ABSTRACT

The research objective was to make chars (carbons) that are more valuable than the chars commonly resulting from mild gasification (MG) of coal. Major program elements were a) preparation and characterization of carbons at the ISGS, b) characterization and catalyst testing at the Amoco Research Center, c) completion of diesel engine testing at the University of Illinois Champaign-Urbana (UI-UC) begun under a previous contract, and d) completion of adsorption studies of activated carbons at the UI-UC. Materials prepared included a) low-ash coal, b) coal chars (MG chars), c) activated low-ash carbons (AC), d) oxidized activated carbons (OAC).

Two inventions were made. The first discovery was how to modify the surface of an activated carbon to improve its ability to adsorb metal ions and organo metallics. This invention has practical implications for the control of trace elements, both for preventing their emissions into the environment and for their control in the chemical processing of hydrocarbons and related materials.

The second discovery was a new method for making a catalytic form of oxidized carbon for catalysis of elimination reactions. This method avoids air oxidation at high temperatures. It was the inability to control air oxidation for the regeneration of catalyst beds that frustrated the commercial development of the 1960s patents on oxidized carbon catalysts.

Tests using a two-cylinder diesel were made to compare dispersions (20 and 35 wt%) of low-ash coal in diesel fuel with diesel fuel alone. Only a minor modification of the fuel injection system was required to feed the slurries.
EXECUTIVE SUMMARY

Two inventions were made. The first discovery was how to modify the surface of an activated carbon to improve its ability to adsorb metal ions and organo metallics. This invention has practical implications for the control of trace elements, both for preventing their emissions into the environment and for their control in the chemical processing of hydrocarbons and related materials.

The second discovery was a new method for making a catalytic form of oxidized carbon for catalysis of elimination reactions. This method avoids air oxidation at high temperatures. It was the inability to control air oxidation for the regeneration of catalyst beds that frustrated the commercial development of the 1960s patents on oxidized carbon catalysts.

The primary research objective was to provide information for making coal chars (carbons) a valued raw material for producing high-value products, the most valuable material in the product list for a given coal utilization strategy. This project’s approach lets other products reach their highest value under a "high quality, clean char" constraint. Setting clean char as the priority does not lower the quality of other products if the first step is removal of essentially all of the mineral matter. Without doubt, one barrier to using coal in internal combustion engines or gas turbines will have been removed by taking out all of the abrasive, ash-forming minerals! One can anticipate that the properties and yields of the liquids produced in mild gasification (MG) of ultra low-ash coal will be enhanced, especially if the initial ash removal process increases the coal’s volatile matter. Some properties of AC produced from low-ash coal can also be expected to be superior to those of ACs from conventionally-cleaned coals.

Materials prepared with assistance from subcontractors were 1) low ash coal isolated from Illinois No. 6 coal (IBC-109) by ChemCoal processing and by acid dissolution of the mineral matter, b) coal char (MG char) produced by mild gasification of IBC-109 and the low-ash coal prepared from it, c) activated carbon (AC) by MG of char, and d) oxidized activated carbon (OAC), a catalyst variety produced from AC. Amoco Research Center supported Champaign-Urbana investigators with its state-of-the-art analytical capabilities and with development of testing procedures to measure catalyst activity.

Seven base-line carbon samples were prepared from a commercial activated carbon and they were characterized by proximate and ultimate analyses. Additionally, their N₂ BET surface areas and apparent densities were determined. Because there is evidence that oxygen values obtained by difference may be unreliable for this work, other methods, including CO/CO₂ desorption and X-ray photoelectron spectroscopy, were used to quantify the amount of surface oxygen present on the various
carbons. The base-line adsorption studies showed that 1) oxygen values obtained by difference may be unreliable and may be inferior to TPD and XPS for quantifying the amount of surface oxygen on the carbons produced from low ash coal, 2) PNP adsorption isotherms for six treated samples indicated that oxidation of carbon with nitric acid decreased adsorption capacity while oxidation in air increased adsorption capacity, 3) TPD data confirmed that a carbon treated with nitric acid had significantly more CO and CO₂ desorbing groups than the as-received activated carbon (AR000).

Activated carbon samples were treated in different ways to produce a series having different surface chemistries. TPD studies of this series revealed 1) the amounts of CO and CO₂ evolved by outgassing diminishes as the temperature is increased and 2) high outgas temperatures may provide carbon surfaces which preferentially chemisorb oxygen at room temperature and this oxygen may desorb as CO₂ below 350°C. XPS analysis found a correlation at the 90% confidence level of catalyst activity for dehydrochlorination of 1,1,2,2-tetra-chloroethane with oxidized carbon (C-O and C=O) as indicated by the 286 eV binding energy. The activity correlation was lower with the XPS percent of oxygen atoms on the surface.

The supply of low ash coal produced by a modification of the ChemCoal process was insufficient to meet the needs for diesel engine tests. Slurry formulation development and tests during modification of the engine's injection system were made with a low ash coal provided by AMAX R&D Center. Successful engine tests in a two-cylinder diesel engine were performed with AMAX low ash coal dispersed in diesel fuel at solid loadings of 20% and 35%. Test were made with the 20% slurry at 1800 and 2200 rpm, under 75% load and 10 in Hg intake manifold boost. The higher speed proved to be more reliable. The slurry burned with a slightly improved thermal and combustion efficiency at both speeds. At 2200 rpm, heat release profiles from the coal-slurry and the diesel fired cylinders were almost identical. When all systems were ready for the final tests with the low ash coal from the ChemCoal process, the slurry was prepared from the limited amount of this coal. A different in particle size distribution is believed to have been responsible for plugging the fuel injector and effectively destroying it at time the funding of this segment of the work was terminated.

The potential to capture a significant share of a diesel fuel market by coal/oil slurries is doubtful. Despite technical success, we hear that there is little industrial interest in coal/oil or even coal/water slurries. Most researchers agree that to shift consumers from oil to slurries of any kind will require a large price differential between coal and oil. We agree with those who believe that a coal/water slurry will prevail over coal/oil because the oil in the coal/oil slurry formulation will escalate at the same rate as the oil that the slurry is attempting to replace.
OBJECTIVES

The integrated set of objectives proposed initially was altered, partly for technical reasons, but mainly to stay within the approved budget. The primary goal was to determine what value could be added to products and byproducts of mild gasification (MG) by lowering the amount of ash-forming minerals. MG is the uncatalyzed heating of coal at atmospheric pressure to produce minor amounts of gas, some tar, but mostly char. Char is a product not only of MG but also of other coal utilization approaches. Char is typically the product having the lowest value because most of coal’s non-fuel, ash-forming minerals are concentrated in it. The first step of this project’s approach used the ChemCoal (CC) process (Knudson, 1986) to remove a high percentage of the ash-forming minerals, including pyrite and as much of the organic sulfur as possible, from IBC-109. IBC-109 is a low-ash, low-sulfur, Illinois No. 6 coal from the Illinois Basin Coal Sample Program.

Determining the combustion characteristics of the low-ash coal in a Diesel engine was another objective. An initial goal was to rank a low-ash fuel with other coal-derived fuels through comparisons not only of the fuel in a Diesel engine but also in a combustion bomb apparatus at the Morgantown Energy Technology Center. Slurry media were to have included MG oils. The scaled-down two-year budget that was approved required limiting the Diesel engine tests to one year and deleting the coal-derived slurry medium for ChemCoal solids.

Making high-market-value derivatives from the ultra low-ash char was another goal. Step one was to convert char to an activated carbon (AC) and step two was to produce an oxidized-activated carbon (OAC) catalyst from that AC. OACs produced under the right conditions catalyze elimination reactions; hydrogen chloride from alkyl halides, water from alcohols, ammonia from amines and hydrogen sulfide from mercaptans and sulfides. Procedures for characterizing these materials were developed in a previous project (Kruse et al, 1991). The continuing ISGS objective is to make OACs that have both catalyst activity and adsorptive properties and to use the OACs to not only adsorb a variety of volatile organic compounds (VOCs) but also to convert them to recyclable hydrocarbons by eliminating their heteroatoms (Cl, N, S, O).

Because the CC process produces clean coal having more volatile matter than the feed, an initial goal was to determine the effect this modified volatile matter had on the yield and properties of MG liquids. It became apparent that the previous yield data on smaller tests would not be applicable to the larger runs because there was evidence of a difference in the degree of coal depolymerization. The yield data was not available from the production runs because they were made strictly for production. Without material balances, the value
of the work planned for the liquids would have been greatly diminished and isolation of MG liquids was also dropped.

IBC-109 coal and two low-ash coals were subjected to hydro-
pyrolysis under conditions found in tests at Sandia National
Laboratories to be effective for bituminous coals. The goal
was to provide additional comparisons of yields and energy
balances. The inclusion of an Illinois coal in comparative
hydroprocessing tests at Sandia Laboratory was encouraged as a
means of developing data on a coal conversion technology that
lies between MG and traditional direct liquefaction. The
results, not available at the time of this writing, will be
included in a contract report by Dr. E. Klawetter, US
Department of Energy (US DOE), for contract AC04-76DP00789
administered by the US DOE Pittsburgh Energy Technology Center.

Tasks

Task 1: Production of low ash coal (UNDEERC/ARDL/SIU/IGSS). ChemCoal solids
were separated by Applied Research and Development Laboratory, Inc. (ARDL)
from the reactor slurry supplied in September 1991 by the University of North
Dakota Energy and Environmental Research Center (UNDEERC). These solids were
dried in a vacuum oven at the IGSS to remove the remaining meta-cresol. IBC-
109 was also treated by Dr. Celling's group at SIU with acids (including
HP) to remove mineral matter.

Task 2: Mild gasification of coals - (IGSS). ChemCoal solids of Task 1 were
subjected to MG at 870°C in a fluidized bed following procedures established
in a previous contract on premium liquids by MG.

Task 3: Fuel assessments in a diesel engine - (UI-UC). This task, begun under
a previous contract, included modification of a two-cylinder diesel engine
to accept a slurry of coal in diesel fuel. The clearance gap of the injector
was enlarged by taping the needle with enery paper. The modification worked
with an AMAX low-ash coal that was used as a prototype to developing the
modified injector, but it plugged when a slurry of ChemCoal solids was tested.

Task 4. Activated and oxidized/activated low ash char

Task 4a. Preparation of chars - (IGSS). ChemCoal solids were gasified with
steam/carbon dioxide at 870°C at less than 50% conversion.

Task 4b. Characterization and use - (Amoco). Sample characterization using
a variety of methods conducted about half the work. The remaining work
involved developing a test to determine relative activities of char
catalysts for elimination reactions and then applying the method to QAC
produced at the IGSS.

Task 4c. Adsorption studies - (UI-UC). This study by a UI-UC graduate
student, Cuneyt Feizulof, under the direction of Dr. Vernon Snoeyink,
sought to correlate functional groups on carbons with the carbon's
adsorption characteristics.

INTRODUCTION AND BACKGROUND

Coal's low hydrogen-to-carbon ratio gives coal its solid state
and the combustion properties that are not the most desirable.
Coal's problem is dealt with in conversion technologies by
either: 1) chemically adding hydrogen, as in direct liquefac-
tion or high-BTU gasification, or 2) the production of char,
as in MG. The first option is neither cost-effective nor
environmentally desirable when greenhouse gases are a consid-
eration. One mole of carbon dioxide is produced for every two moles of hydrogen needed in liquefaction. Despite a preferred hydrogen to carbon ratio in the resultant liquid fuel, the overall accounting shows more carbon dioxide is produced than would be released by burning the coal used to make the liquid fuel.

A low market value of char is the primary drawback of the second option. Making value-added, non-fuel products from char could significantly improve the economics of overall operations, avoid the greenhouse gas problem, and result in competitively-priced premium hydrocarbon fuels. The research goal of a growing number of research groups is to produce and describe carbon products that will command prices higher than the carbon (coal) from which they were produced. To have a reasonable impact on the Illinois coal economy, markets for materials derived from coal char must be large and must have a potential price structure much higher than fuel value. Markets for ACs could satisfy the price demand now. It remains to be determined how what the markets could become when new production technology and economy-of-scale reduce the cost of manufacturing AC. The use of AC for water purification and for adsorbing compounds from nonaqueous solutions or suspensions is growing. Not only is the potential volume attractive, but the price of products against which a char-derived carbon would compete is more than $1000/ton for a high quality product.

Opportunities for developing specialty chemicals and advanced materials from coals were recently reviewed (Song and Schobert, 1993). One- to four-ring aromatics from coal may be necessary to feed the rapidly growing engineering applications of aromatic polymer materials. Development of high-performance carbon materials, such as carbon fibers, graphites, and advanced adsorbents for environmental applications, is another approach for moving coal's carbon into non-fuel uses (Economy et al., 1992; Thwaites et al., 1993). Carbons suitable for methane storage are being produced (Quinn and MacDonald, 1992). Carbon molecular sieves manufactured for commercial pressure swing adsorption (PSA) systems are now competing with zeolites for air separation applications. Illinois coals have been shown to be good feedstocks for making molecular sieves (Lizzio and Rostam-Abadi, 1993). European and Japanese researchers are reportedly testing carbons for adsorption of radon (Kinner et al., 1993; Nakayama et al., 1993). There are biotechnology applications involving carbon as a support (Rittmann, 1993). Commercial use of activated carbon to reduce SO\textsubscript{2}, NO\textsubscript{x}, and mercury in the flue gas from waste incineration plants is well-advanced in Germany (Brueggendick and Pohl, 1993) and Japan (Tsuji and Shiraishi, 1991).

Systems are needed which remove and destroy unwanted organic compounds that have been identified in chlorinated potable waters, cooling waters, and sanitary effluents (Harden &
Ramsey, 1986). Additionally, chemical processes often produce environmentally objectionable compounds which must be removed from aqueous solutions or organic solvents. This project’s PI has a long-standing interest and experience in developing dehydrohalogenation catalysts, having been an inventor of record for three patents covering the preparation and use of oxidized carbonaceous materials as catalysts (Kruse et al., 1966, 1967, 1969). Exploiting OAC’s capability to not only adsorb VOCs but, when heated, to catalyze chemical transformations that convert the unwanted adsorbed compounds into useful ones was an objective of this research and previous research (Fatemi et al., 1993). The trade-offs both technically and economically to achieve a balance between catalytic properties and adsorptive properties must be evaluated. Fresh, dry OAC was shown in previous work to remove 37 volatile organic compounds (VOCs) from aqueous solutions (Kruse et al., 1991; Beaulieu et al., 1992). These are VOCs for which federal and state discharge permits usually require screening. Some of the analytes were more strongly adsorbed than others. Further examination of OAC’s adsorptive and catalyst properties was an objective of this project.

EXPERIMENTAL PROCEDURES

Production of low ash coal

Deashing was accomplished by 1) solubilizing the coal, IBC-109, in a phenolic solvent, m-cresol, under CC process conditions (CO and H₂O at about 2000 psig, 350°C, and Na⁺) followed by a) separation of the coal solution from insoluble ash/coal-by centrifugation or filtration, and b) precipitation of coal from solution by dilution with methanol. Hydrogen is produced in situ by a reaction of CO with water. The goal was to limit the depolymerization to the amount necessary to achieve separation of coal from its minerals. The solids that precipitated from the phenolic solution by dilution with methanol and water retained coal-like properties. Fourteen gallons of reactor product from two CC runs made in a larger autoclave at UNDEERC was delivered to the ISGS. This material was delivered to an ISGS subcontractor, ARDL, in Mt. Vernon, Illinois, for processing. ARDL’s work-up was suspended when product quality did not match previous experience. A 1-quart sample of the untreated crude product was returned to the ISGS for study. It was worked up in three portions. This work confirmed that the procedure supplied by the project PI to ARDL gave coal having more than 0.6% ash. UNDEERC personnel suggested that the viscosity of the crude reactor product be reduced by adding 9% by weight of methanol. Despite this improvement in viscosity and the improvement in the ease of handling, the product’s ash remained high. The ISGS test on 1-quart of effluent gave 137 grams of CC-solids having no more than 5% m-cresol.
ARDL, employed a revised procedure to complete isolation of low-ash coal. The slurry was diluted with methanol (90:10 slurry/methanol) to improve its viscosity. The inorganic matter (IOM) and ash were then removed by centrifugation at 2,500 rpm for 20 min. The liquid was decanted. Methanol was added in a 1:1 ratio of methanol to liquid decanted to precipitate the low-ash coal. It was separated by a second centrifugation at 2,500 rpm for 20 minutes. The liquid was decanted leaving the low-ash coal product to be washed with methanol/water (90:10), with 5% formic acid solution to remove sodium ions, and finally with distilled-deionized water before drying in a vacuum oven at 80°C.

TGA showed that more than 10% of the product volatilized at m-cresol’s boiling point. The CC solids from ARDL were dried under vacuum at 200°C in a nitrogen atmosphere to remove the m-cresol. The CC batches from ARDL lost about 15 wt% in drying. The batches from the drying operation were mixed to produce a uniform composition. Proximate analysis of the composite showed it had 1.0% moisture, 43.3% volatile matter and 0.80% ash. Approximately 3500 g was available for charring and other tests.

A second ultra-low ash coal was to have been produce by hydrochloric acid and hydrofluoric acid leaching as practiced by Dr. Jack Crelling’s group at Southern Illinois University (SIU). The pilot test gave higher ash than initially projected, 0.95% (mf). Particle size reduction was carried out to achieve an ash content lower than 0.95%. However, the ash content was 1.42% (mf) on a 2 kg production run. A second attempt was made with another sample of IBC-109. The 2.9 kg delivered had 1.36% ash. Low temperature ashing gave 2.26% residue. The higher value was not unexpected because low temperature ashing does not remove mineral volatile matter. SEM-EDX revealed abundant widely dispersed Ti that is in grains smaller than 10 μm, and too small to resolve. A similar amount of Fe was present in micrometer-sized spherical grains of pyrite (or marcasite). SEM indicated about 15 percent of the ash is pyrite + marcasite. X-ray diffraction showed some anatase (TiO₂), a trace of quartz and some sulfate crystalline material that, when mixed with water, converts to gypsum.

Fuel assessment in a diesel engine

Michalis Syrimis, under the direction of Professor Dennis Assanis, described this work in an 85-page thesis (Syrimis, 1992). The inability of the PI to provide sufficient quantities of fuel was a serious constraint. Low-ash coal provided by AMAX was used for development tests. It was produced by caustic dissolution of the ash-forming minerals. This coal remained from the preparation of slurries by AMAX for contracts funded by U.S. DOE. The coal was ground in a fluid energy mill to an average size of 5 microns. Arriving at a
working formulation for the coal-diesel slurry required the use of .5% Castor Oil, and 0.5% (to the coal) LP6, a surfactant made by ICI. Castor oil, a substance well known for its lubricative and adhesive properties, was added to the fuel for better lubrication of the nozzle.

In each test the engine was run with diesel fuel in both cylinders for about an hour and a half for engine conditions to stabilize, before the fuel of cylinder 2 was changed to slurry. Data acquisition started half an hour before the change of fuel in the cylinder. Comparison of the two fuels was made by comparing performance variables, and also heat release results of the two cylinders.

A few hundred grams of CC, Professor Zondlo's material extracted with N-methylpyrrolidone, and low ash graphite were available for testing near the end of the funding period for this portion of work. An attempt to run a 35% graphite slurry on the engine was unsuccessful. The slurry formulation used was the same as with the low-ash coal. The fuel injector of cylinder 2 plugged, and the cylinder stop firing. The engine test facility is described in detail in the FINAL TECHNICAL REPORT for the project titled LIGNIN-AUGMENTED BITUMINOUS COAL DEPOLYMERIZATION: A ROUTE TO CLEAN FUELS and in a thesis (Syrmis, 1992).

Chars by mild gasification

The CC solids were a fine powder having particle sizes as low as 1.4 microns. It could not be charred in the Fluidized Bed Reactor (FBR). The CC solids were pelletized to give nominal 1" diameter by 1/2" material. The pellets were shattered and material 1/4" by 10 mesh was separated by screening for the charring in a 2-inch fluidized bed reactor (FBR) described in previous ISGS reports (Stephenson and Liu, 1987). In a typical run, a 200-gram quantity of pelletized CC was heated to 600°C at 20°C per minute and held there for 15 minutes in a nitrogen atmosphere. The nitrogen flow rate was 10 liters per minute.

Activated and oxidized/activated char

Activation - The MG char was crushed in a mortar with a pestle and sieved to produce 10x30 mesh char to be gasified. Gasification was conducted in a 1-inch FBR described in previous reports to the CRSC on MG to produce premium liquids (Stephenson et al., 1987). The chars were heated at 20°C/min in nitrogen up to 870°C where they were gasified in 50%CO2/50%H2O at a flow rate of 2 l/min for 2.5 hrs. Then the gasified chars were allowed to cool in nitrogen.

Air oxidation - Forty gram batches of MG char were oxidized in the 1-inch FBR used for gasification. Each batch was fluidized in nitrogen and heated to 450°C before the fluidizing gas was
switched to a mixture of 10%O₂/90%N₂ flowing at 4 l/min. The
temperature was maintained at 450°C for 15 minutes. The
oxidized char was then cooled in the 10%O₂/90%N₂ gas mixture.

**Nitric acid oxidation of activated carbons** - One hundred grams
of an activated carbon was placed in a round-bottomed boiling
flask which was filled with 500 ml of 1.0 M nitric acid (HNO₃).
Heat was applied to bring the sample to the reflux temperature
for 30 minutes, after which the carbon was removed by
filtration and washed thoroughly with deionized water.

**Outgassing of nitric acid-oxidized carbons** - This operation was
carried out in a tubular furnace in combustion boats. The
sample was heated at 20°C/min to the desired temperature under
a flow of ultra high purity nitrogen. The electrical power was
shut off but the sample remained at the peak temperature
several minutes because of the residual heat.

**XPS characterization surfaces** - X-ray Photoelectron Spectroscopy
(XPS) was used to study the surface compositions and
chemistry of Calgon F-400 AC and the samples prepared from it.
Elemental surface composition (relative elemental weight
percent) and a summary of binding energies (BE), as determined
by XPS were determined.

**Dehydrochlorination procedures** - Dehydrochlorination was
carried out in the gas phase in the final months of the
project. In these experiments, 50.0 ml of a chlorinated
compound was transferred into a micro evaporator. The sample
was then heated to assist vaporization and the vapor was passed
over a bed of the OAC to be tested. The bed was held at 450°C.
A flow of nitrogen pushed the vapor through the hot bed of
char. The collected product was analyzed using a Varian ion-
trap GC/MS. In a few experiments, the HCl from the condenser
was trapped in a 0.1M NaOH solution via a trap adapter with a
bubbler. The NaOH was then back titrated with 0.1 HCl and the
HCl evolved was 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 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 μl 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 at a heating rate of 10°C/min.
The injector and detector temperatures were both set at 300°C
and the transfer line temperature was 280°C.
Preparation, and characterization of treated commercial granular activated carbons (GAC) for adsorption studies

A commercial 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 was designated AR000. AR000 was used to prepare ACs with varying surface chemistry. AR000 was acid leached with ten bed volumes of 1.0 M hydrochloric acid and ten bed volumes of 1.0 M nitric acid to remove mineral impurities that might have interfered with subsequent work. 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. This acid washed sample was designated AW100. AW100 was subjected to heat treatment in an inert atmosphere. The sample was placed in a fluidized bed reactor and heated to 950°C at 20°C per minute in ultra-high purity (UHP) nitrogen gas. AW100 was fluidized at 950°C for 30 minutes before allowing it to cool in UHP nitrogen. This sample, designated FN950, was split into five batches. One batch underwent no further treatment. One batch of FN950 was placed in a fluidized bed reactor and heated to 300°C at 20°C per minute in an atmosphere of 10% O₂/90% N₂. The sample remained fluidized at 300°C for 5 minutes. The sample was then allowed to cool in an atmosphere of 10% O₂/90% N₂. This sample was designated AO305. Another sample, designated AO330, was prepared in an identical fashion, except it remained fluidized at 300°C for 30 minutes. Another batch of FN950 was subjected to oxidation by HNO₃. One hundred grams of FN950 was placed in a round-bottomed boiling flask which was filled with 500 ml of boiling 0.5 M HNO₃. The sample was allowed to reflux for 30 minutes. This sample was designated HN050. A sample designated HM100 was prepared in an identical manner, except 1.0 M nitric acid was used as opposed to 0.5 M. Analyses for these samples appear in Table 1.

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

The apparent density (AD) of the samples was determined according to the ASTM "Standard Test Method for Apparent Density of Activated Carbon" (ASTM, 1992). Its units are mass of GAC per unit volume of an unstratified, packed bed of GAC. The volume measured is that of a GAC bed packed by a free-fall of GAC into a graduated cylinder. Therefore, the volume term of this density measurement includes inter-particle and intra-particle voids. All of the samples were placed in a drying oven for 24 hours prior to AD measurements in order to drive off any moisture which may have been present.
Table 1.
Sample Characterization (Proximate & Ultimate Analyses, Nitrogen Surface Areas, Apparent Densities) and Surface Composition (wt.%, Relative) Data from XPS Analyses.

<table>
<thead>
<tr>
<th></th>
<th>AR000</th>
<th>AW100</th>
<th>FN950</th>
<th>AO305</th>
<th>AO330</th>
<th>HN050</th>
<th>HN100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Matter$^1$</td>
<td>6.5</td>
<td>12.0</td>
<td>10.5</td>
<td>10.6</td>
<td>10.8</td>
<td>15.0</td>
<td>15.1</td>
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<tr>
<td>Fixed Carbon$^1$</td>
<td>87.3</td>
<td>82.2</td>
<td>81.8</td>
<td>83.0</td>
<td>82.9</td>
<td>78.5</td>
<td>77.4</td>
</tr>
<tr>
<td>H-T Ash$^1$</td>
<td>6.3</td>
<td>5.7</td>
<td>7.7</td>
<td>6.4</td>
<td>6.3</td>
<td>5.5</td>
<td>7.6</td>
</tr>
<tr>
<td>Hydrogen$^1$</td>
<td>0.26</td>
<td>0.22</td>
<td>0.43</td>
<td>0.25</td>
<td>0.32</td>
<td>0.26</td>
<td>0.21</td>
</tr>
<tr>
<td>Carbon$^1$</td>
<td>90.55</td>
<td>87.55</td>
<td>88.46</td>
<td>90.71</td>
<td>90.37</td>
<td>87.54</td>
<td>85.27</td>
</tr>
<tr>
<td>Nitrogen$^1$</td>
<td>0.95</td>
<td>1.02</td>
<td>0.89</td>
<td>0.95</td>
<td>0.85</td>
<td>1.15</td>
<td>1.48</td>
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<tr>
<td>Oxygen$^1$</td>
<td>1.27</td>
<td>4.66</td>
<td>1.94</td>
<td>0.87</td>
<td>1.37</td>
<td>3.82</td>
<td>4.79</td>
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<tr>
<td>Sulfur$^1$</td>
<td>0.72</td>
<td>0.83</td>
<td>0.62</td>
<td>0.82</td>
<td>0.82</td>
<td>0.74</td>
<td>0.69</td>
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<tr>
<td>Surface Area$^2$</td>
<td>(m$^2$/g)</td>
<td>1061</td>
<td>1073</td>
<td>1124</td>
<td>1058</td>
<td>1121</td>
<td>1012</td>
</tr>
<tr>
<td>Apparent Density (g/cc)</td>
<td>0.443</td>
<td>0.452</td>
<td>0.445</td>
<td>0.438</td>
<td>0.442</td>
<td>0.459</td>
<td>0.469</td>
</tr>
</tbody>
</table>

$^1$ Values given on a moisture-free basis
$^2$ Values given on an ash-free basis

Sample Key
- AR000: Calgon F-400 commercial active carbon (as-received).
- AW100: AR000 acid washed in 1.0 M HCl & 1.0 M HNO$_3$.
- FN950: AW100 fluidized at 950°C in N$_2$ for 30 min.
- AO305: FN950 air oxidized at 300°C in 10% O$_2$/90% N$_2$ atmosphere for 5 minutes.
- AO335: FN950 air oxidized at 300°C in 10% O$_2$/90% N$_2$ atmosphere for 30 minutes.
- HN050: FN950 oxidized with 0.5 M HNO$_3$.
- HN100: FN950 oxidized with 1.0 M HNO$_3$.

Adsorption isotherms of para-nitrophenol (PNP) on the various carbons were obtained by the procedures shown (next page).

RESULTS AND DISCUSSION

Low ash coal and diesel fuel assessment

The yield of CC solids after drying (3500 grams) was less than the one pound/gallon of reactor slurry predicted on the basis of results obtained in a previous project. More of the coal stayed in solution. This is interpreted to be evidence that the depolymerization progressed further in the UNDEERG runs in the larger autoclave than in the one gallon autoclave used previously.

Dr. Crelling’s group at Southern Illinois State University made two attempts to produce an ultra low ash coal from IBC-109. Both samples had well over 1% ash. There was never a good explanation of why the procedure did not work as well on IBC-109 as on other coals processed by the ISU group.

Procedure for adsorption isotherms

1. A 0.01 M stock solution of PNP was prepared.
2. A small sample (about 2 g) of GAC was dried for 24 hours and pulverized in a SPEX 8000 Mixer/Mill for 5 minutes.
3. The quantities of pulverized carbon weighed into ten 125 ml serum bottles were: 0, 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 0.00001 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 tumber, and allowed to equilibrate.
7. The bottles were removed from the tumber 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.

Mild gasification chars

Approximately 1900 g of CC solids from IBC-109 was converted to 1100 g of char. The average weight loss was 42%. The char’s nitrogen surface area was 10 m²/g, the CO₂ area approximately 280 m²/g, and the ash 2.0%. Approximately 2600 g of IBC-109 char was produced in one continuous feed charring run (CF-40) at 35.2% weight loss. This char had 12.7% ash and only 1.4 m²/g nitrogen surface area.

Activated and oxidized/activated char

Chars with good adsorbent properties was the goal of the gasification of the chars. Surface area generally correlates with adsorption capacity. A series of pilot tests indicated the maximum nitrogen surface area would be generated near 40% conversion (Figure 1). The surface area that could be generated from CC char was lower than from the IBC-109 char. Several batches of gasified CC chars having nitrogen surface areas greater than 300 m²/g were mixed to make a 280 gram composite.

Figure 1. Surface areas vs. carbon conversion for activation of the chars shown.
Weight loss during oxidation averaged 5% for the CC chars and 3% for the IBC-109 char. Ten oxidation runs were made with the CC char to produce 192 g of OAC. Only one run was made to produce 19 g of OAC from IBC-109 char.

Determining OAC catalyst activity - The development of a better procedure for differentiating catalytic activity among catalyst samples was needed. The initial method using a tertiary C₆ alkyl chloride, such as 3-chloro-3-methylpentane at its boiling point, was not reliable. The dehydrochlorination data indicated that the ability of oxidized-activated char to catalyze chlorinated compounds depends strongly on the structure of the individual compound and the reaction conditions. In a private conversation with Dr. Boehm at the Adsorbent Carbon Workshop meeting June 9-11, 1993 in Atlanta, Kruse learned that Boehm and Japanese workers achieved better success in measuring differences in the activity of carbon catalysts when they used chlorides which require temperatures above 400°C for dehydrochlorination. Dehydrochlorination of 1,1,2,2-tetrachloroethane at 450°C became the method of choice for the latter part of this work (Table 2).

The effect of char bed temperature and chemical vapor residence time on the dehydrochlorination reaction of 1,2-dichloroethane was studied. In the first set of experiments, the char bed temperature was increased from 200°C to 450°C. In the second set, the flow of nitrogen was increased from 5 to 35 ml/min. The data from these reactions are shown in Table 3. 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.

Adsorption/destuction of volatile organic compounds - OACs capacity to adsorb volatile organic compounds (VOC) from water was demonstrated in 1991 (Beauleau et al., 1992). Experimentation consisted of equilibrating char samples with water samples deliberately contaminated with a methanol solution of 37 organic compounds, each at 1000 ppm (Accustandard).

<table>
<thead>
<tr>
<th>Compounds (purity)</th>
<th>Conversion (%)</th>
<th>O3T3-9</th>
<th>ACC</th>
<th>OACC</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-chloro-3-methylpentane (98.7)</td>
<td>79.6</td>
<td>58.3</td>
<td>60.3</td>
<td></td>
</tr>
<tr>
<td>1,2-dichloroethane (99.9)</td>
<td>3.0</td>
<td>1.4</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane (98.6)</td>
<td>78.8</td>
<td>48.0</td>
<td>67.1</td>
<td></td>
</tr>
</tbody>
</table>

Reactions were carried out in the gas phase at 450°C.
To simplify analyses when extending the previous work to include this year's destruction of the adsorbed VOCs, a solution of 7 analytes (175 µg/ml in toluene) was used instead of the 37-analyte blend used previously. The seven compounds (dichloromethane, carbon disulfide, toluene, o-xylene, 1,1,1-trichloroethane, trichloroethylene, and methyl ethyl ketone) were a cross sectional representation of last year's 37 compounds. Experimentation consisted of equilibration of OSA3-9 catalyst, produced in a previous study (Kruse et al., 1991), with water samples deliberately contaminated with the solution of 7 VOC in methanol to give aqueous concentrations of 19 µg/ml for each component. Concentrations of the remaining VOC in the water solutions were measured by a Varian Saturn GC/MS instrument equipped with flame ionization detector (FID). The char was then removed from the solution and weighed to establish a relationship between the total weight of the wet char and the weight of the dry char added to the solution. A portion of the wet char was analyzed using a CDS 2000 Pyroprobe pyrolyzer (the material was heated to 850 °C, flash pyrolysis held for 30 sec.) on-line with the Varian GC/MS. The data from these analyses was used to calculate the amount of VOC that adsorbed, desorbed, and remained on the OAC. Two separate sets of experiments were performed, the first using DRY char fresh from storage, and the second using char which had been pre-soaked in water for 4 hours. The amount of char used in all experiments was 0.1 gram. A blank and a control sample were also prepared and analyzed.

Adsorption efficiencies of dry and pre-soaked chars for three organic compounds (toluene, o-xylene and 1,1,1-trichloroethane) are shown in Table 4. Percent desorption of the three organic compounds from the char during flash pyrolysis are also shown in Table 4. The differences between the percent desorption and 100 were assumed to be the percent of materials that remained on the char or the materials which were destroyed by the char during the rapid heating. In general, the adsorption levels were in the range reported previously and the efficiency was significantly higher for the dry char than the pre-soaked char. The dry OAC removed 64% toluene from the contaminated water and the pre-soaked char removed only 40%. The efficiency for the removal of o-xylene and 1,1,1-trichloroethane by the pre-soaked char was even lower. The data in Table 3 suggests that, when dry char was used for the removal of VOC, about 50% of toluene

### Table 3. Optimizing conditions for the dehydrochlorination of 1,2-dichloroethane

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200-250</td>
<td>0.01</td>
</tr>
<tr>
<td>250-275</td>
<td>0.27</td>
</tr>
<tr>
<td>300-325</td>
<td>0.93</td>
</tr>
<tr>
<td>400-450</td>
<td>2.92</td>
</tr>
</tbody>
</table>

N₂ Flow (ml/min) (a)

<table>
<thead>
<tr>
<th>Flow (ml/min)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5.0</td>
<td>8.80</td>
</tr>
<tr>
<td>-10.0</td>
<td>13.25</td>
</tr>
<tr>
<td>-20.0</td>
<td>4.24</td>
</tr>
<tr>
<td>-35.0</td>
<td>3.36</td>
</tr>
</tbody>
</table>

(a) Reactions were carried out in the gas phase at 450 °C.
and almost 90% of o-xylene and 1,1,1-trichloroethane remained on the char or were destroyed by rapid heating of the contaminated char. This efficiency dropped significantly when pre-soaked char was used for the removal of VOC. The adsorption/desorption data from the pre-soaked char experiments clearly suggest that a) pre-soaked char has a lower efficiency for the removal of VOC from water, and b) compared to the DRY char, the VOC are not as strongly bonded to the pre-soaked char matrix and hence they desorb more easily upon heating.

### Adsorption studies

Activation conditions for carbons may be such that the inner cores of the larger particles are not completely activated, resulting in a decrease in adsorptive capacity with increasing particle size. Because there may be significant variations in adsorptive capacity with particle size (Randtke and Snoeyink, 1983) this work was carried out with a narrow size range, 16x20 mesh. Care was taken to remove mineral impurities with hydrochloric acid that might interfere with subsequent tests. Additionally, because some samples would be treated with nitric acid and nitric acid might dissolve mineral matter during those treatments, the base carbon was also washed with nitric acid.

AW100 was heated in nitrogen to 950°C to remove oxygen functional groups from the surface of the carbon. Heating of carbon to high temperatures desorbs surface oxygen as CO or CO₂. This sample was cooled in nitrogen to room temperature and then exposed to the atmosphere to produce sample FN950, a sample having basic surface oxides (Boehm, 1966).

Acidic surface oxides are formed when carbon is treated with oxygen at temperatures near its ignition point and also on reaction with oxidizing solutions (Boehm, 1967). Thus, samples AO305, AO330, HN050, and HN100 should behave as acidic carbons. The purpose of the different residence times used in preparing the AO carbons and the different concentrations of HNO₃ used in preparation of the HN carbons was to put differing amounts of oxygen on the surface of the carbon. Examination of Table

<table>
<thead>
<tr>
<th>Organic Compounds</th>
<th>Concentration (%)</th>
<th>Adsorption</th>
<th>Destroyed</th>
<th>Adsorption</th>
<th>Destroyed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>OST3-9</td>
<td>OACC</td>
<td>OST3-9</td>
<td>OACC</td>
</tr>
<tr>
<td>A. Dry Char</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>58</td>
<td>63</td>
<td>87</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>69</td>
<td>72</td>
<td>57</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>34</td>
<td>42</td>
<td>81</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>55</td>
<td>57</td>
<td>90</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>33</td>
<td>38</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>32</td>
<td>43</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>B. Pre-soaked Char</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>55</td>
<td>59</td>
<td>70</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>65</td>
<td>70</td>
<td>20</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>35</td>
<td>40</td>
<td>6</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>55</td>
<td>55</td>
<td>94</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>20</td>
<td>36</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>34</td>
<td>40</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
</tbody>
</table>

ND = Not Detected
1 reveals that the AO carbons have less oxygen (obtained by difference) than the FN950 from which they were prepared. This is not expected; however, this phenomenon has been previously observed (Kruse et al., 1991). Oxygen values obtained by difference were found to be lower for air oxidized samples than for their precursors, while oxygen values obtained by direct measurement for the same air oxidized samples were higher than those of their precursors.

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

Inspection of Table 1 shows that the carbons treated with nitric acid have higher apparent densities than the other carbons. This is expected since treatment with nitric acid adds significant amounts of oxygen to the surface of carbons. Puri (Puri et al., 1965) found that the oxygen content of an outgassed charcoal could be increased to greater than 20% by oxidation with nitric acid.

Attention in the second year of this project was focused on a second series of carbons with differing surface chemistries. The four samples, DS405, DS525, DS725 and DS950, were produced by desorption of surface oxygen by heating nitric acid-oxidized samples of Calgon AC to 405°C, 525°C, 725°C and 950°C, respectively. The main objective is to evaluate the effects of an activated carbon's surface chemistry on aqueous adsorptive properties. In order to determine whether a relationship between the presence of specific surface groups and PNP capacity exists, the series of samples was characterized by temperature-programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS).

Temperature-programmed desorption (TPD) is an effective means to qualitatively and quantitatively analyze surface oxygen groups present on carbon. TPD of samples DS405, DS525, DS725, and DS950 and the carbon from which they were made confirmed that the overall amount of CO and CO₂ evolved diminished as the outgas temperature was increased. The results also reveal that significant amounts of CO₂-groups evolve at temperatures below 350°C for samples DS405 through DS950. This indicates that these samples most likely chemisorbed oxygen at room temperature after desorption to the elevated temperatures and this chemisorbed oxygen evolved upon heating as CO₂. In addition, some evidence shows that the samples which were heated to higher outgas temperatures, chemisorbed greater amounts of CO₂-evolving oxygen. Outgassing at increased temperatures may have provided a clean, reactive surface conducive to the formation of CO₂-groups which evolve below
350°C. It has been previously reported that surface oxygen is detrimental to the adsorption of PNP.

Surface oxygen did detract from PNP adsorption (Figure 2) but a difference in 1/n, a measure of the strength of adsorption, for the DS525 carbon prompted a quest for it meaning. Because this maximum in the strength of adsorption occurred in the temperature range known to be effective for producing catalytic carbon by air oxidation, and adsorption strength could be associated with catalysis, the decision was made to determine the temperature where the adsorption would be strongest and look for a correlation with catalysis. A second set of nitric acid-oxidized desorbed activated carbons (NAODACs) carbons was produced at 475°C, 525°C, 575°C and 625°C (Figure 2, right); 575°C appeared to be the temperature sought. NAODACs were also made from IBC-109 char and CC-char, the central focus of this project (see flow chart, Figure 3, left). The percent conversion in the vapor phase dehydrochlorination of 1,1,2,2-tetrachloroethane at 450°C over a bed of the carbon was used as a measure of catalyst activity for the set of 11 ACs (Figure 3, right). Surface area measurements indicated, as before, that little change is caused by the oxidative or desorptive treatments. However, there may be subtleties in the micropore distribution not distinguished by the method applied.

Catalyst activity correlations

XPS analyses were used to identify the surface atoms and determine the surface concentration of types of functional. Catalyst activity correlates well with several XPS surface values when the three carbons made from Calgon AC are considered alone. The activities of c1, c2 and c3, were 94%, 66%, 59%, respectively (Figure 3). These conversions are inversely related to the desorption temperatures, 525°C, 575°C, 625°C (Figure 2) in the temperature range covered here. Activity is close to being directly proportional to the % oxygen atoms on the surface as measured by XPS, 10%, 6%, and 6%, respectively (Figure 4). To see how well this relationship with oxygen atom coverage holds for all samples, consider carbons c, e, f and h as a group. They form a second tier of activities among the 11 carbons in this test series. Their conversions averaged 76% or about 80% that of c1 (94%). Their surface coverage of oxygen atoms, 9.3%, 10.8%, 4.9%, and 10.8%, respectively, are generally higher than the remaining samples that have lower catalyst activity and two are even higher than c1's 9.6%. The exception is carbon f. Despite having one of the lowest oxygen coverages it has one of the higher activities. Carbon b is the other carbon with less than 5% low oxygen coverage. Notice that f and b are related. They are both activated carbons made at 870°C. Their chemisorbed oxygen would be expected to be low because of the high temperature. The correlation coefficient for a linear regression analysis of the relationship of activity to surface oxygen for all 11
Figure 2. Freundlich equation plots for p-Nitrophenol adsorption on NAODACs produced at various temperatures.

Figure 3. Dehydrochlorination at 450°C of 1,1,2,2-tetrachloroethane to 1,1,2-trichloroethylene.
### Figure 4. Surface areas and surface atoms

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Area (m²/g)</th>
<th>Atom % on Surface (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calgon F-400, NA-oxidized, DS 525C</td>
<td>878</td>
<td>75</td>
</tr>
<tr>
<td>Calgon F-400, NA-oxidized, DS 575C</td>
<td>855</td>
<td>75</td>
</tr>
<tr>
<td>Calgon F-400, NA-oxidized, DS 625C</td>
<td>811</td>
<td>75</td>
</tr>
<tr>
<td>CC char, STM-ACT, Air-oxidized</td>
<td>648</td>
<td>75</td>
</tr>
<tr>
<td>CC char, STM-ACT, NA-oxidized, DS 575C</td>
<td>609</td>
<td>75</td>
</tr>
<tr>
<td>IBC-109 char, STM-ACT, Air-oxidized</td>
<td>580</td>
<td>75</td>
</tr>
<tr>
<td>IBC-109 char, STM-ACT, NA-oxidized, DS 575C</td>
<td>562</td>
<td>75</td>
</tr>
</tbody>
</table>

### Figure 5. Binding energy (eV) data from XPS analyses

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>C 1s (%)</th>
<th>O 1s (%)</th>
<th>N 1s (%)</th>
<th>S 2p (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calgon F-400, NA-oxidized, DS 525C</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
<tr>
<td>Calgon F-400, NA-oxidized, DS 575C</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
<tr>
<td>Calgon F-400, NA-oxidized, DS 625C</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
<tr>
<td>CC char, STM-ACT, Air-oxidized</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
<tr>
<td>CC char, STM-ACT, NA-oxidized</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
<tr>
<td>CC char, STM-ACT, NA-oxidized, DS 575C</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
<tr>
<td>IBC-109 char, STM-ACT, Air-oxidized</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
<tr>
<td>IBC-109 char, STM-ACT, NA-oxidized</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
<tr>
<td>IBC-109 char, STM-ACT, NA-oxidized, DS 575C</td>
<td>293.3 eV</td>
<td>294.5 eV</td>
<td>295.5 eV</td>
<td>296.5 eV</td>
</tr>
</tbody>
</table>
was low, only 0.41. The data support the view that a factor or factors in addition to the concentration of surface oxygen control catalysis.

Carbon d had an anomalous activity. It was expected to have a higher activity than c, because it was the desorbed member of the nitric acid-oxidized pair. It did not. Note that its oxygen coverage, 7.1%, is significantly lower than that of the NA-oxidized sample, 9.3%, from which it was made. This large drop (24%) was not seen for the pair of NA-oxidized carbons made from raw IBC-109 char, g and h. Char h retained 98% of its oxygen coverage during desorption to 575°C and its activity, 72%, was well above that of its undesorbed counterpart (57%). Why did NA-oxidized CC char lose surface oxygen more readily than NA-oxidized IBC-109? We speculate that the pore size distribution, perhaps the micropore size distribution, could be a factor. It was not possible to activate CC-char to as high a nitrogen surface area as was achieved from IBC-109 char. This suggests differences in the micropore structure of these carbons. Note that their initial nitrogen surface areas before activation were different. CC-char’s area was 10 m²/g. IBC-109’s area was only 1.4 m²/g.

Look now at the relationships among classes of functional groups and catalyst activity. Consider first only the three samples produced from Calgon AC, the first three in Figure 5. Activity is very close to being directly proportional for groups identified by binding energies of 286, 289, 536, 401 and 169 eV. These data suggest that catalyst activity may be related to the concentration of oxidized carbon (C-O and/or C=O), carboxyl groups, carbonate, ammonium derivatives, and sulfonates on the surface (Table 5). When a linear regression analysis is made for these binding energies for all 11 samples, only one appears to be significant, the 286 eV binding energy associated with oxidized carbon. The correlation coefficient indicates a better than 90% confidence level that a direct relationship exists (Figure 6).

![Figure 6. Catalyst activity and oxidized carbon groups](image)

**INVENTIONS**

Two disclosures of invention are an outcome of this work. The first was recognized during the first year and it was described in an ADDENDUM TO INTERIM FINAL TECHNICAL REPORT for the period
September 1, 1991 through August 31, 1992. The second was cited in the INTERIM FINAL TECHNICAL REPORT for the period September 1, 1992 through August 31, 1993 but enabling details were not given. We report for the first time the reduction to practice of the second invention showing how to produce an OAC catalyst by other than air oxidation at elevated temperatures. The engineering problems associated with the production and regeneration of an OAC catalyst by controlled air oxidation was an obstacle to commercial development of patents taken in the 1960s. The method of this second invention avoids the air oxidation at elevated temperatures where carbon burns readily, and scale-up of this new method is expected to be uncomplicated.

Novel Adsorber and Catalyst Support - Reduction to practice

An oxidized carbon surface that was produced by action of nitric acid on an activated carbon extracted zinc and copper very quickly from a water solution produced by contact of distilled water with a brass valve. XPS showed the metal masked two of the three nitrogen binding energy peaks. The two binding energies reappeared when the metals were removed by washing the carbons with hydrochloric acid. This was interpreted to support the view that the metal ions were deposited in the vicinity of active surface nitrogen atoms. This adsorption phenomena is projected to be observed with trace elements in contaminated water or any other organic/aqueous solutions. The phenomena is believed to involve pores in addition to the surface which can be seen by XPS, and the optimum dimensions are believed to be required for a given substrate. Amoco made preliminary tests to determine the effectiveness of the oxidized carbons for removing dimethylmercury (150 μg/ml) and triphenylarsine (110 μg/ml) from hexane solutions. The results are summarized in Figures 7 and 8. Material refluxed with 1 M nitric acid for 15 minutes was superior to untreated AC.

The inventors propose to use OAC surfaces having active nitrogen sites, including the type made for catalyzing elimination reactions, in two ways: 1) for removal of a wide range of environmentally objectionable trace elements found in coal from gaseous or liquid streams by passing them through OAC beds

<table>
<thead>
<tr>
<th>Table 5. Functional groups and their binding energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sulfates and sulfonates</strong></td>
</tr>
<tr>
<td><strong>Elemental and organic sulfur species</strong></td>
</tr>
<tr>
<td><strong>Hydrocarbon (C-C and C-H)</strong></td>
</tr>
<tr>
<td><strong>Oxidized carbon (C-O and C=O)</strong></td>
</tr>
<tr>
<td><strong>Carbonate/carboxylic carbon</strong></td>
</tr>
<tr>
<td><strong>Amines, alkylamines, aromatic amines and pyridines</strong></td>
</tr>
<tr>
<td><strong>Pyrolic nitrogen, amides and amino groups</strong></td>
</tr>
<tr>
<td><strong>Ammonium derivatives</strong></td>
</tr>
<tr>
<td><strong>Nitrites</strong></td>
</tr>
<tr>
<td><strong>Metal oxides</strong></td>
</tr>
<tr>
<td><strong>Numerous special carbon-oxygen species and superoxide (O2−)</strong></td>
</tr>
<tr>
<td><strong>Carbonates</strong></td>
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</table>
having the proper pore size distribution, and 2) for producing unusual catalyst supports for metals including, but not limited to, Ni, Co, Pt, Zn and Mo, that have potential applications as catalysts for the hydrogenation of coal-derived liquids.

Figure 7
Adsorption effectiveness for removal of Hg and As (1 g char/15 ml for 15 min)

Figure 8
Adsorption effectiveness for removal of Hg and As (3 g char/15 ml for 15 min)

Preparation of a Carbon Surface that Catalyzes Elimination Reactions Such as Dehydrochlorination of Alkyl Halides - Reduction to practice

Background - The use of an adsorption isotherm is a relatively simple method used to determine the feasibility of using granular activated carbon for a particular application (Cheremisinoff, 1978). The adsorption capacity of a carbon is frequently represented by the Freundlich equation:

\[ q_e = K C_e^{1/n} \]  
Equation 1

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 ([mg/g]·[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:

\[ q_e = (C_o - C_e) (V/m) \]  
Equation 2

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). Taking the logarithm of both sides of the Freundlich equation gives:

\[ \log(q_e) = \log(K) + 1/n[\log(C_e)] \]
This is the equation of a straight line whose slope is \(1/\lambda\) and whose intercept is \(\log K\) at \(C_e=1\). A plot of \(\log q_e\) against \(\log C_e\) yields a straight line of slope \(1/\lambda\), and \(1/\lambda\) is a measure of the strength of adsorption. An unexpected increase in \(1/\lambda\) for the sample produced at 525°C was observed in the series of desorbed samples produced as part of Peizoulof’s study of the adsorption of p-nitrophenol on his series of nitric acid-oxidized activated carbon (NAOAC) that had been desorbed at four temperatures (see plots on left of Figure 2). This stronger adsorption for the sample desorbed at 525°C is in the temperature range where the oxidation of carbonaceous materials with air produces the carbon catalysts for elimination reactions. Kruse questioned whether this increase in the strength of adsorption might correlate with the activity as an elimination catalyst. Could it be that the functional groups left on the surface at this temperature were not only the right groups but were also in the right geometrical relationships and at the right distances from one another to achieve an intensified degree of chelation of a host molecule? TPD data in the literature (Otake and Jenkins, 1993) that was called to Kruse’s attention by Anthony Lizzio added more credibility to the idea. The oxygen groups remaining on the surface of a NAOAC heated to the 500°C range appeared to be those that were produced by air oxidation in that same temperature range.

Before proceeding to testing the correlation of \(1/\lambda\) with catalyst activity, the phenomenon of the maximum \(1/\lambda\) was duplicated by another investigator, Ilham Demir, in the temperature range from 475°C to 625°C (see plots on the right of Figure 2). Because the maximum slope was at 575°C, this temperature was chosen to produce similar products from the two activated carbons featured in this proposal, i.e. activated carbon produced from IBC-109 coal and from the low-ash variety of this coal produced by the CC process (See Figure 3, carbons b and f, respectively). The diagram in Figure 3 shows the eight samples (letters a through h) made for a series of comparative tests of catalyst activity for the dehydrochlorination of 1,1,2,2-tetrachloroethane at 450°C. Three of the four desorbed samples produced from Calgon F-400 AC were also included in the battery of tests for which results are shown on the bar graph at the right of Figure 3).

The results demonstrated a reduction to practice of the invention for a catalyst which we are calling NAODAC (Nitric Acid-Oxidized Desorbed Activated Carbon) but there were surprises. The highest activity was produced at 525°C, a temperature lower than the 575°C that corresponded to the maximum \(1/\lambda\). We now believe that this may be the result of using an inappropriate "gauge" for strength of adsorption. We need to determine Freundlich constants for the 1,1,2,2-tetrachloroethane itself, or whatever the molecule to be catalyzed, not a larger molecule like p-nitrophenol. The NAODAC made from IBC-109 AC (h) compared favorably to the
NAODAC made from Calgon AC at the same desorption temperature, 72% and 66% conversion, respectively. The NAODAC from CC-char was an anomaly. The NAOAC gave a higher conversion (78%) than the NAODAC produced by desorption to 575°C. Because the catalyst was tested at 450°C, we should technically consider the NAOAC to be a NAODAC produced at 450°C. TPD would doubtless show considerable evolution of CO₂ at 450°C. This anomaly provides evidence that the properties of the activated carbon are parameters that should be considered in achieving the highest catalyst activity. The behavior of CC-solids from IBC-109 differed from that of the IBC-109 which had not gone through a dissolution step. It was not possible to make an activated carbon from the CC-solids that had as high a surface area as was obtained from IBC-109 char (See Figure 1). We believe detailed studies may show a difference in the micropore sizes and distribution which may be helpful in explaining why the optimum desorption temperature for an NAODAC from OAC is lower than that for NAODOC from IBC-109 char.

Catalyst preparation - A catalyst that is effective for catalysis of elimination reactions was produced from a suitable activated carbon by 1) treating the activated carbon with 1 molar nitric acid at its boiling point for 30 minutes, 2) washing the treated carbon with distilled water until the pH of the wash water remains constant, 3) drying the treated carbon at 100°C, 4) heating the nitric acid-treated carbon to 525°C in a flow of nitrogen gas, and 5) cooling the desorbed carbon to room temperature under a nitrogen gas atmosphere. This type of carbon will be designated NAODAC carbon to indicate its method of preparation, i.e. Nitric Acid-Oxidized Desorbed Activated Carbon. NAODAC catalyst was demonstrated to be effective for eliminating hydrogen chloride from 1,1,2,2-tetrachloroethane. A broad base of activity is expected including an ability to eliminate not only hydrogen chloride from alkyl halides but also other small molecules from organic compounds including water from alcohols, ammonia from amines, and hydrogen sulfide from mercaptans. NAODAC is also expected to catalyze certain types of polymerization.

An OAC, produced by air oxidation of carbons in the 500-700°C temperature range, was patented in the 1960s for dehydrohalogenation and polymerization (C.W. Kruse and G.C. Ray, Dehydrohalogenation of hydrocarbon halides, US Patent 3,240,834 March 15, 1966; J.E. Mahan, R.E. Reusser, C.W. Kruse, Dehydrohalogenation process US Patent 3,352,935, November 14, 1967; C.W. Kruse, Polymerization US Patent 3,437,695 April 8, 1969). Scale-up of the production and regeneration of the OAC by controlled air oxidation was difficult and this problem frustrated the commercial development. The method of this invention avoids the controlled air oxidation at elevated temperatures where carbon burns readily, and scale-up is expected to be uncomplicated. It should be possible to treat large beds of activated carbon with nitric acid, wash the bed and then heat
it to the appropriate activation temperature without opening the vessel.

The method of this invention has not been publicly disclosed. A paper has been submitted for the CLEAN COAL TECHNOLOGY Symposium sponsored by the Division of Fuel Chemistry at the 207th American Chemical Society National Meeting in San Diego, California, March 13-18, 1994 (Kruse, et al., 1994). In that paper we speculate on the kind of structure that may be catalytic but do not describe the NAODAC preparation. One paragraph of the paper reads:

"It is postulated that the observed catalytic activity may be the result of specialized spatial arrangements of specific functional groups within the pores of the carbon. XPS would not reveal special spatial arrangements of two or more functional groups on pore walls which may be responsible for catalysis. Figure 9 diagrams one of many arrangements that could catalyze elimination in high yields without rearrangement of the carbon skeleton. This lack of rearrangement was of special importance to the industrial research goals in the 1960s because biodegradability of commercial detergents depended on preserving the linearity of the olefins."

CONCLUSIONS

Coal particles dispersed in diesel fuel burned in the high-speed diesel engine used. Burning of the particles was demonstrated by the improved performance, and minor changes in the heat release profile on the cylinder burning slurry during testing at 2200 rpm with both the 20 and 35 wt % coal slurries in diesel fuel. The higher of the two speeds examined, 2200 rpm, was more favorable for slurry operation. At this speed, the fuel injection system maintained adequate fueling to the slurry cylinder (cylinder 2) and resulted in improved engine performance. Improvement in performance was demonstrated by 1) increased Net Indicated Mean Effective Pressure (IMEPnet), a measure of the measure of the power output of the cylinder, 2) maximum cylinder pressure, 3) exhaust temperature, and 4) thermal efficiency of cylinder 2; also, from the higher degree of combustion completion shown by the heat release analysis. At this speed, the slurry net heat release profiles were
practically identical to the diesel heat release profiles, indicating that coal particles successfully substituted for diesel fuel.

The base-line adsorption studies on a commercial carbon and six treated samples of this carbon showed that 1) oxygen values obtained by difference may be unreliable and may be inferior to TPD and XPS for quantifying the amount of surface oxygen on the carbons produced from low ash coal, 2) PNP adsorption isotherms for six treated samples indicate that oxidation of carbon with nitric acid decreases adsorption capacity while oxidation in air increases adsorption capacity, 3) TPD data confirmed that a carbon treated with nitric acid (HN100) had significantly more CO and CO desorbing groups than the as-received activated carbon (AR000).

Activated carbon samples were treated in different ways to produce a series having different surface chemistries. TPD studies of this series revealed 1) the overall amounts of CO and CO evolved diminishes as outgas temperature is increased and 2) increased outgas temperatures may provide carbon surfaces which preferentially chemisorb oxygen at room temperature and this oxygen will desorb as CO₂ below 350°C.

XPS experiments found a correlation at the 90% confidence level of catalyst activity for dehydrochlorination of 1,1,2,2-tetra-chloroethane with oxidized carbon (C-O and C=O) as indicated by the 286 eV binding energy. The correlation was less with percent of oxygen atoms seen on the surface by XPS.

Two inventions were made. The first discovery was that modification of an activated carbon's surface by nitric acid oxidation improves its ability to adsorb metal ions and organo metallics. This invention has practical implications for the control of trace elements, both for preventing their emissions into the environment and for their control in the chemical processing of hydrocarbons and related materials.

The second discovery was a new method for making a catalytic form of oxidized carbon for catalysis of elimination reactions. This method avoids air oxidation at high temperatures. It was the inability to control air oxidation for the regeneration of catalyst beds that frustrated the commercial development of the patents on oxidized carbon catalysts in the 1960s. The current work proved that a combination of chemisorbed oxygen functionalities introduced at temperatures below 150°C become catalytic as some are desorbed in heating to the 450°C to 575°C range. The highest activity catalyst was produced from a Calgon AC at 525°C. It appeared that the highest activity would have been achieved at a temperature below 525°C and above 450°C for the OAC made from low ash coal produced by the ChemCoal process. Additional work is needed to define conditions for making catalyst with the highest activity from
a given type of activated carbon. Despite a lower nitrogen surface area for activated carbon made from the ultra low-ash carbon, which was the focus of this project, it appears this deficiency with respect to adsorption does not carry over to catalysis.

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