precedes mild gasification and compare this with results on the same coal by hydrolysis under conditions found in tests at Sandia National Laboratories to be effective with Illinois Herrin coal.

The tasks, the organization involved and their objectives are:

### Task 1 Production of low ash coal

Task 1a Low ash ChemCoal solids - UNDEERC/ARDL UNDEERC produced as much crude reactor product as funds permitted with matching funds from the last year's contract (12 gallons of slurry and 2 gallons of mineral matter-rich bottoms) and workup of the reaction product by ARDL provides CC-solids for tests and feed to mild gasification.

Task 1b Low ash coal control - ISGS - A second low-ash coal for use as a control will be that produced by dissolution of coal's mineral matter with acids ( $\text{HF}$ ,  $\text{HCl}$ ) and, if needed, lithium aluminum hydride for pyrite reduction. 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/NIPER - 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 by methods described in previous contracts.

Task 2b Low ash chars - ISGS - Some low ash char will be produced by the mild gasification run to collect tar. Additional char will be made without tar recovery to provide the bulk of the low-ash char used for subsequent tests.

Task 3 Fuel assessments in a diesel engine - UIUC - Feeding the solid fuel to the a diesel engine is a carry-forward objective of previous work. A small two cylinder Lister Petter diesel research engine was set up in the Automotive Systems Laboratory at the Department of Mechanical and Industrial Engineering of the University of Illinois. Reasonably stable slurries are needed. Initial efforts are directed toward identifying chemical additives that will solve this problem as demonstrated in an injection test rig which allows testing of the slurry fuel before using it in the diesel engine. 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.

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. Catalysis properties are gained by subsequent oxidation at a lower temperature.

Task 4a Preparation of chars - ISGS - 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<sub>2</sub>-BET surface areas of 500 m<sup>2</sup>/g-600 m<sup>2</sup>/g. Following activation, the chars are oxidized in a fluidized bed reactor to produce catalysts. The planned work will attempt to further quantify the effects of oxygen content vs. catalytic activity. OAC from this task supplies Amoco Research Center and the Civil Engineering Department 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 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. This task is a fundamental study exploring the selective adsorption of organic compounds from competitive media.

Task 5 Catalytic Hydropyrolysis and Liquefaction - Sandia - This work will be carried out by Dr. Klavetter. Dr. Klavetter proposes to perform noncatalytic and catalytic fixed-bed hydrolysis tests on the IBC-109 coal 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 hydrolysis and comparison of the resulting liquids with liquids 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 both physical and chemical coal cleaning, 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 path to making the desired 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 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. AOC is used 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 much 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. There may be an economy of scale for producing an ultra low-ash coal. If it exists, it will 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 catalysts [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 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.

We wish to determine the commercial potential for using oxidized char in two steps to convert undesirable compounds into readily manageable compounds. In the first step, undesirable organic compounds like those found in ground water, drinking water, or industrial waste streams would be adsorbed. In the second step, adsorbed material would be decomposed by elevating the temperature to the range where the oxidized carbon catalyzes elimination or oxidation reactions.

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 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]. Puri found that when placed in a benzene-methanol mixture, charcoals could be made selective for either benzene or methanol adsorption [4]. 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 a large autoclave at University of North Dakota Energy and Environmental Research Center (UNDEERC) totaling 12 gallons of slurry and 2 gallons of mineral matter-rich bottoms was 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, an injection test rig for testing pumping and atomization characteristics of the fuel slurries has been assembled. The rig is made with components identical to those used in the engine, i.e. injection pump, fuel line, and fuel injector. The rig permits the operator to make necessary adjustments to the mechanical components and to the fuel.

Plugging of the rig indicates that the fuel is 'unstable'. Shearing of the fuel causes coal to separate, and so the additives concentration, surfactant and stabilizer, are changed. The rig allows the recovery of the fuel, and also the use of regular, and high speed photography for the study of the spray.

The source and type of chemical additives used are:

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 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 will be designated AR000 from this point forward. A portion of the AR000 was 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 [15]. Results of proximate and ultimate analyses may be found in Table 1. The surface area of AR000 was measured using adsorption of N<sub>2</sub> 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. Micropore and mesopore volumes of the carbon were also determined. This data is tabulated in Table 1.

A representative fraction of the AR000 was separated and stored for future characterization. The remaining AR000 was placed in an acid washing column and washed with 10 bed volumes of 1.0 M hydrochloric acid followed by 10 bed volumes

Table 1. Characterization of AR000

Proximate Analysis (moisture-free basis)		Ultimate Analysis (moisture-free basis)		Surface Area and Pore Volumes	
Moisture	1.1	Hydrogen	.25	BET Surface Area*	1035 m <sup>2</sup> /g
Volatile Matter	5.4	Carbon	91.80	Micropore Volume*	.421 cc/g
Fixed Carbon	88.3	Nitrogen	.72	Mesopore Volume*	.231 cc/g
H-T Ash	6.2	Oxygen	.40		
		Sulfur	.59		

\*- Indicates values are on a dry-ash free basis.

of 1.0 M nitric acid. The carbon was then rinsed with 20 bed volumes of deionized water followed by 5 bed volumes of a carbonate solution buffered at pH=6. The carbon was then rinsed with 5 bed volumes of distilled-deionized water. The acid-leached AR000 will be designated as AW100. AW100 has been submitted for proximate and ultimate analyses and its surface area will be determined by N<sub>2</sub> adsorption.

Adsorption capabilities of granular activated carbon in distilled-deionized water - An adsorption isotherm of para-nitrophenol (PNP) on AR000 was obtained. The following procedures were used in obtaining the adsorption isotherm.

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, 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.

The adsorption curve is given in Figure 1.

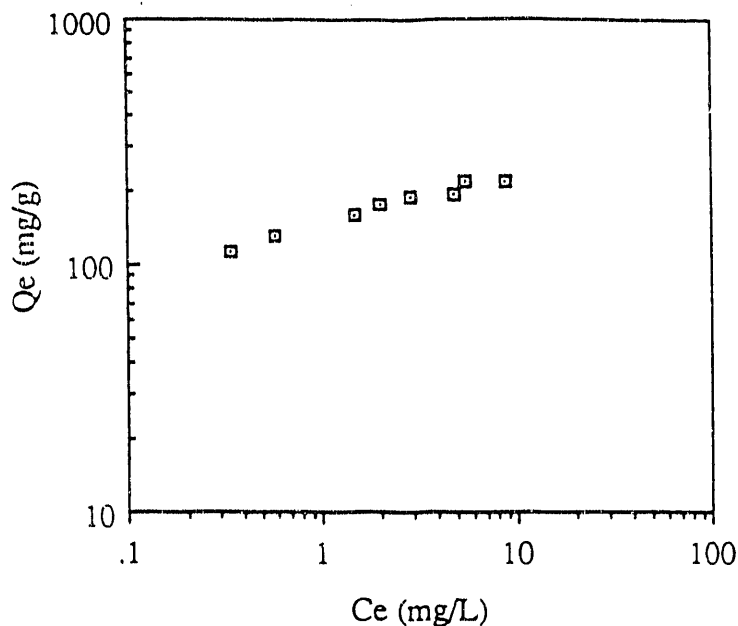


Figure 1. PNP adsorption on AR000

#### Baseline chloride for catalyst activity determination

A Varian Saturn GC/MS instrument equipped with FID (flame ionization) detector was used for the analysis of 3-chloro-3-methyl pentane. A modified dual detector combination system was used to obtain as much information about the chemical as possible. In this system, two identical DB-5 columns (30m long with 0.25 mm ID and 0.25  $\mu\text{m}$  film thickness) were connected to a single injector using a vitreous silica inlet splitter (VSIS). The use of VSIS allow a simultaneous two detector (FID and MS) analyses of the effluent from a single sample injection. The sample was diluted by adding two drops of 3-chloro-3-methyl pentane into 10 ml of dichloromethane. An aliquot of 1.0  $\mu\text{l}$  of this solution was injected into the columns using the split mode. The GC column was programmed to reach 330  $^{\circ}\text{C}$  from an initial temperature of 40 $^{\circ}\text{C}$  with a heating rate of 4 $^{\circ}\text{C}/\text{min}$ . The injector and detector temperatures were both set at 300 $^{\circ}\text{C}$  and the transfer line temperature was set at 280  $^{\circ}\text{C}$ .

### RESULTS AND DISCUSSION

#### Low ash ChemCoal solids

Based on experience in Champaign of duplicating the procedure for precipitation and recovery of CC-solids developed at UNDEERC, we did not expect our subcontractor, ARDL, to have difficulty isolating the product from the twelve gallons provided. ARDL reported in January 1992:

"Significant problems have been encountered in our efforts to process this material following the procedure given us to us by your office....After precipitation of product from the decanted supernatant with methanol, the solids were separated by vacuum filtration. This operation was extremely slow and tedious. Filtration rates on the initial precipitate were in the order of 100 ml/hr. Slight increases in filtration rate were observed as washing progressed by the material was never truly filterable".

The first two samples of CC-solids supplied by ARDL to the PI contained significant m-cresol and their ash analyses were above 0.6% on a m-cresol-free basis. There was a possibility that reactions of the crude reactor product with the tin-coated cans in which it had been stored for several months had resulted in a chelated metal form which escaped the centrifugation. This was ruled out when an elemental analysis of the ash disclosed no increase in tin. ARDL corrected a problems with its vacuum dryer but the high ash persisted.

A 1-quart sample of the untreated crude product was returned to Champaign for study. It was worked up in three portions. We confirmed that the procedure supplied by the PI to ARDL produced product with more than 0.6% ash. After consultation with UNDEERC personnel, we confirmed that the initial viscosity of the crude reactor product could be reduced significantly by adding 9% by weight of methanol. Despite this improvement in viscosity and the attendant improvement in ease of handling, the ash in the product remained high. We obtained 137 grams of CC-solids having no more than 5% m-cresol from the 1-quart. This extrapolates to about one pound of CC-solids per gallon. We expect to renegotiate workup of the remainder of the material by ARDL by procedure which avoids filtration. Figure 2 shows the TGA (pyrolysis) curves for the three tests and a reference curve on the composite produced during a previous contract.

#### **Fuel assessments in a diesel engine**

The injection test rig is now operational. The rig allows testing of the slurry fuel before using it in the engine, photographic study of the spray. A FASTAX 16 mm, high-speed, motion camera will be used to take motion pictures of the spray at approximately 1000 frames/second.

To assist in the set-up of the experiment, pictures of the diesel spray were taken with a regular camera at a shutter speed of 1/2000 sec and various aperture openings. The shutter speed was selected to correspond to the shutter speed of the FASTAX camera when shooting at 1000 frames/sec. Although these preliminary pictures show less detail than the ones to be taken with the FASTAX camera (since the motion camera uses a macro lens), they indicate how the lighting and the camera must be set up for the best possible results.

Subsequently, a quantity of 300 grams of slurry fuel, 10% coal and 0.5% Forestall surfactant made by ICI America and CW-01 (stabilizer made by Henkol, was pumped through the test rig. Even though the slurry passed through the system, it plugged the injector. This was realized only after the injector was removed and dismantled. The needle of the injector was stuck in the tip and could not be removed.

Another attempt was made with a different nozzle, and reduced injector crack pressure, 2500 psi instead of 3000 psi. The injector became plugged very soon, thus causing a significant changed in the spray pattern. Fuel was emerging from the orifices in almost straight streams with poor atomization. Insufficient fuel atomization in a diesel engine causes poor performance and excessive smoke production. It was concluded that a reformulation of the coal slurry and further adjustment of the injector opening pressure will be necessary to improve the injection characteristics before engine tests are conducted.

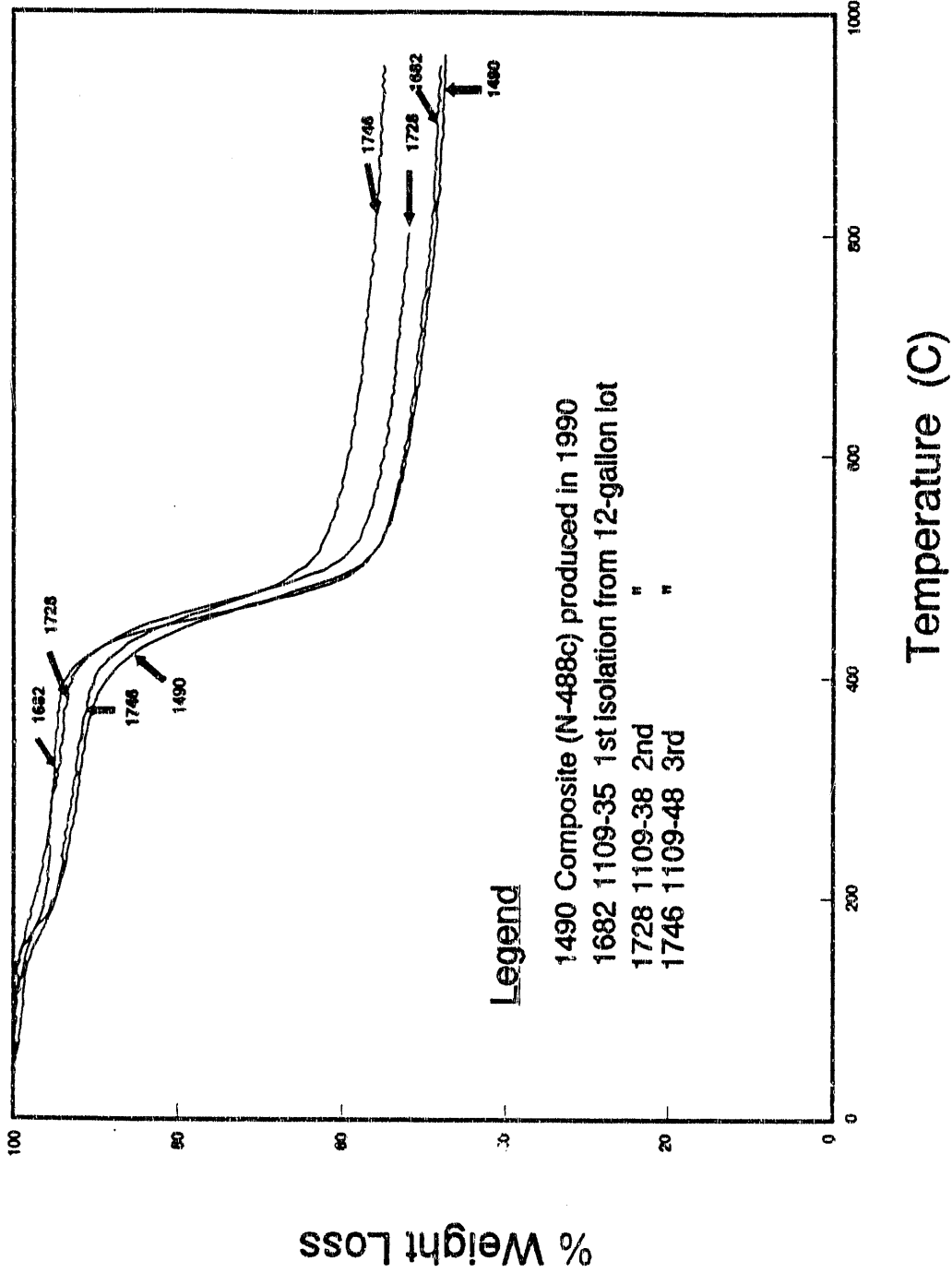


Figure 2. TGA (Pyrolysis) of CC-Solids

## 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. Examination of Table 1 reveals that the volatile matter of AR000 is quite low, 5.4%. This is expected since the activation of most commercial carbons takes place at temperatures between 850°C and 1000°C in steam saturated atmospheres. In addition, the ash content of 6.2% is in good agreement with ash values obtained by other investigators examining this carbon [16]. The high surface area of AR000 indicates it is a carbon which has undergone extensive activation. The micropore volume of the carbon is nearly twice as great as its mesopore volume. This is expected, since micropores are the major contributor to the surface area of a carbon.

AR000 was acid leached in an attempt to remove mineral impurities which may interfere with future work. AR000 was first washed with 10 bed volumes of hydrochloric acid which removes a variety of impurities. This was followed by 10 bed volumes of nitric acid. This was done for two reasons. First, although it has been found that HCl removes some pyritic iron, HNO<sub>3</sub> is much more effective at the removal of pyrite [17]. Second, since future oxidation tests will include treatments with HNO<sub>3</sub> and exposure to oxygen at low to moderate temperatures, it was deemed appropriate to remove HNO<sub>3</sub> solubles from the precursor carbon. If the pre-oxidized carbon was not washed with nitric acid, the oxygen oxidized carbon would still contain HNO<sub>3</sub> solubles while the nitric acid oxidized carbon would not. Therefore, washing with nitric acid prior to oxidation procedures will eliminate the extraneous parameter of HNO<sub>3</sub> solubles when evaluating the effects of varying methods of oxidation. The proximate and ultimate analyses of AW100, as well as its BET surface area will be compared to AR000 to examine the effects of acid-washing.

Adsorption capabilities of granular activated carbon in distilled-deionized water - The adsorption capacity of a carbon is frequently represented by the Freundlich equation:

$$q_e = KC_e^{1/n}$$

where  $q_e$  is the solid-phase concentration at equilibrium (mg/g),  $C_e$  is the liquid-phase concentration at equilibrium (mg/L), and  $K$  and  $1/n$  are the Freundlich constants ( $[\text{mg/g}][\text{L/mg}]^{1/n}$  and dimensionless, respectively). The liquid-phase concentration is determined analytically often by batch experiments and the solid-phase concentration is determined by a mass balance:

$$q_e = (C_o - C_e)(V/m)$$

where  $V$  is the total volume of the solution in the batch test (L),  $m$  is the mass of the carbon used (g), and  $C_o$  is the initial concentration of the compound being studied (mg/L). The PNP adsorption isotherm (see Figure 1) yielded:

$$q_e = 146C_e^{.211}$$

PNP adsorption tests will be conducted on carbons with varying surface characteristics to examine the effect of a carbon's surface chemistry on the adsorption of PNP.

## Baseline chloride for catalyst activity determination

Amoco personnel analyzed 3-chloro-3-methyl pentane from Wiley Organics by gas chromatograph/mass spectrometer (GC/MS) to establish a baseline for the dehydrochlorination work using activated-oxidized char from mild gasification. Two 500.0 gram bottles of this chemical were provided to Amoco by the Illinois Geologic Survey (IGS).

The color of the chemical Amoco received from ISGS as 3-chloro-3-methyl pentane also suggested impurities. The MSDS information on this compound describes 3-chloro-3-methyl pentane as a colorless chemical. The chemical provided by Wiley Organics as 3-chloro-3-methyl pentane, however, was brownish in color.

Portions of 3-chloro-3-methyl pentane from both Aldrich and Wiley Organics were sent for  $^1\text{H}$  and  $^{13}\text{NMR}$  analyses. The NMR data also indicated the 3-chloro-3-methyl pentane from Aldrich has a higher purity (99+% by NMR). However, the purity of 3-chloro-3-methyl pentane from Wiley Organics analysis showed to be only 95+%. Several different isomer impurities could be seen in the Wiley's 3-chloro-3-methyl pentane sample which could not be unequivocally identified and quantified without further separation work. Based on the data reported here the decision was made to discard the 3-chloro-3-methyl pentane from Wiley Organics and to use the Aldrich product for the continuation of our work.

### CONCLUSIONS AND FUTURE WORK

- The remaining pound quantities of ChemCoal solids which will supplement the small amount of material carried forward from the previous project should be available in early April from our subcontractor, ARDL.
- A final additive package for a slurry to be fed to the diesel engine has not been selected. Initial tests in the slurry test rig indicate additional testing is needed.
- The control activated carbon for adsorption studies (AR000) was characterized by proximate and ultimate analyses, and BET surface area, micropore volume, and mesopore volume were determined.
- AR000 was acid washed with hydrochloric and nitric acid. This sample, designated AW100, is currently being characterized.
- Future work will focus on further characterization of AR000 and AW100 so that they may be compared to activated chars manufactured from Illinois bituminous coals. In addition, the effects of the carbon's surface chemistry on adsorptive capacity will be examined. Carbons 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. A subcontract can now replace the letter of intent sent by the University of Illinois and a pure 3-chloro-3-methyl pentane is available for testing catalyst activity.

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## PROJECT MANAGEMENT REPORT

December 1, 1991, through February 29, 1992

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

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C. Feizoulof	U of I	C. L. Knudson	UNDEERC
D. N. Assanis	U of I	S. M. Fatemi	Amoco

Other Participants

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

Project Monitor: Franklin I. Honea CRSC

### COMMENTS

The hiring of a technical person to work on this contract at the ISGS was delayed until February 1992. We employed a subcontractor for the initial work (the isolation of ChemCoal solids from crude product produced at the University of North Dakota Energy and Environmental Research Center). Amoco received its subcontract from the University of Illinois in late February 1992. The delay in Amoco's subcontract accounts for the expenditures being about \$12,000 below those projected through February 1992.

EXPENDITURES - EXHIBIT B  
 INTEGRATED PRODUCTION/USE OF  
 ULTRA LOW-ASH COAL, PREMIUM LIQUIDS AND CLEAN CHAR

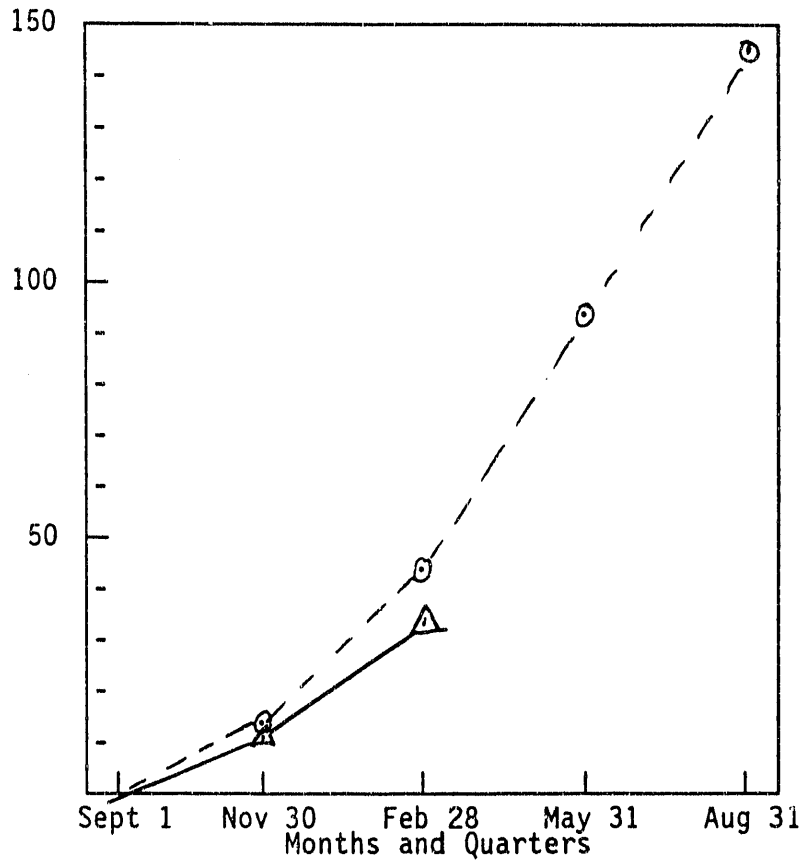
Projected and Estimated Actual Expenditures by Quarter

Quarter	Types of Cost	Direct Labor	Material's and Supp's	Travel	Major Equip	Other Direct Costs	Indir't Costs	Total
Sept 1, 1991 to Nov. 30, 1991	Projected	3,000	1,625	500	0	10,000	1,512	16,637
	Actual	2,820	1,515	738		5,500	1,057	11,622
Sept 1, 1991 to Feb. 28, 1992	Projected	15,500	3,250	750	0	23,000	4,250	46,750
	Actual	19,918	3,500	480	0	5,600	2,950	32,448
Sept 1, 1991 to May 31, 1992	Projected	38,750	4,875	1,100	0	42,500	8,722	95,947
	Actual							
Sept 1, 1991 to Aug 31, 1992	Projected	65,293	6,500	1,100	0	62,524	13,542	148,959
	Actual							

\*Cumulative by quarter

COSTS BY QUARTER - EXHIBIT C

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



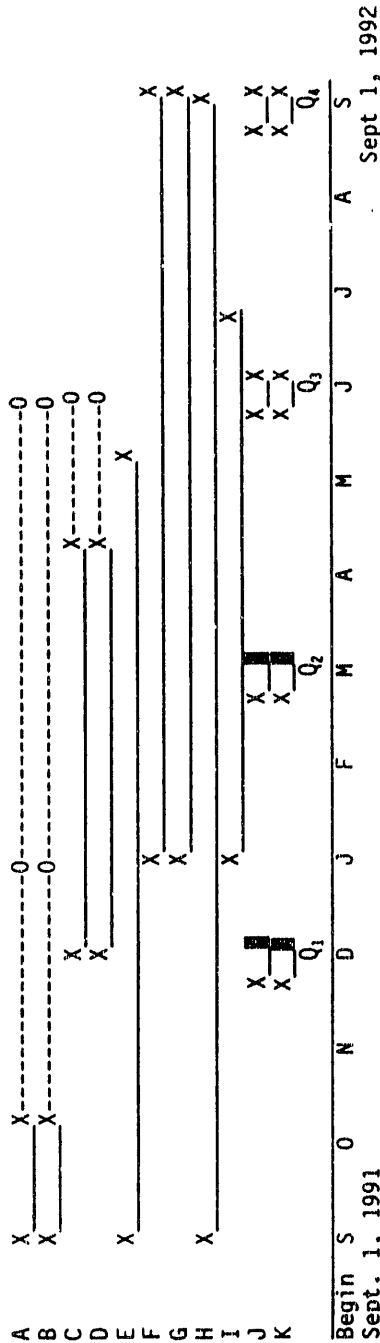
O = Projected Expenditures - - - - -

Δ = Actual Expenditures \_\_\_\_\_

Total CRSC Award \$ 148,959

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
- 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/Feizoulof
- Task 5 Catalytic Hydrolysis and Liquefaction
- Technical reports
- Financial reports

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**END**

**DATE  
FILMED  
9/01/92**

