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TECHNICAL REPORT

December 1 through February 28, 1993

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

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ABSTRACT

The objective of this research is to invert the conventional scale of values normally assigned to products of coal utilization processes and make special coal chars (carbons) that, because of their special properties, can be among the most marketable materials in the product slate.

Reconstruction of a continuous feed charring oven of the type used at the ISGS in 1979 was completed and its operation has been tested on an Illinois No. 6 coal. Pounds of per hour can be processed with this device and it accepts coal of all particle sizes. Effects on char properties related to the depth of the bed charred can be studied in this oven.

Attempts are continuing to develop and prove procedures for comparing the catalyst activity of oxidized activated carbons. In the new studies, dehydrochlorination reactions were carried out in the gas phase and they were applied to alkyl chlorides less reactive than the tertiary chlorides used previously.

Adsorption studies show the capacity of carbons made in this study, as measured by the Freundlich equation, have significantly less capacity than that of AR000, a commercially available activated carbon manufactured from bituminous coal.

The series of samples having differing ratios of CO and CO₂ surface groups has been prepared and submitted to Amoco Research Center for characterization by x-ray photoelectron spectroscopy (XPS). Data obtained from TPD experiments will be analyzed in conjunction with results obtained from x-ray photoelectron spectroscopy to determine which specific surface functional groups may be responsible for enhanced PNP adsorption.

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EXECUTIVE SUMMARY

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

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

Evaluation of the fuel value of intermediates and products on the production pathway to char was an initial goal of this project. This goal was abbreviated and the part that was accomplished, i.e. testing the combustion characteristics of the ultra low-ash coal in a diesel engine located in the University of Illinois automotive testing facilities, was terminated at the end of year one (August 1992) due to budget restrictions. Because the modified ChemCoal™ process produces a clean coal-like solid with significantly higher volatile matter than the feed coal, a goal was to have been the determination of how this increase affects the properties of mild gasification liquids produced during the production of ultra low-ash char. This goal was dropped for budget considerations but a portion of the task planned at Sandia National Laboratory remains. IBC-109 coal, and the two low-ash samples produced from it, will be subjected at Sandia National Laboratories. The conditions will be those found in tests at Sandia National Laboratories to be effective with Illinois Herrin coal. The goal is to provide additional comparisons of yields and energy balances.

Major program elements this year are a) preparation and characterization of materials at the ISGS, b) further characterization of carbons and catalyst testing by the Amoco Research Center and c) completion of a two-year adsorption study.

Installation of a continuous feed charring oven at the ISGS has been completed. Its advantages include not only decreased time required to char fine coal but an ability to char any particle size with equal facility. The study of effects of bed depth on subsequent carbon properties is possible in this unit. Shakedown tests using Herrin seam (Illinois No. 6) coal from Peabody's Randolph cleaning plant in Marissa, Illinois have been made. This -60 mesh coal simulates the fine demineralized coal to be used in this project. The three adjustable parameters that control the char's quality are bed depth, residence time, and temperature.

Materials prepared previously by the ISGS with outside assistance are a) two low-ash coal samples, one via ChemCoal processing of IBC-109 and the other by dissolution of IBC-109's mineral matter with acids, b) ChemCoal char (CC), c) activated ChemCoal carbon (ACC), d) oxidized activated ChemCoal carbon. Characterization of these samples included, Proximate and Ultimate Analysis, Inductive Coupled Plasma (ICP) Analysis, X-Ray Diffraction (XRD), Nitrogen (BET) Surface Area and Surface Composition and Binding Energies from XPS analysis.

Catalyst activity for dehydrochlorination - There are ambiguities in results from catalyst activity comparisons. The activities of catalyst samples appear in different orders depending on the experimental procedure. A number of problems are recognized. They include the selection of an alkyl chloride of the right reactivity for determining differences in catalyst activity. Impurities in some alkyl chloride samples compete with the oxidized activated char as a dehydrochlorination catalyst. Material balances are time-consuming. If there were no side reactions, one should be able to determine the extent of reaction by measuring the absolute concentration of either the alkyl chloride or one of its products, the olefin or HCl. The fact that olefins may dimerize or even trimerize in the presence of HCl, or one olefin molecule may be alkylated by the alkyl chloride molecule if an appreciable olefin concentration exists in liquid phase alkyl chlorides is an additional concern. Measuring the HCl production follows the disappearance of alkyl chloride but a given alkyl chloride may also be disappearing by conversion to higher molecular weight chlorides without HCl production. Furthermore, HCl production need not track with olefin production because of the side reactions of the olefins. The principal investigator is reluctant at this time to draw any conclusions from comparative tests made with tertiary alkyl chlorides at 250°C and above. Experienced workers in the field have suggested the use of more stable chlorides, such as 1,2-dichloroethane, that have a significant temperature difference between catalyzed and uncatalyzed dehydrochlorination.

Adsorption studies - The existence of oxygen-containing functional groups on the surface of carbon is well documented. Their presence is indicated by the evolution of CO_2 and CO upon heating the carbons. In order to determine whether a relationship between the presence of oxygen groups and p-nitrophenol (PNP) capacity exists, a series of carbons with various amounts of surface oxygen were prepared and described in the previous quarterly report. One of these samples was HN100, an HNO_3 -oxidized sample of Calgon F-400 commercial activated carbon that had been previously been degassed at 950°C for 30 minutes in a stream of ultra-high-purity nitrogen. Temperature-programmed desorption (TPD) confirmed that HN100 has significant amounts of surface oxygen groups which evolve as CO and CO_2 upon heat treatment in an inert atmosphere.

Determination of surface areas using nitrogen adsorption at 77K and application of the BET equation revealed that the surface areas of all four DS series samples were approximately 950 to 980 m^2/g on a moisture-free basis. This is comparable to the other samples prepared from AR000 and provides evidence that outgassing of HN100 to the temperatures shown did not cause significant changes in the physical characteristics.

Temperature-programmed desorption (TPD) is an effective means for qualitatively and quantitatively analysis of surface oxygen groups present on carbon. Four samples, DS405, DS525, DS725 and DS950, have now been prepared by outgassing HN100 in a flow of ultra high purity nitrogen at 405°C , 525°C , 725°C and 950°C , respectively. The outgassing temperatures of the DS samples were selected in order to give different CO_2/CO ratios as obtained by temperature-programmed desorption. All four samples have been submitted to Amoco for characterization by the methods previously used. The four samples in the DS series were degassed at different temperatures to determine whether a relationship between CO/CO_2 ratios and PNP adsorption exists. Data obtained from TPD experiments will be analyzed in conjunction with results obtained from x-ray photoelectron spectroscopy to determine which specific surface functional groups may be responsible for enhanced PNP adsorption.

Adsorption capacity of carbon adsorbents in distilled-deionized water - The adsorption capacity of a carbon is frequently described by the Freundlich equation. The application of this equation showed that the PNP capacity of ACC and OACC is significantly less than that of AR000, a commercially available activated carbon manufactured from bituminous coal. At an equilibrium concentration of 1 mg/l ($C_e=1$) the PNP capacities of ACC and OACC are less than half that of AR000.

OBJECTIVES

The principal objective of this project is to attain high-value, coal-derived products from Illinois coal, especially varieties of char. Step one of this Integrated Production/Use progression is to obtain ultra low-ash coal for the producing premium coal tar and low-ash char by mild gasification (MG). Ash-forming minerals are removed from coal by 1) the ChemCoal™ process [1] and 2) dissolution of the minerals with acids. The MG of step two produces low-ash char and coal tar. Increasing the value of the ultra low-ash char by converting it into an activated carbon (AC) is the goal of step three. Some ACs are marketed today for hundreds of dollars per ton. Additional value can be imparted by a fourth step, an oxidation step turning AC into a catalyst identified herein as oxidized activated carbon (OAC). Procedures for characterizing these materials were developed in the preceding project. Extending the fundamental knowledge by comparing the properties of carbons as a function of mineral matter content is a goal.

Work on evaluation of the fuel value of intermediates and byproducts on the production pathway to OAC, an initial project goal, was curtailed to meet funding limits. The testing of combustion characteristics of the ultra low-ash coal in a diesel engine was suspended at the end of year (August 1992). Because the modified ChemCoal™ process produces a clean coal-like solid with significantly higher volatile matter than the feed coal, a determination of how this increase affects the properties of mild gasification liquids produced during the production of ultra low-ash char was an initial goal. Budget considerations prevented work on the MG liquids but a portion of the task planned at Sandia National Laboratory remains. IBC-109 coal, and the two low-ash samples produced from it, will be subjected to hydropyrolysis at Sandia National Laboratories.

Three multi-year Task 4 subtasks were carried forward from year one.

Task 4a Preparation of chars and preliminary characterization at the ISGS.

- 4a.1 Determination of CO and CO₂ desorption as a function of temperature.
- 4a.2 Iterative char preparation based on findings of 4a.1 coupled with catalyst activity testing in 4b.2.
- 4a.3 Preliminary cost estimates for producing char catalysts.

Task 4b Characterization and applied uses at Amoco (the full report for this subcontract appears in Appendix A).

- 4b.1 Spectroscopic studies.

4b.2 Adsorption & elimination reaction testing.

4b.3 Iterative spectroscopic studies.

4b.4 Iterative applied tests as needed.

Task 4c Adsorption studies at UI-UC (the uncut report of this work appears in Appendix B).

4c.4 Adsorption capabilities of acid/basic carbon using trichlorophenol and trichloroethylene.

4c.5 Evaluation of acidic/basic surfaces in adsorption.

4c.6 Effect of different functionalities on adsorption capacity.

4c.7 Paper for ACS presentation and publication.

Task 5a Catalytic hydrolysis - Sandia

INTRODUCTION AND BACKGROUND

Marketing of one product is acknowledged to be less complicated than finding markets for a set of products having interrelated properties and yields. Nevertheless, there are examples of successful multiproduct strategies for utilization of natural resources, petroleum refining for example. Because coal and petroleum have so much in common, a multi-product approach to coal utilization may also prove attractive.

This project provides portions of knowledge needed to evaluate the technical potential of coal-derived products, especially ultra clean coal and chars made from it. The INTEGRATED PRODUCTION/USE approach to coal utilization produces a low-ash coal, a mineral rich coal fraction, and coal-derived liquids via mild gasification on the way to OAC. The marketability of the char is the principal factor for economic viability. To have a reasonable impact on the economy of the State of Illinois and other coal producing states, any market considered for char should be large and have a price greater than that of fuel for utility boilers. Uses of activated carbon for water purification and adsorbing components from nonaqueous solutions or suspensions have not only the desired large potential volume for adsorbents made from coal but also the potential price, more than \$1000/ton.

An important projected advantage of OAC is the capacity to catalyze chemical decomposition of the toxic organic compounds. OAC may also catalyze desirable reactions of coal-derived liquids. The adsorption capacity of carbon made from coal containing substantial mineral matter (relatively high ash) is expected to be lower than values obtained for commercial activated carbon. The trade-offs both technically and economically in achieving a balance between ash content and adsorptive capacity, between catalytic properties and

adsorptive properties and between cost of treatment steps and improvement of properties must be evaluated. When the technical benefits are known for taking practically all of the mineral matter out of coal before further processing, it should be possible to assign a monetary value to this upgrade. An economy of scale, if it exists, for producing an ultra low-ash coal 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 for this project is an inventor of record on three United States patents on oxidized carbonaceous materials as catalysts [2]. Exploiting the properties of OAC oxidized/activated carbon, an objective of previous collaborative work with Amoco personnel [3], is carried forward into this project. More than 300 chlorinated organic compounds have been identified in chlorinated potable waters, cooling waters, and sanitary effluents. Systems are needed that will remove and destroy toxic organic compounds that are introduced into drinking water during purification by chlorination. Additionally, chemical processes often produce aqueous solutions of environmentally objectionable compounds in aqueous solutions. Filtration through activated carbon is the conventional technology for ridding water of objectionable organics. One objective of this project is to assess the technical potential for using oxidized char not only to adsorb undesired organic compounds from ground water, drinking water, or industrial waste streams, but to also decompose the adsorbed material.

The objective of an adsorption studies segment of the project is to evaluate the effects of an activated carbon's surface chemistry on aqueous adsorptive properties. Papirer and co-workers [4] state that the existence of surface groups on carbons largely determines their specific interaction capacity. Capacity is a property which besides texture, is of great importance for the use of active carbons.

EXPERIMENTAL PROCEDURES

Thin bed, continuous feed, charring oven (Figure 1) - The frame, mechanical parts, the oven and sheet metal enclosures for the continuous feed charring were constructed by Swanson Machine Company, Champaign. Modifications were made by ISGS personnel after its delivery. The heated zone was insulated from the sheet metal housing by a fire brick partition, gas ports were added to the housing to provide a nitrogen purge of the cooler portions of the oven's housing during operation, and two travelling thermocouples were installed. The thermocouples are in 3/16" OD stainless steel tubing (side by side) centered above the conveyor and running the oven's length at approximately 1" above the floor of the conveyor.

One thermocouple is used to monitor the temperature along the length of the reactor and the other, positioned at the hottest point in the reactor, sends its output to the temperature controller. This oven is very similar to one built by the principal investigator in 1979 at the ISGS. Pyrolysis data from that oven that resulted in an ISGS patent [5].

The oven will be used to make chars at temperatures of up to 700°C with variable bed depths and residence times. The desired temperature is maintained by a programmable temperature controller on electric tubular heating rods above and below the conveyor belt. The feeder has a slide that regulates the depth of the material fed to the conveyor and the speed of the motor driving the conveyor is adjustable to achieve the desired residence times in the heated zone. The nitrogen flows counter to the direction the conveyor belt moves. As the material passes through a heating zone of successively higher temperatures the inert gas removes volatile pyrolysis products to a lower temperature zone insuring that the pyrolysis products do not condense on char that has reached a higher temperature.

Shakedown tests in the new oven have used Herrin seam (Illinois No. 6) coal from Peabody's Randolph cleaning plant in Marissa, Illinois. This -60 mesh coal simulates the fine demineralized coal to be used in this project. The three adjustable parameters that control the char's quality are bed depth, residence time, and temperature.

Low Ash Coal - An 0.95% ash coal was produced from relatively coarse IBC-109 in a small pilot at SIU using hydrochloric acid and hydrofluoric acid to dissolve the ash-forming minerals. A lower value was expected using micronized IBC-109. The ash content of a 2 kg lot was 1.42% (mf), almost twice that expected. Low temperature ashing showed that all the acid soluble minerals had been removed. The concentration of pyrite (not soluble in the acids) was more than we have found in a dozen analyses of IBC-109. Contamination by grinding in a large fluid energy mill that is not easily cleaned of material previously ground is suspected.

Two size fractions of IBC-109, 10x30 and -30 mesh, prepared by sieving IBC-109 are shown in Table 1. The ash value and the pyrite value are lower in the 10x30 mesh size fraction. Four kg of the 10x30 mesh material was selected for a second attempt to get the ash below 1% by the hydrochloric acid and hydrofluoric acid treatment. Dr Crelling delivered 2.9 kg of the demineralized IBC-109 to the Illinois State Geological Survey. The ash value was 1.36% for this second lot (2.9 kg) of demineralized coal. The sample has been submitted for low temperature ashing to confirm that acid soluble ash remains.

Table 1. Proximate analysis of screened fractions of IBC-109

	As received	10x30mesh	-30 mesh
Volatile Matter	35.2	35.1	34.0
Fixed Carbon	56.5	57.4	56.6
H-T Ash	8.3	7.5	9.4
Sulfur	1.1	1.1	1.1
Forms of Sulfur			
Sulfatic	0.0	0.1	0.2
Pyritic	0.5	0.3	0.5
Organic	0.6	0.7	0.4

Figure 1. Thin-bed, continuous-feed, charring oven

Applied tests at Amoco - catalysis of dehydrochlorination -
Experiments were designed to compare the catalyst activity of oxidized activated char made this contract year from low ash coal with OST3-9 made last year from IBC-109 without ash reduction. Three char samples, produced from low ash IBC-109 coal (ChemCoal solids) were characterized at Amoco last quarter (see previous quarterly report).

- 1) ChemCoal Char (CC) by MB ChemCoal solids. (1173-31-C)
- 2) Activated ChemCoal Carbon (ACC) by CO₂-steam gasification of the previous carbon (CC). (1173-31-B)
- 3) Oxidized Activated ChemCoal Carbon (OACC) - by oxidizing ACC with 10%O₂/90%N₂ at 450°C. (1173-30-B)

Experimental details for this quarter's dehydrochlorination tests appear in APPENDIX A, page A-2 and the summary of data is in Tables I through IV, pages A-5 and A-6.

Adsorption studies - APPENDIX B IS The uncut report of our UI-UC collaborator's work, Task 4c. Please refer to it for experimental details.

RESULTS AND DISCUSSION

Low Ash Coal - Low ash coal was produced from IBC-109 in the first year of this project by two methods: 1) ChemCoal processing at the University of North Dakota Energy and Environmental Research Center (UNDEERC) with workup at the Applied Research and Development Laboratory, Inc. (ARDL) in Mt. Vernon, Illinois, and the ISGS laboratory in Champaign, and 2) dissolution of the ash-forming minerals from micronized IBC-109 with hydrochloric acid and hydrofluoric acid by Dr. Jack Crelling's group at Southern Illinois University (SIU). Despite obtaining 0.95% (mf) for a pilot test on relatively coarse IBC-109, two attempts to produce larger quantities of material with less than 1% ash have failed. The ash values were 1.42% and 1.36%. Contamination with pyrite from a work during milling is suspected in the first attempt. The problem with the second try has not been identified, but we remain hopeful that 0.6-0.8% ash range will be achieved.

Charring in the continuous feed charring oven - The amount of volatile matter left in the char is a reliable indicator of the severity of the treatment. The Peabody coal used for shakedown tests has approximately 35% volatile matter. Charring this coal to a maximum of 600°C with 11 minutes residence time and a 22 mm coal bed depth gave char with 20.5% volatile matter. Charring at a maximum temperature of 600°C, 16 minutes residence time, and a bed depth of 15 mm produced char with 14.0% volatile matter. The entrance temperature in both cases was 450°C. These runs have been repeated to confirm the reproducibility. To decrease the percentage of volatile matter further the maximum temperature and the residence time can be increased, and the bed depth can be decreased.

Most of the coal charring at the ISGS in recent years has in fluidized bed reactors (FBR). FBRs require coarse material of a relatively narrow size distribution. Finely-divided, low ash coals must be pelletized for fluidized bed processing. This has proven to be a very time-consuming operation. Additionally, we observe that pelletization reduces the amount of volatile matter released in TGA tests. This appears to be related to condensation reactions which occur when tar is not withdrawn quickly as it forms. Our previous work showed the bed depth made a difference in the amount of volatile matter removed. We will be able to vary the depth of charring in the

continuous feed oven to approach chars similar to fluidized bed chars, but this machine will doubtless convert some portions of volatile matter driven off in a fluidized bed into char.

Catalyst activity for dehydrochlorination - Please refer to Appendix A for additional details of this work at Amoco not carried forward to the following summary of the results. There are ambiguities in results from catalyst activity comparisons. The activities of catalyst samples appear in different orders depending on the experimental procedure. A number of problems are recognized. First, tertiary alkyl chlorides are too reactive to be the chloride of choice for determining differences in catalyst activity. The temperature at which they are thermally decomposed is too close to that required for the catalyzed reaction. Additionally, impurities in some alkyl chloride samples compete with the oxidized activated char as a dehydrochlorination catalyst. A second problem concerns material balances. If there were no side reactions, one should be able to determine the extent of reaction by measuring the absolute concentration of either the alkyl chloride or one of its products, the olefin or HCl. A material balance is not possible when appreciable unidentified impurities are present in the alkyl chloride. Additionally, the olefins may dimerize or even trimerize in the presence of HCl, or one olefin molecule may be alkylated by the alkyl chloride molecule if an appreciable olefin concentration exists in liquid phase alkyl chlorides. Measuring the HCl production follows the disappearance of alkyl chloride but a given alkyl chloride may also be disappearing by conversion to higher molecular weight chlorides without HCl production. Furthermore, HCl production need not track with olefin production because of the side reactions of the olefins.

It is uncertain whether the differences shown in catalyst activity for the tertiary chloride (3-chloro-3-methyl pentane) by HCl conversion in Table 1 and by analysis for alkyl chloride and olefins are meaningful. The tertiary chlorides are dehydrochlorinated by almost any surface at 250°C and higher. The principal investigator has experienced unexpected changes in the analysis of tertiary alkyl chlorides on gas chromatographic columns which were traced to formation of a catalyst at a specific locations in the heated column. The column was returned to normal by injection of an alkyl amine to deactivate the catalyst site.

There appears to be a difference in activity between OST3-9 and OACC at 250°C for catalyzed dehydrochlorination of 1,2-dichloroethane shown in Table I. Conversions based on HCl evolution were 0.01 and 0.07 for OST3-9 and OACC, respectively. There was no appreciable difference at 450°C (Table III) where conversions were 3.0% and 2.9% for OST3-9 and OACC, respectively. The low conversions at 450°C call

into question whether the space velocity was appropriate for the length of the catalyst column. Additionally, there is evidence that the ACC has appreciable activity without the added oxidation step. The 450°C may be too high for clear observations of differences between catalyzed and uncatalyzed dehydrochlorination for 1,2-dichloroethane. An unambiguous method for measuring catalyst activity has not yet been achieved. The principal investigator is reluctant draw any conclusions from comparative tests made with tertiary alkyl chlorides at 250°C and above. Experienced workers in the field have suggested the use of more stable chlorides, such as 1,2-dichloroethane, that have a significant temperature difference between catalyzed and uncatalyzed dehydrochlorination.

Adsorption studies - The existence of oxygen-containing functional groups on the surface of carbon is well documented. Their presence is indicated by the evolution of CO₂ and CO upon heating the carbons. In order to determine whether a relationship between the presence of oxygen groups and p-nitrophenol (PNP) capacity exists, a series of carbons with various amounts of surface oxygen were prepared and described previously [6]. One of these samples was HN100, an HNO₃-oxidized sample of Calgon F-400 commercial activated carbon that had been previously been degassed at 950°C for 30 minutes in a stream of ultra-high-purity nitrogen. Temperature-programmed desorption (TPD) confirmed that HN100 has significant amounts of surface oxygen groups which evolve as CO and CO₂ upon heat treatment in an inert atmosphere.

Determination of surface areas using nitrogen adsorption at 77K and application of the BET equation revealed that the surface areas of all four DS series samples were approximately 950 to 980 m²/g on a moisture-free basis. This is comparable to the other samples prepared from AR000 and provides evidence that outgassing of HN100 to the temperatures shown did not cause significant changes in the physical characteristics.

Temperature-programmed desorption (TPD) is an effective means for qualitatively and quantitatively analysis of surface oxygen groups present on carbon. Four samples, DS405, DS525, DS725 and DS950, have now been prepared by outgassing HN100 in a flow of ultra high purity nitrogen at 405°C, 525°C, 725°C and 950°C, respectively. The outgassing temperatures of the DS samples were selected in order to give different CO₂/CO ratios as obtained by temperature-programmed desorption. All four samples have been submitted to Amoco for characterization by the methods previously used. The goal is to determine whether a relationship between CO/CO₂ ratios and PNP adsorption exists. Data obtained from TPD experiments will be analyzed in conjunction with results obtained from x-ray photoelectron spectroscopy to determine which specific surface

functional groups may be responsible for enhanced PNP adsorption.

Adsorption capacity of carbon adsorbents in distilled-deionized water - The adsorption capacity of a carbon is frequently described by the Freundlich equation. The application of this equation has been described elsewhere [6].

Examination of Figures 1 and 2 (APPENDIX B, pages B-5 and B-6) show that the PNP capacity of ACC and OACC is significantly less than that of AR000, a commercially available activated carbon manufactured from bituminous coal. At an equilibrium concentration of 1 mg/l ($C_e=1$) the PNP capacities of ACC and OACC are less than half that of AR000.

CONCLUSIONS AND FUTURE WORK

The reconstruction of a continuous feed charring oven of the type used at the ISGS in 1979 has been completed and it has been test on an Illinois coal. This unit will not only facilitate the rate at which we can char fine coal, it will permit us to examine the differences in properties as a function of bed depth.

There are ambiguities in results from catalyst activity comparisons. The activities of catalyst samples appear in different orders depending on the experimental procedure. The ability of oxidized activated char to catalyze chlorinated compounds in dehydrochlorination reactions strongly depends on the reaction conditions as well as the structure of the alkyl chloride. Impurities in the chlorinated compound have a significant effect on the reaction products and total conversion. Char bed temperature and reaction residence time both have a significant effect on the reaction products and total conversion. Between the two oxidized activated chars, OST3-9 and OACC, when tested on 1,1,2,2-tetrachloroethane, the OST3-9 seemed to be the superior catalyst.

PNP adsorption isotherms of two activated char samples, designated ACC and OACC, produced from an ultra-low ash coal product revealed that the PNP capacities of ACC and OACC are significantly lower than that of the F-400 carbons.

A determine whether or not a relationship between surface oxygen groups and PNP adsorption exists will be forthcoming when results for series of samples sent to Amoco Research Center for characterization by x-ray photoelectron spectroscopy (XPS) are available. TPD and XPS results will be interpreted concurrently in order to identify any surface functional groups which may contribute to enhanced PNP adsorption.

ACKNOWLEDGEMENT

Contributions to this work by Massoud Rostam-Abadi and Tony Lizzio at the ISGS and Rudy Lagman at the Amoco are acknowledged. Dr. Rostam-Abadi advised on interpretation of TGA results used to select parameters for activation of coal chars. Dr. Lizzo has furnished equipment for small scale charring, surface area measurements, and pore size measurements, and he has provided guidance for the use of this equipment.

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APPENDIX A Evaluation of ChemCoal™ Char
Mohammad Fatemi and Rudy Lagman (Amoco)

Technical Report
December 1, 1992, through February 28, 1993
Integrated Production/Use of Ultra Low-Ash Coal, Premium
Liquids and Clean Char

EVALUATION OF CHEMCOAL™ CHAR FOR USE IN DEHYDROCHLORINATION REACTIONS

Detailed characterization of the ultra low-ash ChemCoal™ chars (1173-31-C, 1173-31-B 1173-30-B) was reported in our previous quarterly report. The ChemCoal™ process was used to produce the ultra low-ash coal needed for the production of these samples. In the ChemCoal™ process, coal ash is removed by dissolving the coal in a phenolic solvent (meta-cresol) in the presence of sodium hydroxide, carbon monoxide and water. An ultra low-ash coal is then produced after filtration and removal of the meta-cresol solvent. This ultra low-ash coal was then used to produce ultra low-ash ChemCoal™ char (CC) by mild gasification in a fluidized bed reactor (FBR) and Activated ChemCoal Carbon (ACC) was produced from CC by CO₂-steam gasification in an FBR. Oxidized Activated ChemCoal Carbon (OACC) was produced by oxidizing ACC with 10%O₂/90%N₂ at 450°C. In this study, these chars have been evaluated for their possible use as a catalysts in dehydrochlorination reactions.

The data from these evaluations have been compared with the previously reported data for oxidized steam activated char (OST3-9), which was produced in the first year of this project. The OST3-9 sample was produced from the same coal and under similar activation and oxidation conditions as the ultra low-ash chars. The major difference between the OST3-9 char and OACC is the removal of ash by the ChemCoal™ process for the OACC prior to the activation and oxidation steps.

DEHYDROCHLORINATION STUDY

In our earlier work we showed that the addition of oxidized activated chars (OST3-9 and OST10-14) to a chlorinated compound such as 3-chloro-3-methyl pentane at its boiling temperature results in a rapid evolution of HCl and the formation of lower boiling 3-methyl-2-pentene (cis/trans) components. This report contains the data from our continuing effort on the evaluation of the catalytic capability of oxidized activated chars (OST3-9 and OACC) for dehydrochlorination of chlorinated compounds. The compounds used in this work included 3-chloro-3-methyl pentane; 1,2-dichloroethane; and 1,1,2,2-tetrachloroethane. In this study, the extent of dehydrochlorination reactions was measured using two different approaches. One approach was to use a GC/MS to identify and

measure the olefins produced from the reaction and the other approach was to measure the dehydrochlorination efficiencies by measuring the formation of HCl from the reaction.

1. Experimental Procedure

In the previous studies, dehydrochlorination reactions were accomplished by pipetting 5.0 ml of a chlorinated compound into a 25 ml micro evaporator. The sample was then heated to the desired temperature and allowed to reflux for 5 minutes. At this time, 0.5 g oxidized activated char (OST3-9) was added to the refluxing sample and allowed to reflux for an additional 10 minutes. The mixture was finally allowed to cool to room temperature before filtration. In some experiments, only a water cooled condenser was used for refluxing and in others the distillable materials were distilled away from the reaction and collected for analyses.

In the new studies, however, dehydrochlorination reactions were carried out in the gas phase. In these experiments, 50.0 ml of a chlorinated compound was transferred into a micro evaporator. The sample was then heated to evaporate and the vapor was passed over a bed of oxidized activated char, which was held at 250-450 °C temperature, before going through a condenser. A flow of nitrogen was used to push the vapor through the hot bed of char. The collected product was then analyzed for expected olefins using a Varian ion-trap GC/MS. In a few experiments, the product from the condenser was trapped in a 0.1M NaOH solution via a trap adapter with a bubbler. The NaOH solution with the trapped HCl was then back titrated with 0.1 HCl from which the HCl evolved was then calculated.

The GC/MS analyses were performed using a Varian ion-trap GC/MS instrument equipped with FID detector and a vitreous silica inlet splitter (VSIS). In this system, two identical DB-1 columns (30 m long with 0.32 mm ID) 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. GC column temperature was held at 50 °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.

2. Dehydrochlorination of 3-Chloro-3-Methyl Pentane

Results from the dehydrochlorination reactions of 3-chloro-3-methyl pentane from Aldrich Chemicals (>97% purity) and Wiley Organics (>88% purity) with the three chars (OST3-9, ACC and OACC) are shown in Table I. In these reactions, dehydrochloro-

mination of 3-chloro-3-methyl pentane to 3-methyl-2-pentene (cis/trans) was measured by measuring the formation of HCl from the reaction. The reactions were carried out in gas phase and at a char bed temperature of 250 °C. Data in Table I indicate that HCl production is significantly lower with the 3-chloro-3-methyl pentane from Aldrich Chemicals, which is a higher purity chemical. This is in contrast to our previous data suggesting a higher conversion of 3-chloro-3-methyl pentane to 3-methyl-2-pentene (cis/trans) with a higher purity chemical. The source of high HCl in the reactions involving 3-chloro-3-methyl pentane from Wiley Organic, therefore, could probably be due to the high impurities in this chemical and not from the higher conversion of 3-chloro-3-methyl pentane to 3-methyl-2-pentene (cis/trans). The data in Table I also indicate that OACC char is a better catalyst for dehydrochlorination of 3-chloro-3-methyl pentane than the OST3-9 char. However, data from the GC/MS analysis of the distillates from the dehydrochlorination of 3-chloro-3-methyl pentane suggests differently.

Table II shows the data from the GC/MS analysis of the distillate collected from dehydrochlorination reactions of 3-chloro-3-methyl pentane with the three chars (OST3-9, ACC and OACC). These reactions were also carried out in the gas phase. However, the char bed temperature for these reactions was 450 °C. The data for blank analysis, shown in Table II, were obtained from a run in which the char bed temperature was kept at room temperature. Comparison of the data in Table II indicates that the distillate collected from the reaction using OST3-9 yielded the highest concentration of both cis and trans 3-methyl-2-pentene. This reaction also had the highest total conversion. Surprisingly, there was very little difference in the conversion of 3-chloro-3-methyl pentane to 3-methyl-2-pentene (cis/trans) using either of the two activated ChemCoal™ chars (ACC or OACC).

3. Dehydrochlorination of Other Chlorinated Compounds

Several dehydrochlorination reactions were also carried out using 1,2-dichloroethane and 1,1,2,2-tetrachloroethane. The procedure used for these reactions was the same as the one used for 3-chloro-3-methyl pentane. In one reaction, dehydrochlorination of 1,2-dichloroethane was measured by measuring the formation of HCl from the reaction. This reaction was carried out in gas phase and at a char bed temperature of 250 °C. Data from this reaction are also shown in Table I. As the data indicates, none of the chars had any catalytic activity for dehydrochlorination of 1,2-dichloroethane at these experimental conditions. However, increasing the char bed temperature from 250 °C to 450 °C increased the conversion of 1,2-dichloroethane significantly, Table III. Data from the dehydrochlorination of 1,1,2,2-tetrachloroethane are also shown in Table III. Here again, comparison of the data in

this table suggest that the OST3-9 char is a superior catalyst compared to either of the two ChemCoal™ chars. These data also suggest that under the experimental conditions used in these reactions both OST3-9 and OACC chars were a fairly effective dehydrochlorination catalyst for 3-chloro-3-methyl pentane as well as 1,1,2,2-tetrachloroethane.

In a series of reactions, the effect of char bed temperature and chemical vapor residence time on the dehydrochlorination reaction of 1,2-dichloroethane was also studied. In the first set of experiments, the char bed temperature was increased from 200 °C to 450 °C. In the second set of experiments, the flow of nitrogen, which was used as a carrier of the chemical vapor over the char bed, was increased from 5 to 35 ml/min. The data from these reactions are shown in Table IV. These data clearly indicate that the optimum temperature for dehydrochlorination of 1,2-dichloroethane was at the highest temperature (450 °C). The data also indicates that the optimum vapor residence time for this reaction is achieved at the nitrogen flow rate of 10 ml/min.

CONCLUSION

Dehydrochlorination data obtained from the studies reported previously and in this report suggest that:

- a.) The ability of oxidized activated char to catalyze chlorinated compounds in dehydrochlorination reactions strongly depends on the reaction conditions as well as the structure of the individual compound.
- b.) Impurities in the chlorinated compound used for the dehydrochlorination reaction have a significant effect on the reaction products and total conversion.
- c.) Char bed temperature and reaction residence time both have a significant effect on the reaction products and total conversion.
- d.) Among the two oxidized activated chars, OST3-9 and OACC, the OST3-9 seemed to be the superior char for use as a dehydrochlorination catalyst.

FUTURE WORK

Comparison of the characterization data from the oxidized activated ChemCoal™ char and OST3-90 char clearly indicated that the two chars are significantly different. Evaluation of the oxidized activated ChemCoal™ char for elimination reactions such as dehydrochlorination of several chlorinated compounds was also completed. Comparison of the data from these dehydrochlorination reactions involving OAS ChemCoal™ char and OST3-9 char clearly suggested that the OST3-9 is a superior catalyst for these types of elimination reactions. Further evaluation of ChemCoal™ chars for the adsorption and destruction of unwanted organic compounds is in progress.

Table I.

Tabulated Results from Dehydrochlorination Reactions of Some Chlorinated Compounds with Different Chars^(a)

<u>Compounds</u>	<u>HCl C o n v e r s i o n (%)</u>		
	<u>OST3-9</u>	<u>ChemCoal™</u> <u>ACC</u>	<u>Chars</u> <u>OACC</u>
3-Cl-3-methyl Pentane ^(b)	48	42	79
3-Cl-3-methyl Pentane ^(c)	64	32	90
1,2-dichloroethane	0.01	0.01	0.07

(a) Reactions were carried out in the gas phase at 250 °C.

(b) 3-Chloro-3-methyl pentane from Aldrich Chemicals (97% purity).

(c) 3-Chloro-3-methyl pentane from Wiley Organics (88% purity).

Table II.

Product Distribution of Dehydrochlorination Reactions of 3-Chloro-3-methyl Pentane with Different Chars^(a)

<u>Compounds</u>	<u>Blank</u>	<u>Area Concentration (%)</u>		
		<u>OST3-9</u>	<u>ChemCoal™</u> <u>ACC</u>	<u>Chars</u> <u>OACC</u>
3-chloro-3-methyl pentane	98.7	20.1	41.2	39.1
3-methyl-2-pentene (cis/trans)	0.43	66.9	55.5	53.0
other components	0.83	11.9	2.8	6.8
Conversion (%)	----	79.6	58.3	60.3

(a) Reactions were carried out in the gas phase at 450 °C.

Table III.

Tabulated Results from Dehydrochlorination Reactions of Some Chlorinated Compounds with Different Chars^(a)

<u>Compounds</u>	<u>Purity</u>	<u>C o n v e r s i o n (%)</u>		
		<u>OST3-9</u>	<u>ChemCoal™ Chars</u> <u>OAC</u>	<u>OACC</u>
3-chloro-3-methyl pentane	98.7	79.6	58.3	60.3
1,2-dichloroethane	99.9	3.0	1.4	2.9
1,1,2,2-tetrachloroethane	98.6	78.8	48.0	67.1

^(a)Reactions were carried out in the gas phase at 450 °C.

Table IV.

Effects of Changes on Char Temperature and Nitrogen Flow (Vapor Residence Time) on Conversion of 1,2-dichloroethane During Dehydrochlorination Reaction

<u>Temperature (°C)</u>	<u>Conversion (%)</u>
200-250	0.01
250-275	0.27
300-325	0.93
400-450	2.92
<u>Nitrogen Flow (ml/min)^(a)</u>	
~ 5.0	8.80
~ 10.0	13.25
~ 20.0	4.24
~ 35.0	3.36

^(a) Reactions were carried out in the gas phase at 450 °C.

APPENDIX B

Adsorption Studies, Vernon Snoeyink (C. Feizoulof) - UIUC

INTRODUCTION

The overall objective of this segment of the project is to evaluate the effects of an activated carbon's surface chemistry on aqueous adsorptive properties. Papirer and co-workers [1] 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.

EXPERIMENTAL PROCEDURES**Acquisition, preparation, and characterization of carbon adsorbents**

Two activated char samples were received from the Illinois State Geological Survey. The chars were activated at high temperatures (870°C) in a 50% steam/50% CO₂ atmosphere. The starting material for the activated chars was an ultra-low ash coal product produced via the ChemCoal process. The activated char has been designated ACC (Activated ChemCoal). A portion of the ACC was oxidized at moderate temperatures (450°C) in a 10% O₂/90% N₂ atmosphere. This sample has been designated OACC (Oxidized Activated ChemCoal).

Four samples prepared from HN100 (Table 1) will be examined in order to better evaluate whether a relationship between the presence of surface oxygen and adsorption of p-nitrophenol exists. HN100, a sample relatively rich in surface oxygen groups, was outgassed to varying temperatures in an atmosphere of ultra high purity (UHP) nitrogen. Two samples, one heated to 405°C (DS405) and another to 525°C (DS525) were prepared and described in the previous quarter. Two more samples, one outgassed to 725°C and another to 950°C have been prepared and designated DS725 and DS950, respectively.

The surface areas of DS725 and DS950 were measured using adsorption of N₂ at 77 K and application of the Brunauer, Emmet, and Teller (BET) equation. The samples were outgassed under vacuum at 110°C for approximately 24 hours prior to the analysis.

Temperature-programmed desorption studies began this quarter to determine whether CO- or CO₂-evolving groups effect p-nitrophenol adsorption.

A series of samples was sent to Amoco Research Center for surface characterization by x-ray photoelectron spectroscopy.

Adsorption capacity of carbon adsorbents in distilled-deionized water

Adsorption isotherms of p-nitrophenol (PNP) on the samples ACC and OACC were obtained. The following procedures were used in obtaining the adsorption isotherms.

1. A 0.01 M stock solution of PNP was prepared.
2. A small sample (about 5 g) of GAC was dried for 24 hours and pulverized in a SPEX 8000 Mixer/Mill for 5 minutes.
3. The pulverized carbon was weighed into ten 125 ml serum bottles in the following quantities: 0, 0, 2, 4, 5, 6, 7, 8, 10, and 12 mg.
4. Ten ml of 0.01 M PNP was pipetted into a 1.0 liter volumetric flask and diluted to 1.0 liter with a phosphate buffered solution, giving a 0.0001 M PNP 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 separated 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 filtrate was determined using a Perkin-Elmer Lambda 3B UV/Vis spectrophotometer. The samples were analyzed at a wavelength of 400 nm.

RESULTS AND DISCUSSION**Acquisition, preparation, and characterization of carbon adsorbents**

The main objective of this segment of the overall project is to evaluate the effects of an activated carbon's surface chemistry on aqueous adsorptive properties. The existence of oxygen containing functional groups on the surface of carbon is well documented. In order to determine whether a relationship between the presence of surface oxygen groups and PNP capacity exists, a series of carbons with various amounts of surface oxygen were prepared and described previously [2]. During this reporting period, two samples, DS725 and DS950, were prepared from HN100. The outgassing temperatures of the DS samples were selected in order to give different CO/CO₂ ratios as obtained by temperature-programmed desorption. As the outgassing temperature is increased, less oxygen will be present on the surface of the carbon, since it is evolved as CO and CO₂.

Determination of surface areas using nitrogen adsorption at 77K and application of the BET equation revealed that the

surface areas of samples DS725 and DS950 were approximately 980 m²/g and 960 m²/g, respectively, on a moisture-free basis. This is comparable to the other samples prepared from AR000 and provides evidence that outgassing of HN100 did not cause significant change in the physical characteristics of the carbons.

Temperature-programmed desorption (TPD) is an effective means to qualitatively and quantitatively analyze surface oxygen groups present on carbon. A series of samples has been degassed at different temperatures in order to determine whether a relationship between CO/CO₂ ratios and PNP adsorption exists. Data obtained from TPD experiments will be analyzed in conjunction with results obtained from x-ray photoelectron spectroscopy to determine which specific surface functional groups may be responsible for enhanced PNP adsorption.

Adsorption capacity of carbon adsorbents in distilled-deionized water

The adsorption capacity of a carbon is frequently described by the Freundlich equation. The application of this equation has been described elsewhere [2].

Examination of Figures 1 and 2 show that the PNP capacity of ACC and OACC is significantly less than that of AR000, a commercially available activated carbon manufactured from bituminous coal. At an equilibrium concentration of 1 mg/l ($C_e=1$) the PNP capacities of ACC and OACC are less than half that of AR000.

Table 1. Sample designations and corresponding treatments

<u>Sample I.D.</u>	<u>Treatment</u>
AR000	Calgon F-400 commercial active carbon (as received)
AW100	AR000 acid washed in 1 M HCl and 1 M HNO ₃
FN950	AW100 fluidized in UHP N ₂ at 950°C for 30 minutes
AO305	FN950 air oxidized at 300°C with 10% O ₂ /90% N ₂ for 5 minutes
AO330	FN950 air oxidized at 300°C with 10% O ₂ /90% N ₂ for 30 minutes
HN050	FN950 oxidized with 0.5 M HNO ₃
HN100	FN950 oxidized with 1.0 M HNO ₃
DS405	HN100 outgassed to 405°C in UHP N ₂
DS525	HN100 outgassed to 525°C in UHP N ₂
DS725	HN100 outgassed to 725°C in UHP N ₂
DS950	HN100 outgassed to 950°C in UHP N ₂
ACC	ChemCoal activated in 50% steam/50% CO ₂ at 870°C
OACC	ACC oxidized at 450°C in 10% O ₂ /90% N ₂

CONCLUSIONS AND FUTURE WORK

- The surface areas of two carbon samples were measured using adsorption of N₂ at 77 K and application of the BET equation. The surface areas of DS725 and DS950 were 980 m²/g and 960 m²/g, respectively. These results provide some evidence that outgassing of the samples did not significantly alter the physical characteristics of the carbon.
- PNP adsorption isotherms of two activated char samples, designated ACC and OACC, produced from an ultra-low ash coal product were obtained.
- Adsorption experiments revealed that the PNP capacities of ACC and OACC are significantly lower than that of the F-400 carbons.
- Temperature-programmed desorption studies began this quarter in an attempt to determine whether a relationship between surface oxygen groups and PNP adsorption exists.
- A series of samples was sent to Amoco Research Center for characterization by x-ray photoelectron spectroscopy (XPS). TPD and XPS results will be interpreted concurrently in order to identify any surface functional groups which may contribute to enhanced PNP adsorption.

REFERENCES

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2. Kruse, C. W., S. L. Carlson, V. L. Snoeyink, C. Feizoulof, D. N. Assanis, M. Syrimis, and M. Fatemi. Integrated Production/Use of Ultra-Low Ash Coal, Premium Liquids and Clean Char. **Interim Final Technical Report to the Center for Research on Sulfur in Coal**, August, 1992.

Figure 1. PNP adsorption at pH = 6

Figure 2. PNP adsorption at pH = 8

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