Create a Consortium and Develop Premium Carbon Products from Coal

ANNUAL TECHNICAL REPORT

For Reporting Period Ending May 31, 2004

Principal Authors:
Frank Rusinko, Consortium Director, June 1998-December 2002
John Andresen, Consortium Director, January 2003-November 2004

Report Prepared By: Jennifer E. Hill, Harold H. Schobert, and Bruce G. Miller

Date of Submission: *January 2006*

Work Performed Under Cooperative Agreement No. DE-FC26-98FT40350

Submitting Organization: *The Energy Institute*
The Pennsylvania State University
405 Academic Activities Building
University Park, PA 16802-2398
Phone: (814) 863 8265
Fax: (814) 863 8892

ABSTRACT

The objective of these projects was to investigate alternative technologies for non-fuel uses of coal. Special emphasis was placed on developing premium carbon products from coal-derived feedstocks. A total of 14 projects, which are the 2003 Research Projects, are reported herein. These projects were categorized into three overall objectives. They are:

(1) To explore new applications for the use of anthracite in order to improve its marketability;
(2) To effectively minimize environmental damage caused by mercury emissions, CO_2 emissions, and coal impounds; and
(3) To continue to increase our understanding of coal properties and establish coal usage in non-fuel industries.

Research was completed in laboratories throughout the United States. Most research was performed on a bench-scale level with the intent of scaling up if preliminary tests proved successful.

These projects resulted in many potential applications for coal-derived feedstocks. These include:

- Use of anthracite as a sorbent to capture CO_2 emissions
- Use of anthracite-based carbon as a catalyst
- Use of processed anthracite in carbon electrodes and carbon black
- Use of raw coal refuse for producing activated carbon
- Reusable PACs to recycle captured mercury
- Use of combustion and gasification chars to capture mercury from coal-fired power plants
- Development of a synthetic coal tar enamel
- Use of alternative binder pitches in aluminum anodes
- Use of Solvent Extracted Carbon Ore (SECO) to fuel a carbon fuel cell
- Production of a low cost coal-derived turbostratic carbon powder for structural applications
- Production of high-value carbon fibers and foams via the co-processing of a low-cost coal extract pitch with well-dispersed carbon nanotubes
- Use of carbon from fly ash as metallurgical carbon
- Production of bulk carbon fiber for concrete reinforcement
- Characterizing coal solvent extraction processes

Although some of the projects funded did not meet their original goals, the overall objectives of the CPCPC were completed as many new applications for coal-derived feedstocks have been researched. Future research in many of these areas is necessary before implementation into industry.

TABLE OF CONTENTS

EXECUTIVE SUMMARY

The objective of these projects was to investigate alternative technologies for non-fuel uses of coal. Special emphasis was placed on developing premium carbon products from coal-derived feedstocks. A total of 14 projects, which are the 2003 Research Projects, are reported herein. These projects were categorized into three overall objectives. They are:

(1) To explore new applications for the use of anthracite in order to improve its marketability;
(2) To effectively minimize environmental damage caused by mercury emissions, CO_2 emissions, and coal impounds; and
(3) To continue to increase our understanding of coal properties and establish coal usage in non-fuel industries.

Each of these topics had a broad range of subtopics that was the result of individual research projects. These subtopics are project-specific and include developing high-value carbon fibers and foam via processing of a low-cost extract pitch with well dispersed nanotubes, determining the feasibility of recyclable PACs, and exploring the mechanisms of carbon-catalyzed reactions to design carbon catalysts for additional reactions. Many other subtopics were also explored in this research, and are discussed in the individual final reports for the 2003 projects.

Research was completed in laboratories throughout the United States. Most research was performed on a bench-scale level with the intent of scaling up if preliminary tests proved successful.

The overall success of the projects initiated by the CPCPC was astounding. Most projects successfully met their objectives and those that did not still documented and provided information useful for the growth of the carbon industry outside of fuel-related applications. Many applications for carbon were determined such as:

a. Use of anthracite as a sorbent to capture CO_2 emissions
b. Use of anthracite-based carbon as a catalyst
c. Use of processed anthracite in carbon electrodes and carbon black
d. Use of raw coal refuse for producing activated carbon
e. Reusable PACs to recycle captured mercury
f. Use of combustion and gasification chars to capture mercury from coal-fired power plants
g. Development of a synthetic coal tar enamel
h. Use of alternative binder pitches in aluminum anodes
i. Use of Solvent Extracted Carbon Ore (SECO) to fuel a carbon fuel cell
j. Production of a low cost coal-derived turbostratic carbon powder for structural applications
k. Production of high-value carbon fibers and foams via the co-processing of a low-cost coal extract pitch with well-dispersed carbon nanotubes
l. Use of carbon from fly ash as metallurgical carbon
m. Production of bulk carbon fiber for concrete reinforcement
n. Characterizing coal solvent extraction processes

These applications and many others enable the coal industry to diversify and find moneymaking opportunities outside of the fuel industry. In addition, many of the above mentioned applications use low marketed or waste coals as the feedstock. Also of importance are the environmental benefits these solutions provide. By minimizing coal waste streams and more effectively controlling emissions, the coal industry becomes much more environmentally responsible.

Additional research is needed for these projects as they were only done on a small scale. This research would be beneficial in determining the extent to which these applications can be commercialized and as a basis for an economical analysis. Indeed, these results are most promising.

INTRODUCTION

The overall purpose of the Consortium for Premium Carbon Products from Coal (CPCPC) is to explore new methods and uses for coal outside its traditional use as a fuel. In order to achieve this, three main objectives were the focus of the 2003 projects. They are:

1. To explore new applications for the use of anthracite in order to improve its marketability;
2. To effectively minimize environmental damage caused by mercury emissions, CO_2 emissions, and coal impounds; and
3. To continue to increase our understanding of coal properties and establish coal usage in non-fuel industries.

Using these objectives as guidelines, research was conducted in many different areas and ranged from the possible uses of coal impound ponds to producing high-value carbon fibers and foam using low-cost pitch feed stock.

Within each of the three overall objectives there are many individual goals. These individual goals are summarized below

For **Objective 1**: *To explore new applications for the use of anthracite in order to improve its marketability*, the goals are:

- To explore the mechanisms of two carbon-catalyzed reactions in order to develop the knowledge needed to design a carbon catalyst for existing commercial reactions,
- To develop a method for anthracite exfoliation that is safer than using perchloric acid and to test the exfoliated anthracite as an electrode material,
- To improve the properties of coal-based electrodes and cathodes to maintain and expand the usage of anthracite coal in carbon products, and
- To synthesize high-surface-area powdered anthracites, impregnate them with amine compounds, and determine the feasibility of using these materials for CO_2 capture.

For **Objective 2**: *To effectively minimize environmental damage caused by mercury emissions, CO_2 emissions, and coal impounds*, the goals are:

- Determine the feasibility of using high-surface-area powdered anthracites impregnated with amine compounds for CO_2 capture,
- To determine the feasibility of the removal and recovery of mercury that is sorbed to powered activated carbon (PAC) from coal combustion power plant flue gas streams,
- To develop activated carbon sorbents from coal chars to determine their mercury capacity and compare them to commercially activated carbons, and
- To develop activation techniques for coal recovered from coal slurry water and treatment of coal slurry water to National Pollutant Discharge Elimination System (NPDES) standards.

And finally, for **Objective 3**: To *continue to increase our understanding of coal properties and establish coal usage in non-fuel industries*, the goals are:

- To determine if cyclone-fired boilers can produce fly ash with sorptive potential, activated carbon potential, or metallurgical carbon potential,
- To assess performance improvements associated with the addition of fiber reinforcement in concrete,
- To produce high-value carbon fibers and foam from low-cost extract pitch with well-dispersed carbon nanotubes,
- To use solvent-extracted carbon ore (SECO) to fuel a fuel cell,
- To determine the performance of additional binder pitches, the physical and chemical properties of anode butts, and the interaction between the pitch and different parts of the anode butt,
- To determine what petrographic, physical, and chemical characteristics of bituminous coal lead to the production of maximum yield in N-methylpyrrolidone (NMP),
- To produce a coal extract surrogate for conventional coal pitch, and
- To develop a synthetic coal tar enamel that closely matches commercial products.

The objective of this report is to summarize the findings and conclusions produced as a result of the 2003 projects and to show how each of the projects undertaken meets the objectives of the overall consortium. This will be accomplished in the following format: experimental work will briefly be summarized and referenced to specific projects, overall results will be discussed, and conclusions will be drawn from those results.

EXPERIMENTAL

Experimental work was completed in university and industrial facilities across the country. In each setting, experimental work was completely documented such that additional work could be completed based on the initial work being done. Some experiments were designed and completed in only one facility whereas others were sent to multiple facilities for work. Each experiment followed standard procedures found in literature or common in industry. All equipment used was either thoroughly documented or the standard used in the given application. Accidents and injuries were kept to a minimum by following the required safety guidelines. Most experimental work was done on a bench-scale level with the intent on continuing research if initial tests were deemed successful. For further information on the experimental set-up of individual projects, reference can be made to the project's final report. (See Appendix A for the final reports of the 2003 projects).

RESULTS AND DISCUSSION

This section discusses the results found under each of the three overall objectives and explains their significance to the coal/carbon industry.

Objective 1: To explore new applications for the use of anthracite in order to improve its marketability

Testing done to fulfill this objective shows promising results. Through these tests, it has been found that there are many possibilities for additional uses of anthracite. These opportunities include: use as a sorbent to capture CO_2 emissions, use of anthracite as a carbon catalyst, and use of processed anthracite in carbon electrodes and carbon black. These findings will be explained in more detail below. In addition, exploratory experiments were done to determine the ability to exfoliate anthracite, but were inconclusive, leaving room for additional studies in that area.

Anthracite Sorbents for CO_2 Capture

Because the costs of CO_2 separation and capture are so significant in the fossil fuel industry, there is a demand for more revolutionary capture technologies. Currently, new solid-based sorbents are being investigated; however, the supports used so far (including commercial molecular sieves and activated carbons) are very expensive, making the process uneconomical. This results in a need for low-cost precursors that can compete with expensive commercial supports, and to develop effective solid sorbents that can easily be regenerated. Due to the inherent chemical properties, fine porosity, and relative low price, anthracites would be ideal as sorbent precursors for activated carbon.

Three Pennsylvania anthracites were used in this study. They were activated with steam in a fluidized-bed reactor. The activated anthracites had a highly developed micropore structure (based on nitrogen adsorption isotherms at 77 K), with some mesoporosity. The optimum activation time was three hours, and it was possible to obtain surface areas approaching 800 m^2/g for activation at 800°C, and exceeding 900 m^2/g at 850°C. Interestingly, longer activation times actually reduced surface area as did increasing the activation temperature to 890°C. Surface area alone, however, is not the only part of the story. The anthracite with the highest CO_2 adsorption capacity (66 mg CO_2/g anthracite) was one with a surface area of only 540 m^2/g. Very likely, the crucial relationship is not the absolute pore volume or surface area, but rather that between microporosity and the CO_2 physisorption process. This is further substantiated by the fact that CO_2 adsorption results are not a linear function of surface area. Both ammonia treatment and polyethylenimine impregnation can increase CO_2 capacity, presumably due to the introduction of basic nitrogen-containing functional groups on the anthracite surface. The impact of these reagents on surface area is different, with ammonia treatment increasing surface area, but polyethylenimine causing a drastic decrease (likely by simple physical blocking or occlusion of pores). Again it can be seen that surface area alone is not a reliable indicator of the performance of activated anthracite in CO_2 adsorption.

These results are significant, in that anthracite is a fairly inexpensive feed source for activated carbon and shows potential in the CO_2 capture process.

Development of Anthracite-Based Catalyst

Being able to use anthracite or other forms of carbon as catalysts in place of metal has many benefits. Specifically, anthracite is a low cost material, has reasonably low chemical and electrochemical reactivity, and has an easily reproducible and controllable surface chemistry. The preliminary results show promise in the area of carbon catalysts.

The principal goal of this work was to obtain additional information on the catalytic mechanisms of the reduction of nitrobenzene to aniline by hydrazine and the decomposition of hydrazine. Understanding how these reactions are catalyzed by carbons then opens up the possibility of using anthracites (or other coals or coal-derived products) as catalysts for these reactions. Further, the possibility of carbon catalysis, or even catalysis by coals, could then be extended to other reactions.

The catalytic activity of various commercial carbons (activated carbons, carbon blacks, charcoals, and graphite) was investigated for both reactions, in refluxing *iso*-propanol. The specific reactions of nitrobenzene reduction and hydrazine decomposition are easy to study, by measuring the production of gases as a function of time in a simple gas burette. All of the carbons tested catalyzed both reactions. Reaction rates were proportional to the catalyst concentration and increased with surface area, but were independent of stirring conditions. These observations suggest that the reactions may be surface-controlled. For the specific case of nitrobenzene, an effect of pore diffusion cannot be ruled out, because of a near-linear relationship between initial reaction rates and external surface area and pore volume of the carbons.

For both reactions, the activity of the carbon catalysts varied linearly with the surface area and with the bulk oxygen content (at low oxygen contents). The dependence of activity on surface area actually plots as two straight lines, depending on whether the carbons are acidic or basic. This is an indication that the adsorption of hydrazine and nitrobenzene is affected by two different types (i.e., acidic or basic) of oxygen functional groups.

Hydrazine decomposition is first order at low concentrations of hydrazine, but changes to zero-th order at higher concentrations. The kinetics of nitrobenzene reduction also show a change in order, from a fractional positive value of low nitrobenzene concentrations to a fractional negative one at higher concentrations. The kinetics of the nitrobenzene reaction are complicated by the fact that hydrazine is simultaneously undergoing decomposition on its own and is involved in the reduction of the nitrobenzene. Presumably the hydrazine decomposition begins with a Langmuir adsorption (the slow step) of hydrazine non-dissociatively onto the carbon surface. Subsequently, these adsorbed hydrazine molecules react with other hydrazine molecules still in the solution phase. The rate-determining step in the nitrobenzene reduction is a reaction between an adsorbed nitrobenzene molecule and an adsorbed hydrazine, following the well-known Langmuir-Hinshelwood model.

Processing of Anthracite Coals for Carbon Products

In order to increase productivity, both aluminum and silicon smelters are significantly raising the power input into the smelting furnaces. For this reason, the property requirements for carbon electrode and carbon blacks are becoming more stringent. Without improvement, current anthracite markets will not be able to meet these standards.

Testing in this area showed that heat treatment of anthracite coals is effective at upgrading the coal quality. In addition, testing showed that the optimum temperature range for anthracite use in carbon electrodes and carbon blacks is between 2300º and 2700ºC.

The optimal heat-treatment temperature is in the range of 2300–2700°C. Little additional improvement is obtained by pushing to 3000°C. Heat treatment of electrically calcined anthracite (ECA) has two effects. One is a "true graphitization" that improves the crystallinity of regions essentially free of mineral constituents; the other is a catalytic graphitization effected by the minerals (or vaporized ash-derived species). The amount of "catalytic graphite" increases with increasing heat treatment temperature. X-ray diffraction, electron microscopy, "real" and helium densities, and optical microscopy studies are all consistent with this.

For aluminum smelters, cathodes made from anthracite treated at higher temperatures have lower ash content, lower with-grain CTE, lower sodium uptake, and higher thermal conductivity. They also have more resistance to electrolytic attack. For silicon smelters, electrodes made from the anthracites having higher heat treatment temperatures have better thermal shock resistance. Fracture toughness tests were inconclusive.

If existing ECA furnaces were operated at higher temperatures and with more uniform temperature distribution internally, the results of this work could possibly be implemented. Of course, a detailed economic assessment of the cost would be essential.

Overall

Overall, these tests show possibilities for anthracite usage in commercial areas where anthracite has not traditionally been used. Additional research on a larger scale is needed in these areas along with economic analysis to determine the feasibility of implementation.

The significance of these tests should not be overlooked as there is the potential of both saving industry money and opening up new markets in the anthracite industry. Both parties are benefited by these findings.

More additional information on these findings can be found in the final project reports in Appendix A:

"Anthracite Coal for Cathode/Electrode Applications in Aluminum/Silicon Smelters"
"Development of Anthracite-Based Carbon Catalysts"
"Novel Anthracite Sorbents for CO_2 Capture"
"Potential Applications for Exfoliated Anthracite: Filler in Cathodes"

Objective 2: To effectively minimize environmental damage caused by mercury emissions, CO_2 emissions, and coal impounds

The testing associated with this objective was generally successful. Many aspects of these experiments have significant results for helping the coal industry to meet environmental regulations. Specifically, it was found that anthracite can be used as a sorbent to capture CO_2 emissions, slurry water is treatable through the use of TiO_2, raw coal refuse can be used as activated carbon, reusable PACs are a distinct possibility, and there are possibilities for the use of activated carbon to capture mercury from coal fired power plants. Each of these results is further explained below.

Sorbents for CO_2 Capture

Anthracites have inherent chemical properties, fine pore structure and relatively low price that makes them excellent raw materials for the production of premium carbon products, such as for the synthesis of CO_2 sorbents. The President's Global Climate Change Initiative commits to reduce greenhouse gas intensity by 18% over the next ten years. However, the costs of current CO_2 separation and capture technologies are estimated to be about 75% of the total cost of ocean or geological sequestration. Furthermore, the demand to develop revolutionary direct capture technologies has also been identified by the U.S. DOE. The use of anthracite in this role has been discussed in Objective 1, above.

Metal Treatment in Slurry Water

Coal slurry impoundments hold the effluents from washing processes that coal producers perform on raw coal once it is brought to the surface. The result is usually a large amount of highly acidic water combined with solid particulate matter, contained by dams. Unfortunately, the containment dams are sometimes designed, causing overflows during storms and leakage. These problems are dangerous and costly. Consequently, research was done to determine the feasibility of remediation of the coal slurry water through various means.

It was found that the use of activated carbon was unsuccessful in removing the metals from the slurry water. Also, pretreatment of the water by exposure to UV radiation proved unsuccessful. However, treatment with TiO_2 photocatalyst, with or without UV exposure, was successful under some experimental conditions. Specifically, the pH of the water was an important factor in metal removal. Increasing the pH from 2 to 6–7 precipitated most of the iron and aluminum from solution. Manganese remained in solution because it is soluble to pH 10. Therefore, an additional treatment step would be needed to remove manganese.

Further research is underway to continue to find a cost-effective way to treat coal slurry water. This work shows promising results in impound remediation. In addition, this research is significant to all coal-fired power plants with coal slurry water impoundments. By finding a method to treat this waste, and possibly market some of it, the coal industry will spend less money cleaning up dangerous impoundment overflows, benefiting both industry and the environment.

Raw Coal Refuse for use as Activated Carbon

In addition to the project explained directly above, raw coal refuse was tested to determine the feasibility of its use for activated carbon production. Raw coal received from impoundment had exceptionally low surface areas, on the order of 1 m^2/g. Steam activation at 840–950°C for 2–3 hours resulted in surface areas of 69–137 m^2/g, well below the values of ≥ 600 m^2/g characteristic of commercial coal-derived activated carbons. Chemical activation, using phosphoric acid or sodium hydroxide, produced carbons with surface areas of 260 and 324 m^2/g, respectively, an improvement but still well below values for commercial carbons.

Use of a proprietary third-party treatment with hydrofluoric acid, followed by steam activation at 850–950°C for 2–5 hours produced carbons with surface areas in the range of 382–850 m^2/g. Interestingly, analogous CO_2 activation experiments failed to develop significant porosity in these carbons. The HF chemical pretreatment costs an estimated $0.01/lb. The raw material normally used for activated carbon production is ≈\$0.04/lb. Since the raw coal refuse is nominally of no cost, or even of negative value, this work suggests that the HF-treated coal could potentially serve as a raw material for activated carbon production.

Reusable PACs for Mercury Capture

Due to the new EPA regulations regarding mercury emissions and the negative effects of mercury on water supplies in the world it has become necessary to find ways to control mercury emissions in a cost effective manner. One possibility that is being explored is the use of PACs; however, the current production capacity for PACs is only 10% of the capacity that is necessary to meet these regulations. Therefore, it is desirable to design a PAC system that can be recycled.

Results from this testing show that a recyclable PAC system is indeed feasible. The thermal desorption process involves heating for 30 minutes at 550^{o} C in inert atmosphere. This system will save operating costs by allowing the same PAC to be used over and over instead of being discarded. In addition, mercury was removed from the PAC during the recycling stage of the process. This mercury can then be purified and sold for other applications. Therefore, this system not only saves in operating costs, but allows a potentially hazardous material to be sold instead of disposed.

This work is important to coal-fired power plants because it allows an economical method of mercury control. Additional testing is needed on a larger level and determine what must be done before this process is marketable.

Activated Carbon for Mercury Capture

For the same reasons explained above, research is being done to determine feasible methods for mercury capture. In this work, it was found that fly ash carbons from coal-fired power plants have the potential to capture mercury if they have mesoporous structure (about 50% mesoporousity on a surface basis or 75% on a volume basis) and oxygen and halogen functional groups. Although the chars used in this work had varying levels of mercury capture, values of 1.85 mg/g were obtained, not far off the value of 2.77 mg/g for a commercial activated carbon. They are a potentially low-cost sorbent and addition testing should be done. If additional testing proves successful, fly ash could be a potential new source of material for mercury capture. This would also benefit coal fired power plants and the economy.

Overall

Overall, these projects show potential for mercury capture, CO_2 emissions treatment, and coal water slurry treatment. These treatments would be beneficial to the environment and to the coal industry. Each of these projects focused on either cost-effective treatments or treatments that could actually save the power plant money.

Additional research is necessary to determine the feasibility of these findings in industry as most of these tests were run on a bench-scale level. For more information on these tests, see the final project reports listed below.

"Novel Anthracite Sorbents for CO_2 Capture"
"Remediation of Coal Impounds: Efficacy of Coal for Activated Carbon"

“Processing and Reuse of Activated Carbon Used to Adsorb Mercury from Power Plant Flue Gases”
“Use of Coal Gasification and Combustion Chars for Mercury Capture”

Objective 3: To continue to increase our understanding of coal properties and establish coal usage in non-fuel industries

The testing done to fulfill this objective was much more varied that the testing done for the previous two objectives. Many different types and forms of coal were tested for use in an equally many new ways. These tests explore many aspects of coal and coal byproducts being used for new applications. Specifically, these tests focused on: development of a synthetic coal tar enamel, the study of alternative binder pitches in aluminum anodes, the use of SECO to fuel a carbon fuel cell, the production of a low-cost coal-derived turbostratic carbon powder for structural applications, development of nanotube-enhanced coal extract pitches, investigation of new fly ash sources for metallurgical carbon, and characterizing coal solvent extraction processes. In addition, research into the benefits of using pitch-derived fibers to reinforce concrete concluded that there were no real benefits associated with the addition of these fibers. These results are discussed in further detail below.

Development of Synthetic Coal Tar Enamel

Coal tar enamel is used as coatings for pipelines and other objects that require protection from environmental conditions. Currently the pitch component of coal tar enamel is obtained from the high-temperature carbonization of coal during the production of metallurgical coke and as such is similar to coal tar binder pitch. Because domestic coke production is predicted to decline there is a need for alternate sourcing.

A synthetic coal tar enamel was prepared using solvent-extracted pitch and a commercial “heavy oil.” The pitch was prepared by extracting a West Virginia bituminous coal with tetralin, followed by de-ashing with N-methylpyrrolidone. It was blended with a commercial coal tar distillate called “heavy oil.” Most of the properties of the synthetic enamel are within the specifications of commercial products. The synthetic enamel is more volatile than the commercial product, but not so much so that it would not be usable. Penetration values were lower than for commercial enamels, but not out of specification range. The synthetic enamel can serve as an adhesive for carbon foam–steel composites. Cathodic disbonding tests were not as good as for the commercial enamel. On the whole, however, the overall good results show great promise for this synthetic material.

This research provides additional uses for coal-derived heavy oils and partially solves the problem of declining coke production for coal tar enamels. In addition, this research shows the possibility of synthetic coal tar enamel being used in multiple applications, adding to its appeal as a marketable resource.

Binder Pitches in Aluminum Anodes

Traditionally, coal tar binder pitches were obtained from coal tars that come as a byproduct of bituminous coal coking processes. With this supply declining, it was proposed to find alternate binder pitches.

Research in this area concluded that petroleum pitch offers potential to be used as an additive to the standard coal tar pitches for use as binders in aluminum anode production. Three anode butts were also studied in this project. X-ray CT scanning, pore volume, and density measurements showed a decrease in apparent density but increase in absolute density and specific pore volume from the center of the butt to the surface. Experimental laboratory-scale anodes made from the top and bottom of the butt materials gave lower apparent green densities than anodes made from the middle part of the butt. These results correlate with the high porosity of the top and bottom of the butt materials, which inhibited pitch penetration into the pores. Anodes made from a pitch mixture that contained 20% petroleum pitch and 20% gasification pitch (with standard coal tar pitch) gave comparable baked densities to those made using 100% coal tar pitch.

This research provides possibilities for alternate binder pitches to replace a diminishing supply. Additionally, this research finds alternate uses for petroleum pitch, coal-extracted pitch, and gasification pitch.

Use of SECO in Carbon Fuel Cells

Research was focused on producing a low cost coal-derived turbostratic carbon power and testing it in a carbon fuel cell. The carbon fuel cell produces electrical power through the combustion of carbon with oxygen from ambient air. The products are carbon dioxide and electricity. Turbostratic carbon with microscopic domain size of 30nm or smaller and an ash value less than 0.5% is ideal for the carbon feed of the fuel cell. Research was done to determine the feasibility of a low-cost coal-derived feedstock.

The results showed that a significant reduction in the volatile matter to less than 10% was necessary before the created samples were usable. Heat treatment at 800º C was found desirable as carbon that is more conductive was obtained at higher heat treatments. SECO heat-treated at 800º C has a volatile matter content of 4%, carbon content of 89%, ash yield of 0.3%, and resistivity of 29 ohm-cm. After heat treatment, the SECO showed favorable performance in the carbon fuel cell. It was determined that the low ash characteristic (<0.3%) apparent in these SECO samples makes them very attractive for this application. Additional research in this area will further determine the success of using turbostratic carbon power in fuel cells.

Development of Turbostratic Carbon Powder for Structural Purposes

Again, it was determined that development of low cost coal-derived turbostratic carbon powder had potential as a use in structural processes. Carbon foams consisting of oxidized SECO samples and coal tar pitch were made and their properties were assessed. A crush test was conducted on the sample and resulted in a value of 12.3 MPa. The foam had a density of 0.87g/cm^3. These results were comparable to other carbon foams produced from a variety of feedstocks.

This research is significant in demonstrating yet another application of coal-derived turbostratic carbon. If this product can be produced at a lower cost than the other foams then substantial savings could be made. An economic analysis to this extent should be performed. In addition, further research should be done to optimize the combination of SECO and coal tar pitch for this application.

Nanotube Enhancement of Coal Extract Pitches

High-performance pitch-based carbons are typically made from mesophase pitch; however, the high processing costs and low yields associated with the production of mesophase pitch makes the pitch expensive to produce. Therefore, research was conducted to determine the feasibility of producing high-value carbon fibers and foams via the co-processing of a low-cost coal extract pitch with well-dispersed carbon nanotubes. The testing results on nanotube-doped materials were mixed. For epoxy-coated pitch and pitch/nanotube composite fibers, in one case addition of nanotubes enhanced tensile strength and had no effect (within experimental error) on elastic modulus. However, for a different fiber, tensile strength decreased. A 2% loading of nanotubes increased the thermal diffusivity by about 30% in the range 25–700°C. At 25°C, for example, thermal diffusivity increased from 1.335 mm^2/s to 1.483 with the nanotubes added. For carbon foams derived from pitches, the effect of nanotube addition on bulk density, porosity, and open-cell volume was strongly dependent on the nature of the original pitch. As an example, the addition of nanotubes to Ashland A-240 pitch increased bulk density of the resulting carbon foam from 0.34 to 0.41 g/cc, but, using a coal-based synthetic pitch, the respective values showed a decrease in bulk density, from 0.42 to 0.34 g/cc. Nanotube addition to pitch seemed to have little effect on the compressive yield strengths of carbon foams. For example, with a foam derived from a synthetic pitch, the compressive yield strength was 2.5 MPa without nanotube addition to the pitch, and 2.7 MPa with addition.

If further research proves successful, then the ability to produce higher value materials with a small addition of nanotubes could result in materials of high commercial and military interest. Some examples may include: structures, thermal management, and electromagnetic shielding. This research shows the potential for exceptional cost savings in this application.

New Fly Ash Sources for Metallurgical Carbon

Carbon with an LOI higher than 80% has the potential to be used in electric arc furnaces (EAF). Carbon added to the EAF makes it more energy efficient, increases its refractory life, and minimizes nitrogen and hydrogen in steel. Fly ash from Reliant Energy’s Niles cyclone boiler (CB) is currently being marketed as metallurgical carbon for the above explained use. However, increasing demand of this carbon has initiated research to find other CBs that have fly ash similar to Niles. In all, 36 plants were contacted. Of these 14% make marketable carbon material, 14% make marginal carbon material, 29% have fly ash unsuitable for carbon marketing, 14% currently already market their fly ash, 19% were geographically undesirable, and 10% did not cooperate. These findings show there is a potential for the market of fly ash from CB power plants. This would enable a current waste stream to be recycled into a useful application with the potential for significant cost savings.

Characterization of Coal Solvent Extraction Processes

It was desirable to determine what petrographic, physical, and chemical characteristics of bituminous coals leads to the production of maximum extraction yield in NMP. It was found that coals with mean maximum vitrinite reflectance below 1.0 were difficult to process by filtration because they were colloidal in nature. In addition, those above 1.2 processed well by produced only moderate extraction efficiencies. Those most suitable for NMP extraction exhibited vitrinite reflectance of about 1.10. Yields of extract were nearly 75% in this case. Additional testing showed that low ranking bituminous coals were most affected by NMP in terms of physical alteration. Finally it was found that the coals most suitable to NMP extraction exhibited Gieseler plasticity of about 30,000 dial divisions per minute, produce free-swelling indexes up to 9, and exhibited Audibert-Arnu dilatation of about 300%. Coals with these characteristic usually fall in the hvA bituminous rank. These findings are significant in understanding NMP extraction processes more fully.

Overall

Overall, these research projects show great potential for alternate uses of coal. There are many applications for coal and coal-derived products made available through this research. Additional research should be done in these areas as they were conducted on a small scale and must be scaled up to determine the full potential. For further information on these projects, refer to the final reports listed below.

“Synthetic Coal Tar Enamel Using Solvent Extraction”
“Binding Efficiency of Coal-Derived Binders Towards Anode Butts”
“Turbostratic Carbon Powder”
“Nanotube Enhancement of Coal Extract Pitches: Fibers and Foams”
“Expanding Supply for Fly Ash Derived Carbons”
“Characterization of Coal Solvent Extraction Processes using Petrographic, Chemical, and Physical Methods”
“Pitch Derived Fiber Reinforced Fly Ash Concrete”

CONCLUSION

Research performed under the direction of the CPCPC (i.e., the 2003 research projects) led to the completion of 14 research projects. These were performed in order to expand the use of coal outside the traditional fuel industry. From these projects significant results were found, which have the possibility to open new markets to the coal industry, develop new methods for helping the coal industry to be more environmentally friendly, and to understand coal properties and characteristics at a new level. Future research in these areas based on this initial research could result in a much more diversified coal industry.

APPENDIX A: *List of Final Reports for 2003 Projects*

POTENTIAL APPLICATION FOR EXFOLIATED ANTHRACITE: FILLER IN CATHODES
Final Report

Start Date: March 1, 2003
End Date: June 30, 2004

Principle Investigator: Dr. Caroline E. Burgess Clifford
Report Issue: July 15, 2004

Internal Agreement No. 2486-TPSU-DOE-0350,
For Award No.: DE-FC26-98FT40350

The Energy Institute
Penn State University
209 Academic Projects Bldg.
University Park PA 16802

DISCLAIMER

ABSTRACT

Anthracite has some unique properties as a carbon, but it also has similar properties to graphite as well. Graphite is known to exfoliate, and exfoliation of graphite improves its electrical properties. Therefore, it was thought that exfoliation of anthracite may improve its electrical properties. Exfoliation of anthracite can be accomplished by intercalating perchloric/nitric acids and exfoliating at temperatures of 700-800°C.

However, three factors inhibit the use of exfoliated anthracite as an electrode material. First, with perchloric acid having such explosive properties, scaling the process up to an industrial scale is not feasible. The second factor is there is no basis for choice of a particular anthracite coal because it is not known which properties make anthracite able to be exfoliated. Finally, the only application that exfoliated anthracite has been tested for is as an activated carbon; we anticipate that exfoliated anthracite would be useful in many applications.

The main goal of the current project was to develop a method for anthracite exfoliation that would be safer than with using perchloric acid. Once a method was established, we expected to apply exfoliation to different anthracite coals, and to test the exfoliated anthracite as electrode material.

Several methods of exfoliation were tested, all methods that are known to be successful on graphite. Details of the methods tested are included in the report. The methods could be classified into three types: graphite oxidation, graphite reduction, and methods that required no oxidation or reduction. Exfoliation using acid intercalation was considered an oxidation method, and exfoliation using alkali metals was considered a reduction method.

We successfully exfoliated coal using oxidative methods, particularly the perchloric/nitric acid method in order to determine coals amenable to exfoliation. We successfully exfoliated Summit and Hongay coals using this method, both semi-anthracites. Several coals were obtained from FB Leopold; however, no more coals were tested using this method because of the explosive nature of perchloric acid.

Marginal success was obtained in exfoliating Summit coal using two methods: intercalation using sulfuric/nitric acids with exfoliation at 700-800°C and intercalation by electrochemical oxidation and sulfuric acid with exfoliation at 700-800°C. More data was needed to determine the extent of exfoliation (surface area characterization), but data was not obtained by publication date of this report. Information from the surface area data would be useful in determining the best conditions for anthracite exfoliation.

Graphite reduction exfoliation methods were tested, but were not successful. We were not successful exfoliating anthracite using alkali metals. While it is possible modification of these methods could induce exfoliation, we did not have time to explore further.

Materials were sent to Carbone to make test electrodes, but data was not available by the publication date of this report. Therefore, we could not determine if exfoliated anthracite would make a good electrode material.

TABLE OF CONTENTS:

INTRODUCTION

Anthracite is an abundant and inexpensive natural resource that has not been fully exploited as a useful material. Historically, anthracite coal has been used as a slow-burning, high heating value fuel. It had a use for domestic heating and cooking, as well as industrial applications in iron smelting.[1] Production peaked at 100 million tons per year in 1917 and 1918[2], but now appears to have stabilized at about 3.2 million tons in 1999.[3] More recently, it has found a market as a water filter medium, but only anthracite obtained as-mined is used because of the difficulty (and expense) in grinding.

Anthracite is an intriguing feedstock for premium carbon materials. Most anthracites contain 92–98% carbon, virtually all of which is present as aromatic carbon in large polycyclic sheets.[4] These sheets may contain thirty or more fused aromatic rings,[5,6] resulting in extraordinary properties such as highly ordered carbon that also exhibits a high ultra-microporosity pore volume. Exploiting one or more of these properties of anthracite to produce value-added products offers the potential for developing new markets for this resource.

Typically, anthracites have been most important in amorphous based cathodes, as these cathodes have a moderate thermal conductivity and electrical conductivity, while having high abrasion resistance and crushing strength.[7] Amorphous cathodes can also be made of mixtures of anthracites and graphite, which seems to improve on the properties of anthracite alone. Semi-graphitic carbon blocks have been accepted as replacements for anthracite blocks because they have some improved properties similar to graphitized blocks but are not as costly. If there were a way to increase the thermal conductivity and reduce the electrical conductivity of anthracite without increasing the cost significantly, the material would indeed be desirable to the aluminum and steel industries.[7]

Recently, we have been exploring the exfoliation of anthracite[8-11], a method to cause “flaking” or “breaking apart” of the anthracite, in order to react or structurally reform the original material. We anticipate that by either breaking apart or even opening up the pore structure of the anthracite, that with application of heat, the structure can become more ordered and hence improve the electrical properties while hopefully maintaining the strength of the material compared to graphites. Research has shown that exfoliated graphite had improved electrical properties compared to the original graphite.[12] Anthracites and carbons have been shown to intercalate several compounds. As mentioned, anthracite is an intriguing carbon because structurally, it is not quite a graphite, a crystalline carbon, or an amorphous carbon; and, at the same time, it is an extremely hard, yet microporous material. Intercalation may be restricted in some anthracite coals due to the geometry in the coal.

The key to being able to exfoliate a material is to intercalate ions/compounds/elements that, when rapidly thermally shocked or reacted, will expand inside the structure rather than vaporize out. Intercalation is different from physical adsorption. For physical adsorption, the compound goes into the pores and may have some interaction with the pore surface, but does not become a part of the structure. To accomplish intercalation, two factors must be considered. The first factor is the coal structure must be amenable to intercalating a compound, which means the structure must allow access to the intercalate.[13] The second factor is the intercalating compound/element must be small enough to fit into the structure, but also interact with the structure so it will not vaporize out upon activation. The intercalate must be able to overcome the intermolecular forces between the planes of graphitic carbon planes.[14] The binding energy between carbon layers is estimated to be 1.5 kcal/mol, so this energy must be overcome for a compound to intercalate into carbon.[14] Bartlett and McQuillan[14] suggest mainly two types of intercalation that take place in graphite: intercalation with graphite reduction and intercalation with graphite oxidation. For graphite oxidation, mineral acids have been the intercalate of choice, and for graphite reduction, metal alkalis have been the most studied.

Carbons and anthracites have been shown to intercalate alkalis such as sodium, lithium, and potassium when using organic solvent,[13,15-17] so there is evidence of intercalation by carbon reduction. Carbons and anthracites can also be intercalated by carbon oxidation, using acids such as perchloric and sulfuric acids, but only when used in combination with nitric acid (i.e., chemical oxidation).[8-11,14,18] Anodic electrochemical oxidation can also be used to intercalate acid salts, such as HSO_4^-.[14,18-22] For anthracite in particular, perchloric/nitric acid mixtures have been intercalated into the anthracite; the resulting intercalated carbons were thermally shocked in order to exfoliate it for use as a precursor for activated carbons.[8-11]

The following is the final report for the work done over the year of funding for CPCPC. The main goal was to develop a method for anthracite exfoliation, and with success and if time permitted, determine the best exfoliating coals and the use of exfoliated anthracite as an electrode material. Several methods were employed to attempt intercalation/exfoliation of acids and alkalis, and all methods will be described in detail. All samples were screened using SEM to detect if exfoliation occurred. We expected to have BET surface area characterization done on those samples that were thought to have exfoliated, but we were not able to acquire this data before publication of this report. While it was anticipated that several coals would be tested, only a few were tested, with focus mainly on Summit coal. The following discussion details the methods that accomplished exfoliation and the implications for future work.

EXPERIMENTAL

Choice of Coals

Several coals have been chosen to test in this application. Initial experiments were conducted on Hongay, Summit, and Jeddo coals, with most of the success occurring on Summit coal. FB Leopold provided some additional samples. Proximate analysis information is provided in Table 1. Summit and Jeddo coals were tested in previous work,[23] and Hongay analysis comes from the literature.[8-11] FB Leopold obtained proximate analyses on their coals. These coals are of both anthracite and semi-anthracite rank. It is expected that semi-anthracite coals may exfoliate better, as some anthracite coals may be structurally unable to intercalate alkali metals or acids.

Intercalation and Exfoliation Using Acids

In the literature, only one method of exfoliation has been shown to exfoliate coals.[8-11] This involves the use of a 50/50 mixture of perchloric acid and nitric acid. Previous work was done using this method. Table 2 summarizes the various materials and methods of intercalation and exfoliation using acids.

Perchloric/Nitric Acid Methods

Method 1

Previous work in our lab has been done to attempt exfoliation. We attempted exfoliation using two anthracites. Two -20 mesh samples of Pennsylvania anthracites, one from the Mammoth vein of the Eastern middle seam (Jeddo) and the other unprocessed anthracite from the Tracey vein (Summit), were chosen for exfoliation in this experiment. Each anthracite sample was dried at 105°C under vacuum for one hour to remove moisture from the sample before exposure to the acid treatment.

The coals were intercalated according to the following procedure. To introduce intercalate compounds into the pore structures, the anthracites were treated with varying mixtures of Sigma Aldrich fuming nitric acid and 70% perchloric acid. Each sample of anthracite was placed in excess acid on the order of 10 ml of the acid mixture per gram of sample; perchloric acid concentrations varying from 25 to 75 volume percent, nitric acid making up the rest of the acid mixture.[8]

Each acid mixture was preheated to 120°C before the addition of the anthracite sample. During the acid treatment, the temperature of the mixture was raised 10°C each hour and allowed to stabilize until the mixture reached a maximum temperature of 150°C; once the treatment reached the temperature maximum, it was held there for one hour.[8] After the acid treatment, each sample was filtered and dried under vacuum. The dried samples were placed in a tube furnace under an argon atmosphere and subjected to heat treatment (slow heat-up) on the order of 700 and 800°C for three hours at the peak temperature.

As will be reported in the results section, this method of intercalation and exfoliation did not appear to exfoliate the coals, so acid intercalation and exfoliation was attempted using slightly different conditions, on Hongay semi-anthracite and Summit semi-anthracite.

Method 2

Again, Hongay coal was heated in acid as discussed previously. On the first attempt, only 0.5 g was recovered from the addition of 5 g of coal. The intercalated sample was dried, then later mixed with water to form a paste and heated to 700°C, using a fast heating rate, in a volatile matter furnace, exposed to the atmosphere.

On a second attempt to intercalate Hongay semi-anthracite, an explosion occurred and most of the sample was lost. It also resulted in injury (second degree burns and cuts), so it was decided to modify the procedure to just mix the coal with acids without heating. More than one method of intercalation was used in the literature, one with heat and the other without heat.[8-11]

Method 3

Hongay coal and Summit coal were mixed with 50/50 mixtures of perchloric/nitric acids for 2 hours at room temperature.[8-11] The mixture was filtered and the resulting paste was loaded into crucibles. Crucibles were heated to 700°C in a volatile matter furnace. For the Summit coal, exfoliation was achieved, but for the Hongay coal, sample spontaneously combusted and most of the sample was lost. If this method is attempted in the future, we will heat in a furnace in an inert atmosphere. However, we are still exploring other methods of intercalation and exfoliation to reduce the safety hazards associated with the explosive nature of perchloric acid, using other acid treatments.

Sulfuric Acid Procedure

Method 1

Graphite is commonly exfoliated by intercalating a mixture of sulfuric and nitric acids and thermally shocking the resulting material to 700-800°C for ~1-2 minutes.[12,17] We first tested this method on graphite to determine if indeed exfoliation occurred with this method. Approximately 5 g of Summit coal was mixed with 41 mL of a 3/1 ratio of sulfuric acid and nitric acids for two hours. The mixture was filtered and rinsed with a small amount of water. The resulting material was loaded into crucibles and heated to 700°C. One portion of the sample was heated 45 seconds, and another portion was heated to 700°C for 2 minutes.

Method 2

While the previous method is known to intercalate and exfoliate graphite, several researchers have explored the use of introducing the acid intercalate electrochemically.[14,18-22] Exfoliation occurred in graphites using acids other than sulfuric acid.[18,20] Adding the acid electrochemically provides a driving force to introduce the acid between the layers of the graphite similar to using nitric acid.[14] Doing this electrochemically may either reduce the contact time of the acid, allowing the use of an acid that is weaker and less environmentally hazardous than sulfuric acid, or provide a method to introduce intercalate into carbons that may be more resistant to intercalation.

Figure 1 is a schematic of the method to intercalate anthracite. Coal was added to a polypropylene bag (5 µm pore size), with a stainless steel metal piece (2" x 0.5") inserted into the middle of it (anode). The cathode was another piece of stainless of the same size. The electrolyte in this case was sulfuric acid (98 %). A power supply was connected using 9.6 V, with a resulting current of 0.05 A and a power consumption of 2.2 Ah/kg. The voltage was applied for ~2 h. Vigorous bubbling took place, with the stainless steel electrode turning grey. The voltage was then turned off, the bag with sample removed and dipped into water to remove excess acid. The sample was then loaded into a crucible and heated to 800°C for 50 seconds in a volatile matter furnace.

Intercalation and Exfoliation Using Alkali Metals

Previous reports have shown that lithium will intercalate into crystal structures by soaking the substrate in a solution of *n*-butyllithium and hexanes.[24] *n*-Butyllithium is a strong reducing agent.[25] The Li^+ ion is then a good oxidizing agent and upon intercalation reduction takes place (Eq. 1). Once the lithium is intercalated into the substrate, the substrate is reacted with water to cause exfoliation. The extremely exothermic reaction of lithium and water causes small "explosions" within the substrate, which increases the porosity of the substance (Eq. 2).

$$\text{Sub} + n\text{-BuLi} \rightarrow \text{Sub}^- + \text{Bu}\cdot + \text{Li}^+ \rightarrow \text{LiSub} + \text{octane} \qquad \text{Eq. 1}$$

$$\text{LiSub} + H_2O \rightarrow \text{Sub(exfoliated)} + \text{LiOH} + 1/2H_2 \qquad \text{Eq. 2}$$

Method 1

Preliminary tests were conducted by mixing 1.6 M *n*-butyllithium (in hexane) with Hongay anthracite coal (under inert atmosphere). This was done using a beaker and stir bar within a glove box with an argon atmosphere. The first reaction was done for ~1 h, at which time the solvent hexane evaporated completely. One gram of coal was used with ~7.8 mL of 1.6 M of *n*-butyllithium. After mixing, the sample was reacted in water, using ultrasonication in order to improve the coal/water interaction. Reaction 2 was similar, except ~17 mL of 1.6 M *n*-butyllithium was added and mixing continued for 2 hours. Little activity occurred under these conditions, so the following was implemented to allow for much longer reactions times.

All glassware was dried in an oven overnight prior to the reaction at a temperature above 110°C. The lithium intercalation reaction was done using a two-neck round bottom flask and condenser with a steady stream of nitrogen flowing in through the round bottom and out through the top of the condenser. One neck of the round bottom was connected to the condenser and the other had a septum attached with a needle for the nitrogen flow and also to inject the *n*-butyllithium. The nitrogen output then went through a nitrogen bubbler to maintain an inert atmosphere within the reaction vessel (Figure 2).

The dried glassware was assembled under an inert atmosphere. One gram of the anthracite was added to the round bottom and then the reaction vessel was sealed for the remainder of the reaction. *n*-Butyllithium (10 mL) was then added using the Sure/Seal technique to avoid exposure to air. The reaction was then stirred with water flowing through the condenser to minimize hexane evaporation, for up to 5 days.[24,25] More *n*-butyllithium or hexane can be added if evaporation occurred.

After intercalation, the round bottom was removed from the condenser, but with nitrogen still flowing through the side-arm while the flask was stoppered. In a glove box, the sample was washed with hexane to remove any excess lithium present in solution. Standard gravity filtration was used.

The “intercalated anthracite” was then placed in water. At this point, hydrogen gas forms. Several reports mention the use of sonication to promote lithium intercalation and then lithium reaction with water.[25,26] Therefore, sonication was used to promote the interaction of the water with the intercalated alkali. The anthracite can be dried on a high vacuum line or the house vacuum in a dessicator and then analyzed. Additionally, it was hoped that increasing the reaction temperature would increase the interaction.[27] Because a condenser was used, loss of solvent was not a problem and temperature was added to the reaction.

Method 2

We tried a second method of lithium intercalation, to see what differences would take place.[28] This method uses lithium borohydride ($LiBH_4$), which has similar chemical properties to *n*-butyllthium.[28] The reaction for intercalation (Eq. 3) and exfoliation (Eq. 4) are similar to those using *n*-butyllithium.

$$LiBH_4 + Sub \rightarrow LiSub + 1/2B_2H_2 + 1/2H_2 \qquad \text{Eq. 3}$$

$$LiSub + H_2O \rightarrow Sub + LiOH + 1/2H_2 \qquad \text{Eq. 4}$$

This reaction was first tried using solvated $LiBH_4$ and $NaBH_4$. $LiBH_4$ (2.0 M in THF) and $NaBH_4$ are available and a procedure similar to the procedure used with *n*-butyllithium was followed to intercalate lithium and then exfoliate the anthracite. The reaction temperature would have to remain below 50°C for safety and evaporation reasons. Additionally, KBH_4 is also very a good reducing agent (better than $LiBH_4$); however, it is significantly less stable in air and recommended use would be only with dilute solutions (preferably used in the glove box). The literature suggests that strong reducing agents and larger atomic radii will increase exfoliation, so $NaBH_4$ and KBH_4 may work better than lithium.[25,29]

Several reactions were done with these two lithium intercalation procedures, using a condenser and reacting the sample for 4 days with a lithium or sodium compound dissolved in a solvent, followed by reaction in water. Table 3 summarizes the different conditions tested used on the Hongay anthracite. Each sample was intercalated with the alkali metal, then reacted in water before doing any analytical tests on the material.

Other potential methods of alkali intercalation/exfoliation have been described in the literature.[14,30-34] Most of these methods involve the heating of the alkali metal to a liquid or vaporization temperature. As Na and K are much more reactive in moisture and air, it would be necessary to do experiments in a glove box. Therefore, we decided to postpone further investigation, as having to keep everything in an inert atmosphere would add expense to a process.

Method 3

A method was tried that was based on a method to introduce function groups to exfoliated graphite.[35-37] Exfoliated graphites have been chemically modified by reaction with quinones, with the added quinone functionality improving on the electrical properties of the exfoliated graphite.[35-37]

Other Methods of Exfoliation

Supercritical CO_2 Intercalation/Exfoliation

Supercritical CO_2 intercalation/exfoliation of graphite has been shown in the patent literature; however, details of the method are sketchy at best.[38,39] We developed our own method based on the patent literature and conditions for supercritical CO_2 extraction.[38-41] A horizontal tubing reactor was loaded with 7 g of Summit anthracite coal, and filled to 1500 psi of CO_2 cold. The reactor was heated using heat tape. The sample was heated to 120°C, with a pressure of 4000 psi, and held under those conditions for 15 minutes. While the reactor was still hot, the pressure was released to cause destructive depressurization.

Liquid N_2 Intercalation/Exfoliation

Bartlett and McQuillan suggest that intercalation can take place without apparent oxidation or reduction of the substrate, noting that noble gas fluorides can intercalate into graphite.[14] We tried one method of intercalation using very cold liquid N_2 and thermal shocking using boiling water, as this method could be a way to see how thermal shocking might affect the anthracite. The –20 mesh Summit sample (5 g) was placed in a wire mesh bag (-200 mesh) in order to access the cooling and heating mediums as quickly as possible. The filled bag was dipped into liquid N_2 for several minutes. The sample was then removed and immediately placed into boiling water. The resulting material was then dried for further evaluation.

Characterization of Samples

Scanning electron microscopy (SEM) has been used to characterize the coals before and after reaction. SEM is a useful qualitative method to detect exfoliation and was the method used to screen reacted materials to test for exfoliation.[8-11] SEM was done on two different instruments: one instrument a Philips XL20 with a filament gun, the magnification range for the instrument 20 to 50000X, and the other a Hitachi S-3500N with a similar magnification range.

We expected to determine the BET surface area using a Quantchrome Autosorb 1 instrument, using 5 data points to determine the surface area value. This technique was only to be used on samples that we identified from SEM as materials that may have exfoliated. However, the instrument was still under repair at the time of publication of this report.

RESULTS AND DISCUSSION

Results of Acid Intercalation and Exfoliation

Results Perchloric/Nitric Acid Procedure

Method 1

Figure 3 shows the SEM micrographs of untreated Jeddo anthracite, and Jeddo after acid treatment with 50:50 nitric/perchloric acid followed by heat treatment at 700°C. The heat treatment does not appear to have had much effect on the surface of the coal, but the acid treatment followed by heating at 700°C appears to have affected the surface of the coal significantly. Figure 4 shows the SEM micrographs of untreated Summit anthracite, Summit after heat treatment at 700°C, and Summit after acid treatment with 50:50 nitric/perchloric acid followed by heat treatment at 800°C. Acid treatments (followed by heating at 700°C and 800°C) appear to have had significant effect on the anthracite surface as well as possibly affecting the porosity. The treated anthracites appear to be both flaking and expanding, similarly to what would be expected for natural graphite exfoliation. However, it appears that most of the reaction occurred on the surface, so exfoliation does not appear to have been achieved. It was decided to use a faster heating method to achieve exfoliation.

Method 2

Figure 5 shows the SEM micrographs of untreated Hongay coal and the slightly exfoliated Hongay coal. While it appears slight exfoliation occurred, as will be seen later, this procedure did not fully exfoliate the coal. It is thought that drying the coal prior to the heating step could have prevented exfoliation.

Method 3

Figure 6 shows SEM micrographs of untreated Summit coal and the exfoliated Summit coal. Exfoliation appears to have taken place. As mentioned in the previous section, Hongay coal spontaneously combusted during heating and could not be analyzed effectively. For samples that appear to exfoliate, we will collect surface area data to determine the change in surface area of the whole sample. Surface area data will be used to determine extent of exfoliation and be a more definitive method to determine the best exfoliation method. However, the instrument is in the process of being repaired and data will not be able to be collected before submission of this report.

Results from Sulfuric Acid Intercalation and Exfoliation

Method 1

Figure 7 shows SEM micrographs of Summit coal after treatment with acid/heating (a) 700°C for 45 seconds and (b) 700°C for 2 minutes (the SEM photo of untreated Summit is in Figure 6). For both sets of samples, there are definitely smaller particles and the surface of the material appears to have changed. More changes seemed to occur with the 2 minute heating of the acid intercalated coal at 700 °C. There does seem to be some flaking of the coal particles as well, an indication that exfoliation may have occurred. A control experiment was performed on graphite, raw graphite in Figure 7(c) and exfoliated graphite in Figure 7(d). However, because of the orientation of the exfoliated anthracite particle, it is difficult to detect expansion that looks exactly like the exfoliated graphite particle. There is also the possibility that some of the smaller particles could be silica based, and future experiments using energy dispersive X-ray spectroscopy (EDS) will confirm if there is a significant amount of silica on the sample. It is possible that the acid etched some of the silica from the glass beaker used for stirring the sample. More will be explained in the alkali intercalation/exfoliation section, as silica may also have contaminated the sample. For samples that appear to exfoliate, we will collect surface area data to determine the change in surface area of the whole sample. Surface area data will be used to determine extent of exfoliation and be a more definitive method to determine the best exfoliation method. However, the instrument is in the process of being repaired and data will not be able to be collected before submission of this report.

Method 2

Figure 8 shows SEM micrographs of Summit coal after treatment with electrochemical acid intercalation (a) before heat treatment and (b) after heat treatment at 800°C for 50 seconds. It appears that some expansion may have occurred before heating the sample. Exfoliation appears to have taken place after heating. For samples that appear to exfoliate, we will collect surface area data to determine the change in surface area of the whole sample. Surface area data will be used to determine extent of exfoliation and be a more definitive method to determine the best exfoliation method. However, the instrument is in the process of being repaired and data will not be able to be collected before submission of this report.

Results of Alkali Intercalation

SEM micrographs were taken of the anthracite that was reacted. SEM has been shown to be a useful method to detect exfoliation.[8-11] This was the method used to detect any obvious visual changes. Figure 9 shows the SEM micrographs for reactions BG 1-7 (methods 1-3 for exfoliation). In all cases, the main visual change seemed to be to the surface of the anthracite. There appeared to be striations on the surface, probably due to the reaction of lithium with water, forming a strong base that may have etched the anthracite surface. In a few reactions, particularly BG 2, there appeared to be "fuzzy" particles on the surface, clumps of "puffy" particles, and some porous areas on some of the particles. Initially, we thought we had achieved some sort of exfoliation, but preliminary elemental examination by SEM and EDS indicated the "fuzzy" and "puffy" particles might be silica based. For BG-4 (reacted with method 3), the main feature seems to be cracks in the coal. However, exfoliation did not take place.

In the future, we will continue to analyze to see if BG-2 does indeed contain silica based particles and determine the source of the silica. Coals can contain silica based mineral matter; when enough coal is available, we will test the mineral matter content of Hongay coal. Another source of silica could be the reaction vessels, which were glass. In this case, we would use a different type of reaction vessel, either alumina or Nalgene based, as these materials are not affected by strong acid or base. At this point, we also want to know if lithium is being intercalated under the conditions used. This can be determined by XRD.[30,31] Alkali intercalation of anthracite can be achieved under certain conditions.[30-34] Carbon exfoliation has been achieved by potassium intercalation and exfoliation.[32] However, potassium is the most reactive of the alkali metals, and could also be a source of explosion if not carefully handled. Time was also limited, therefore, we could not complete testing other methods of alkali exfoliation. For samples that appear to exfoliate, we will collect surface area data to determine the change in surface area of the whole sample. Surface area data will be used to determine extent of exfoliation and be a more definitive method to determine the best exfoliation method. However, the instrument is in the process of being repaired and data will not be able to be collected before submission of this report.

Results of Other Methods of Intercalation/Exfoliation

Other methods of Intercalation/Exfoliation were done on coal. As discussed in the introduction, several criteria must be met in order to intercalate and exfoliate a substance. The intercalate must be small enough to go into the pores of the substrate, as well has some kind of driving force to overcome the energy between the layers of carbon sheets.[14] It has been reported recently that graphite can be intercalated using supercritical CO_2 and exfoliated by explosive/destructive depressurization.[38,39] However, this has been reported in patents, which contain little detail on how to accomplish intercalation/exfoliation. We also thought to try using liquid nitrogen as the intercalate, then using a thermal shock with boiling water to cause exfoliation. We continue to have ideas, but will not have time to complete additional ideas during the time of the project.

CO_2 Intercalation/Exfoliation

Figure 10 shows SEM micrographs of Summit treated with supercritical CO_2 destructive depressurization, with (a) at 20 µm, and (b) at 50 µm. Some particles appear to have some surface changes, but many of the particles remain unchanged. While there appear to be changes, it does not appear that exfoliation has taken place. However, the CO_2 intercalation at 120°C and 4000 psi was only done for 15 minutes, and actual diffusion of CO_2 into an anthracite particle may need to take place for a significantly longer period of time. Because there are surface changes on some of the particles, exfoliation may occur if the CO_2 is allowed to diffuse into the particle.

Liquid Nitrogen Intercalation/Thermal Shock

Figure 11 shows SEM micrographs of Summit treated with liquid N_2/thermal shocking (a) at 200 µm and (b) at 20 µm. It does not appear that any type of particle expansion took place, although the process may have fragmented the coal to some extent. This was expected, as nitrogen does not have the ability to oxidize or reduce chemically. It also indicates that some chemical interaction does need to take place in order to cause exfoliation.

Testing of Materials as Electrodes

Three raw coals were sent to Carbone to make test electrodes, but data from those electrodes will not be available before the final report must be submitted. While it does appear that exfoliation was successful with Summit coal, not enough material was generated to date in order to make a test electrode.

CONCLUSIONS

Research has shown that exfoliated graphite improves upon the electrical properties of graphite before pretreatment.[12] It was hypothesized that if anthracite coal could be exfoliated, the electrical properties could be improved.

Graphite can be exfoliated using several methods: (1) perchloric/nitric acid intercalation followed by exfoliation at 700°C for ~2 minutes, (2) bromine intercalation/reversible exfoliation,

(3) supercritical CO_2 destructive depressurization, (4) alkali intercalation followed exfoliation in water or ethanol, and (5) intercalation with sulfuric/nitric acids or by electrochemical oxidation of sulfuric acid and exfoliating at 700-1000°C for a few seconds to a couple of minutes. Several methods of exfoliation were tested on anthracite. One method was completely successful: perchloric/nitric acid intercalation followed by exfoliation at 700°C for ~2 minutes. Literature reports this to be a successful method,[8-11] however, due to safety concerns, the goal of the project was to determine other successful methods of exfoliation that would be useful in an industrial setting. Marginal success was achieved with (5), intercalation with sulfuric/nitric acids or by electrochemical oxidation of sulfuric acid and exfoliating at 700-1000°C for a few seconds to a couple of minutes. Some particles appeared to have exfoliated, but some particles did not exfoliate and there may have been some contamination by silica from the beaker used. Conclusive evidence of extent of exfoliation and of silica contamination could not be confirmed by the time the report had to be completed. To determine the best conditions for full exfoliation of anthracite, these issues must be solved.

Alkali intercalation/exfoliation was not achieved on anthracite using the Li/Na metal methods. It is expected that alkali intercalation can be achieved by other methods. Older methods for alkali metal intercalation use the pure metal (preferably as powders or fine particles) in conjunction with solvents such as THF and DMSO.[32,33] This method is particularly dangerous because the solvent must be dried thoroughly either through distillation or using a solvent system that is closed off to air. Exposure to traces of water should be absolutely avoided for Li, Na and K metals.

While electrode fabrication and testing of raw anthracites is currently underway, completion will not be achieved by the time the report will be submitted. It was also difficult to obtain enough exfoliated material for fabrication an electrode (1 kg needed for electrode), therefore this task was unable to be completed.

REFERENCES

1. Wallace, A.F.C., *St. Clair: A Nineteenth Century Town's Experience with a Disaster Prone Industry.* Alfred Knopf, New York, 1987.
2. Hower, J., Levine, J., Skehan, J., Danial, E., Lewis, S., Davis, A., Gray, R., Altaner,. S., *Org. Geochem.* **70** (1993) 519.
3. *Keystone Coal Industry Manual.* Intertec Publishing, Chicago, 2001.
4. Pappano, P.J., Mathews, J.P., Schobert, H.H., *Preprints, Amer. Chem. Soc. Div. Fuel Chem.* **44** (1999) 567.
5. Gerstein, B.C., Murphy, P.D., Ryan, L.M., In: *Coal Structure.* Academic Press, New York, 1982, Chapter 4.
6. van Krevelen, D.W., *Coal: Typology–Chemistry–Physics–Constitution.* Elsevier, Amsterdam, 1981.
7. Sørlie, M. and Øye, H.A., *Cathodes in aluminum electrolysis,* Aluminum-Verlag GmbH: Dusseldorf, 1994, pp. 1-20.
8. Pettijean, D., Klatt, M., Furdin, G., and Hérold, A., *Carbon*, 1994, **32** (3), 461.
9. Albiniak, A., Furdin, G., Begin, D., Mareche, J.F., Kaczmarczyk, J., and Broniek, E., *Carbon*, 1996, **34** (11),1329.
10. Furdin, G., *Fuel*, 1998, **77** (6) 479.
11. Daulan, C, Lyubchik, S.B., Rouzaud, J-N., and Béguin, F., *Fuel*, 1998, **77** (6), 495.

12. Chung, D.D.L., *J. Mat. Sci,* 1987, **22** (12), 4190 and reference therein.
13. Inagaki, M., *Solid State Ionics*, 1996, **86-88**, 833-839.
14. Bartlett, N., McQuillan, B.W., "Graphite Chemistry," in *Intercalation Chemistry*, Ed. M. Stanley Whittingham and Allan J. Jacobson, Academic Press:London, 1982, pp. 19-53.
15. Inagaki, M. and Tanaike, O, *Carbon,* 2001, **39**, 1083-1090.
16. Narita, N., Nagai, S., and Shugo, S., *Phys. Rev. B.,* 2001, **64**, 245408.
17. McKay, S.F., *J. Appl. Phys.,* 1964, **35**, 1992-1993.
18. Toyoda, M., Katoh, H., and Inagaki, M., *Carbon*, 2001, **39**, 2231-2237.
19. Ubbelode, A.R., *Proc. R. Soc. London, Ser. A,* 1969, **309**, 297.
20. Ubbelode, A.R., *Proc. R. Soc. London, Ser. A,* 1971, **321**, 445.
21. Toyoda, M., Sedlacik, J., Inagaki, M., *Synthetic Metals,* 2002, **130**, 39-43.
22. Kang, F., Zheng, Y-P., Wang, H-N., Nishi, Y, Inagaki, M., *Carbon*, 2002, **40**, 1575-1581.
23. Pappano, P.J., *M.S. Thesis.* The Pennsylvania State University, University Park, PA, 2001.
24. Murphy, D.W., Di Salvo, F.J., Hull, G.W., and Waszczak, J.V., *Inorg. Chem.,* 1976, **15** (1),17.
25. Heising, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.,* 1999, **121,** 11720-11732.
26. Miremadi, B. K.; Morrison, S. R. *J. Appl. Phys,* 1988, **63**, 4970-4974.
27. Yang, D.; Frindt, R. F. *J. Phys. Chem. Solid,* 1996, **57**, 1113-1116.
28. Tsai, H. L.; Heising, J.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater,* 1997, **9**, 879-882.
29. Hérold, C; Marêché, J. F.; Lagrange, P. *Carbon*, 1996, **34**, 517-521.
30. Berger, D., Carton, B., Metrot, A., and Herold, A. in *"Chemistry and Physics of Carbon,"* 1975, **Vol. 12**, Ed. P.L. Walker and P.A. Thrower, pp. 1-37.
31. Anderson, S.H., and Chung, D.D.L., *Carbon*, 1984, **22** (3), 253-263.
32. Viculis, L.M., Mack, J.J., and Kaner, R.B., *Science*, 2003, **299** (5611), 1361-1361.
33. (a) Vadla, J.J., Quandt, H.C., Rich, D.J., Metall., 1980, **34** (12) 1102-1105. (b) Diez, M-A., Marsh, H., Light Metals, 2001, 739-746, (c) Marsh, H., Murdie, N., Edwards, I.A.S. and Boehm, H.P., "Interactions of Carbons, Cokes, and Graphites with Potassium and Sodium," in Chemistry and Physics of Carbon, 1987, **Vol. 20**.
34. Dresselhaus, M. S.; Dresselhaus, G. *Adv. Phys.,* 1981, **30**, 139.
35. Agarwal, R.K., Noh, J.S., and Schwarz, J.A. *Carbon* (1987), **25**, 219.
36. Ramesh, P. and Sampath, S., *Chem. Commun.* (1999), 2221.
37. Ramesh, P. and Sampath, S., *Analyst* (2001), **126**, 1872.
38. Manke, C.W., Gulari, E, Mielewski, D.F., Lee, E.C., U.S. Patent No. 6,469,073, Oct. 22, 2002.
39. Kaschak, D.M., Reynolds III, R.A., Krassowski, D.W., Ford, B.M., U.S. Patent Application, No. 20040033189, Feb. 19, 2004.
40. Li, w., Lazar, I.M., Wan, Y.J., Butala, S.J., Shen, Y., Malik, A., Lee, M.L., *Energy Fuels,* 1997, **11**, 945-950.
41. Williams, D.F., *Chem. Engr. Sci.,* 1981, **36** (11), 1769-1788.

TABLES AND FIGURES

Table 1. Characteristics of Jeddo and Summit Anthracite

Anthracites	Rank	Moisture (wt %)	Ash (wt %)	Volatiles (wt %)	Fixed Carbon (wt %)
Hongay[a]	Semi-anthracite	3.0	2.7	5.6	91.7
Jeddo[b]	Anthracite	4.7	8.1	6.1	85.9
Summit[b]	Semi-anthracite	2.6	17.6	11.1	71.2
AFM-700[c]	Anthracite	4.6	12.22	5.77	82.0
AFM-1400[c]	Anthracite	3.8	14.9	6.7	78.4
AFM-2300[c]	Anthracite	3.6	19.6	5.9	74.5

a Data obtained from literature references 8-11.
b Data obtained from literature references 4 and 23.
c Coals and data obtained from FB Leopold

Table 2: Summary of reaction conditions for acid intercalation exfoliation.

Sample ID	Material Intercalated	Acid Mixture (volume/volume)	Intercal[a] Time (h)	Temp (°C)	Exfoliation Time	Exfoliation Condition (°C)
HT1	Jeddo coal	50/50 Nitric/Perchloric	1	150	3 hours (slow)	700/800
HT2	Summit coal	50/50 Nitric/Perchloric	1	150	3 hours (slow)	700/800
HT3	Jeddo coal	25/75 Nitric/Perchloric	1	150	3 hours (slow)	700/800
HT4	Summit coal	25/75 Nitric/Perchloric	1	150	3 hours (slow)	700/800
HT5	Summit coal	75/25 Nitric/Perchloric	1	150	3 hours (slow)	700/800
ABCB 1	Hongay coal	50/50 Nitric/Perchloric	1	150	1-2 minutes	700
ABCB 2	Hongay coal	50/50 Nitric/Perchloric	1	150	1-2 minutes	700
ABCB 3	Hongay coal	50/50 Nitric/Perchloric	2	25	1-2 minutes	700
ABCB 4	Summit coal	50/50 Nitric/Perchloric	2	25	1-2 minutes	700
SUM 1	Summit coal	75/25 Sulfuric/Nitric	2	25	45 seconds	700
SUM 2	Summit coal	75/25 Sulfuric/Nitric	2	25	2 minutes	700
SUM 4, 6	Summit coal	75/25 Sulfuric/Electro[b]	2	25	50 seconds	800

a – intercalation

b – electrochemical oxidation instead of using nitric acid

Table 3: Reaction conditions for alkali intercalation; for each reaction, the alkali was intercalated and then sonicated in water for several hours.

Sample ID	Method No.	Reaction Time	Alkali Substrate	Solvent	Type of Mixing	Temperature (°C)
BG-1	1	4 days	*n*-butyllithium	Hexane	Stirring	25
BG-2	1	4 days	*n*-butyllithium	Hexane	Stirring	70
BG-3	1	4 days	*n*-butyllithium	Hexane	Sonication	40
BG-5	1	4 days	*n*-butyllithium	Hexane	Sonication	25
BG-6	2	4 days	$NaBH_4$	THF	Stirring	25
BG-7	2	4 days	$LiBH_4$	THF	Stirring	25

Figure 1: Schematic of experimental setup for electrochemical intercalation of sulfuric acid into Summit coal.

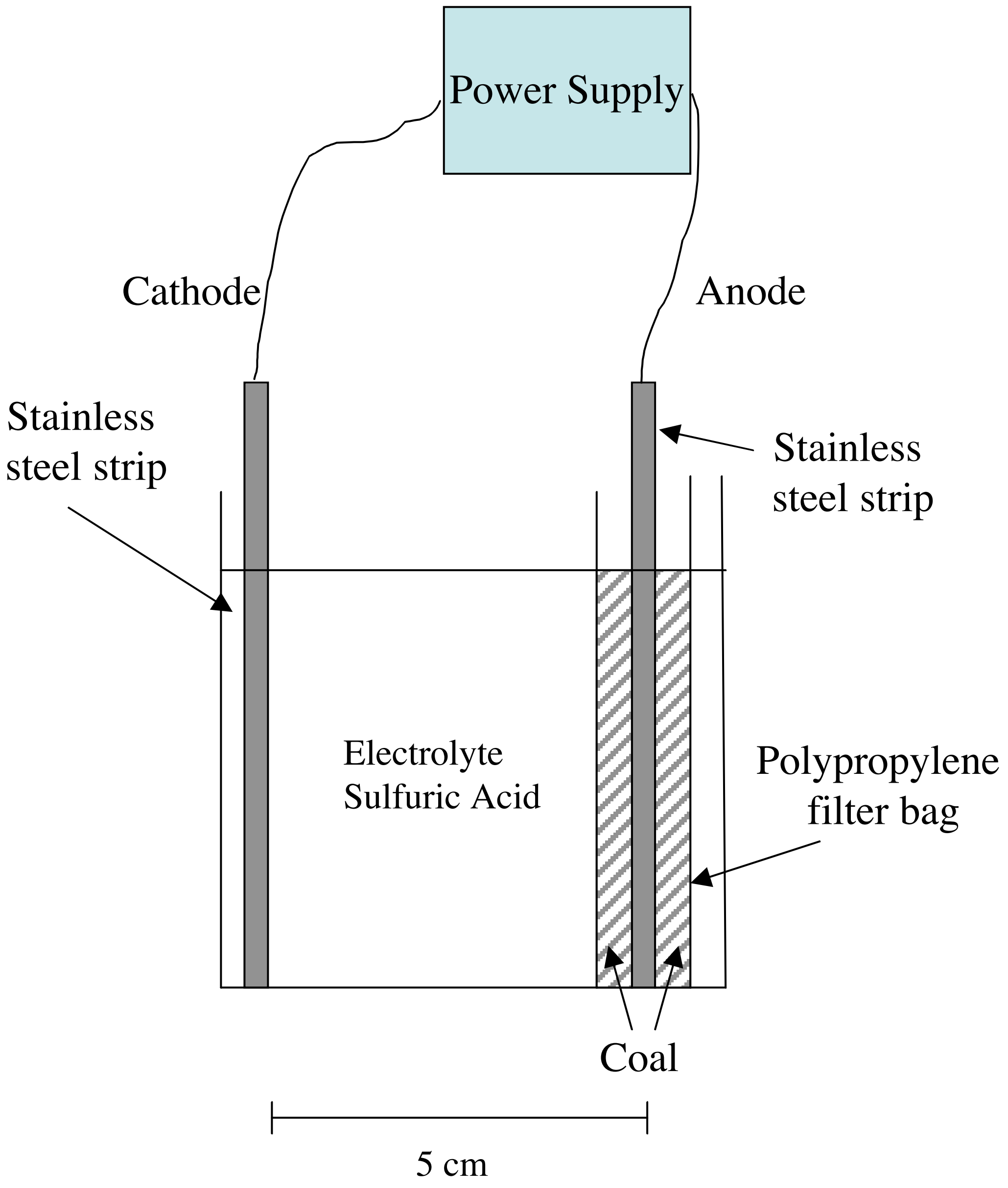


Figure 2: Reaction Setup for alkali intercalation, to prevent air and moisture from sample.

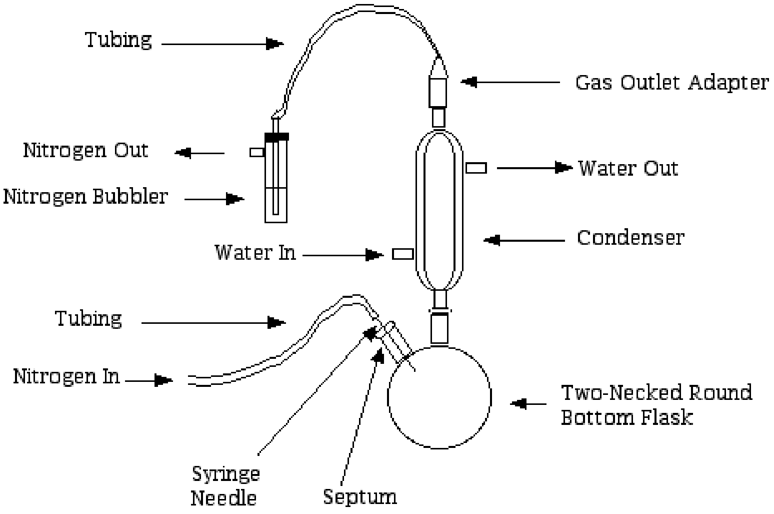


Figure 3: SEM micrographs of untreated Jeddo anthracite and products of various treatments. SEM micrographs of (a) raw Jeddo anthracite and (b) Jeddo anthracite acid treated in 50:50 nitric/perchloric acid with heat treatment at 700°C.

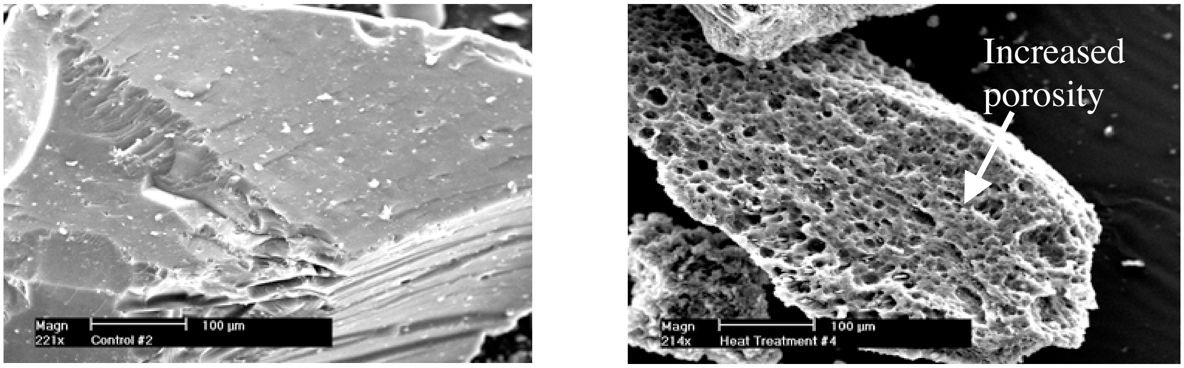

(a) (b)

Figure 4. SEM micrographs of untreated Summit anthracite and products of various treatments. SEM micrographs of (a) raw Summit anthracite, (b) Summit anthracite treated at 700°C, (c) Summit anthracite acid treated in 50:50 nitric/perchloric acid with heat treatment at 800°C.

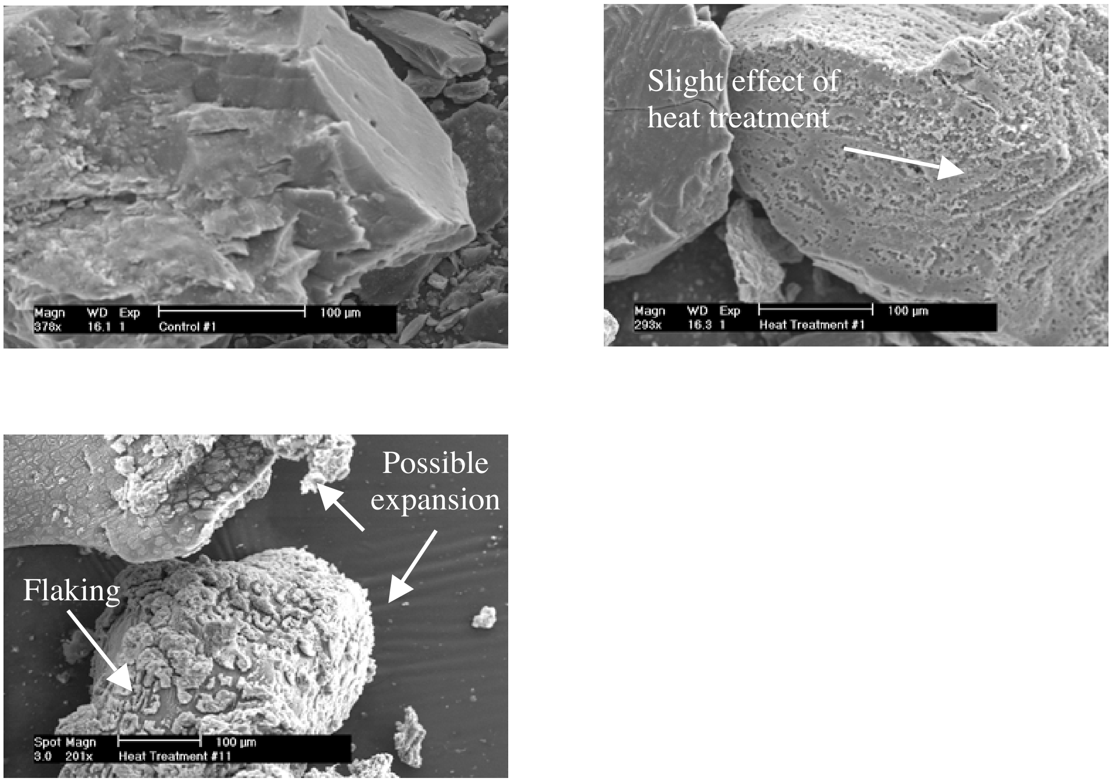
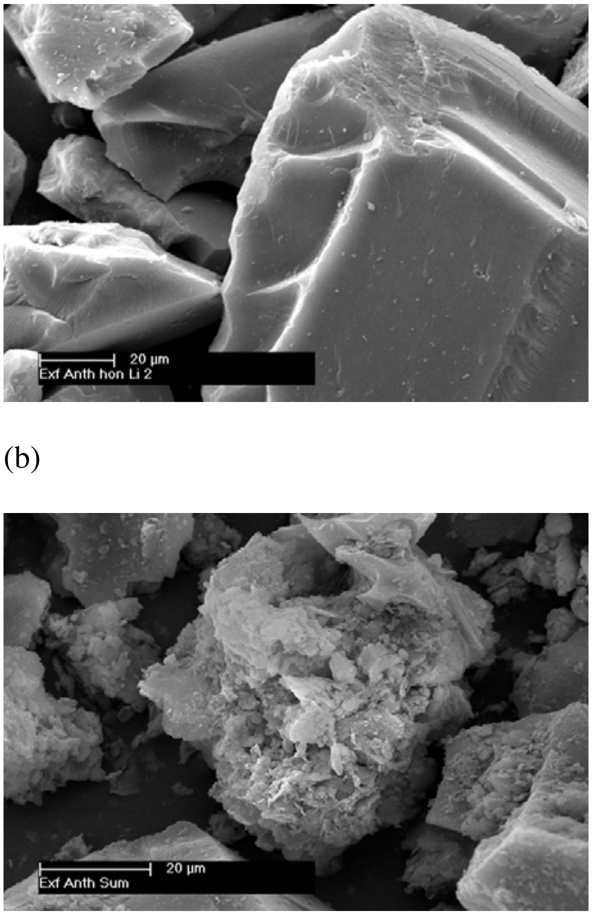

(a) (b) (c)

Figure 5: SEM micrographs of (a) untreated Hongay coal and (b) slightly exfoliated Hongay coal.



(a)

(b)

Figure 6: SEM micrographs of (a) untreated Summit coal and (b) acid/heat-treated Summit coal from perchloric/nitric acid treatment.

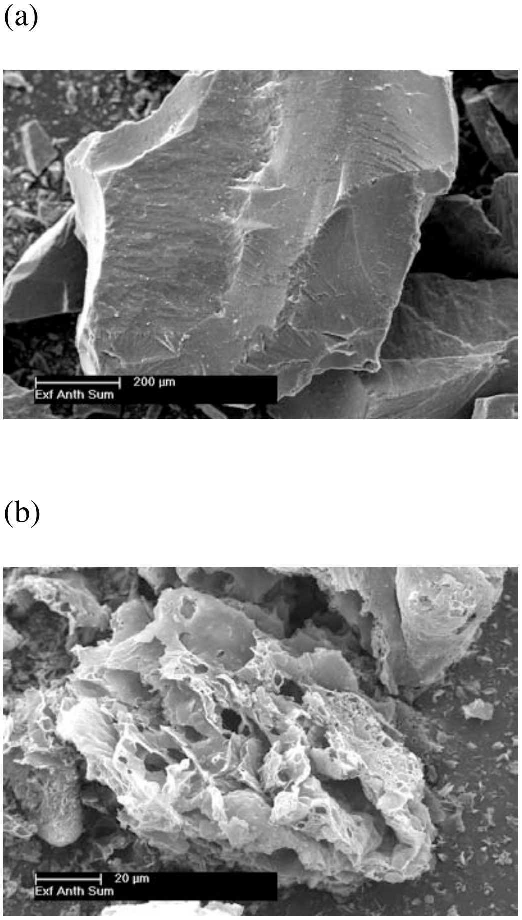


Figure 7: SEM micrographs of treated Summit coal from sulfuric/nitric acid treatment (a) 45 second heat treatment and (b) 2 minute heat treatment and of (c) graphite and (d) treated graphite.

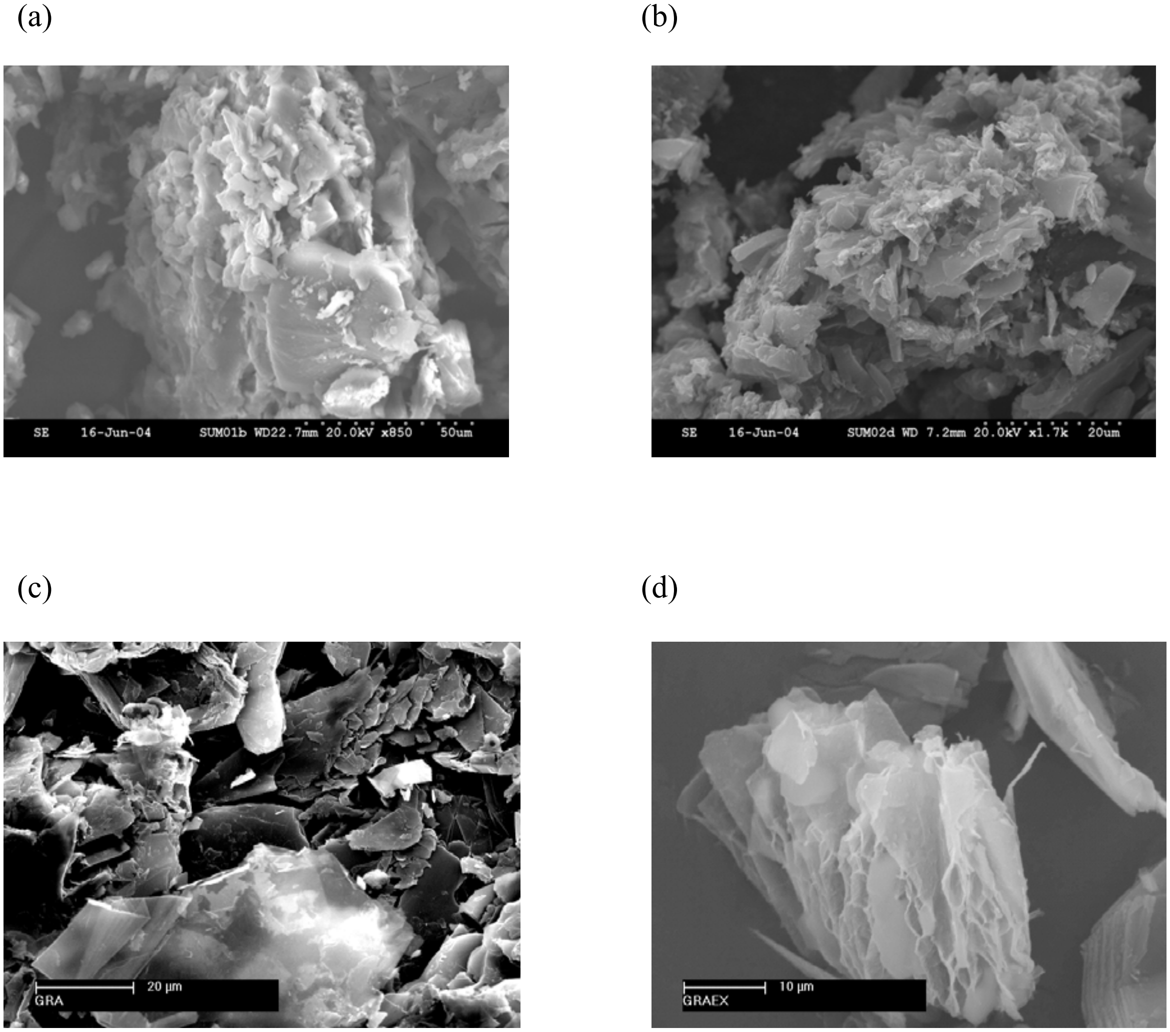


Figure 8: SEM micrographs of treated Summit coal from electrochemical sulfuric acid treatment (a) before heat treatment and (b) after 50 second heat treatment.

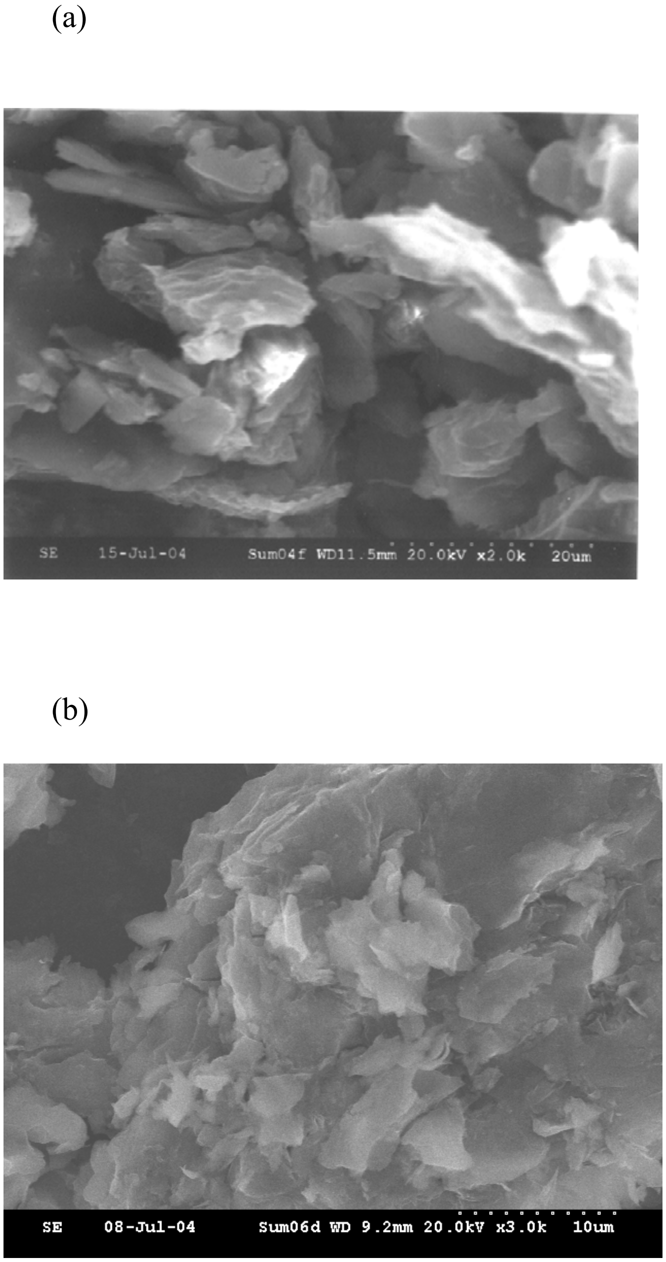


Figure 9: SEM micrographs of Hongay coal after intercalation with lithium and reaction in water (a) BG-1, (b) BG-2, (c) BG-3, (d) BG-5, (e) BG-6, (f) BG-7, and (g) BG-4.

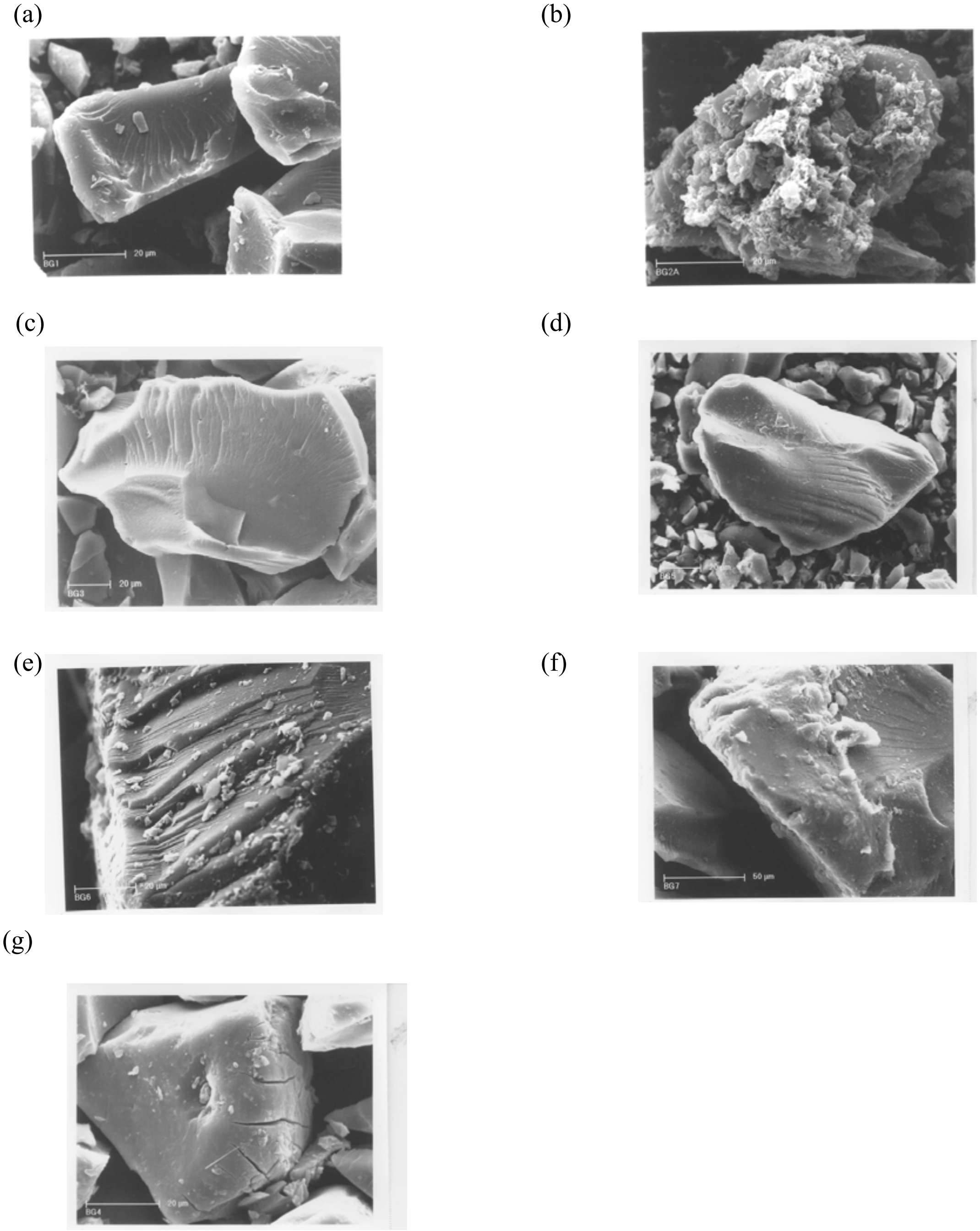
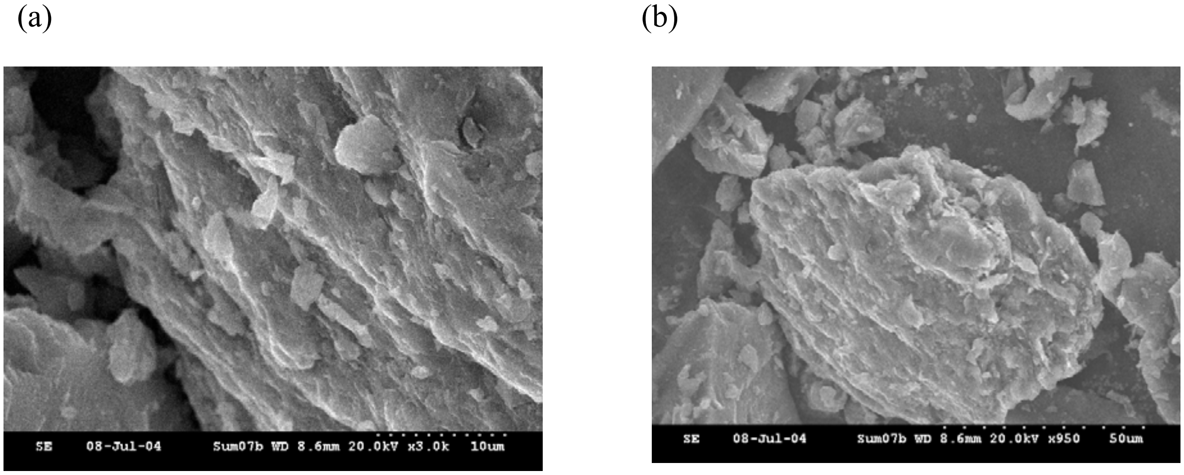
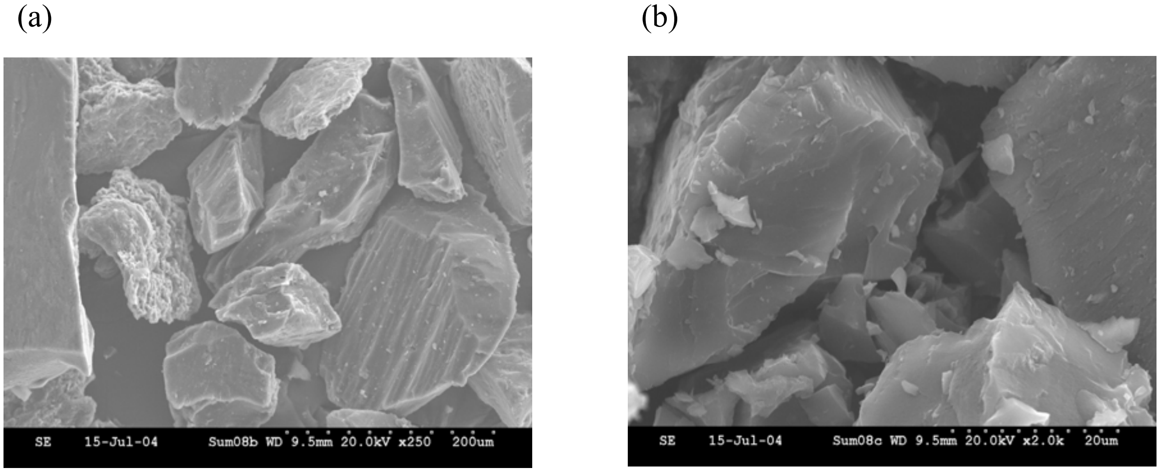


Figure 10: SEM micrographs of Summit treated with supercritical CO_2 destructive degradation (a) at 20 µm and (b) 50 µm


(a)

(b)

Figure 11: SEM micrographs of Summit treated with liquid N_2 thermal shocking (a) at 200 µm and (b) at 20 µm.


(a)

(b)

FINAL TECHNICAL PROGRESS REPORT
SUBMITTED TO

CONSORTIUM FOR PREMIUM CARBON PRODUCTS FROM COAL
The Pennsylvania State University
C211 Coal Utilization Laboratory
University Park, PA 16802-2398

USE OF COAL GASIFICATION AND COMBUSTION CHARS FOR MERCURY CAPTURE

Reporting Period Start Date: *March 1, 2003*

Reporting Period End Date: *June 30, 2004*

Submission Date: *September 1, 2004*

Principal Authors: *Dr. M. Mercedes Maroto-Valer, PI*
Mr. Bruce Miller, Co-PI
Dr. Yinzhi Zhang

DOE Award number: *DE-FC26-98FT40350*

Submitting Organization: The Energy Institute
The Pennsylvania State University
405 Academic Activities Building
University Park, PA 16802-2398
Phone: (814) 863 8265

Disclaimer

Abstract

Due to the increasing restricted use of landfill, the coal industry needs to find uses for high carbon chars from coal-fired combustors or gasifiers instead of their current disposal practice. Following this demand, a one-step activation protocol was developed by the proposers to produce activated carbons from coal chars. Compared to the conventional two-step process that includes a devolatilization of the raw materials, followed by an activation step, chars only require a one-step activation process, since they have already gone through a devolatilization process while in the combustor or gasifier. The produced activated carbons with a fine particle size are not only rich in micropores, but they also present a high content of mesopores, which leads to good mass transfer properties during the adsorption process, and therefore, activated coal chars could be a superior mercury sorbent candidate. Accordingly, the overall objective of the proposed research program is to develop activated carbon sorbents from coal chars to determine their mercury capacity and compare them to commercial activated carbons.

In this work, under Task 1 “Procurement and characterization of coal gasification and combustion chars” eleven char samples, including six samples from boiler systems and five samples from gasifiers were collected and analyzed. These samples consisted of 4 biomass-based samples and 7 coal-based samples. In addition, two commercial activated carbons, which have been widely adopted as a baseline for mercury sorbent studies, were also analyzed. Of the samples collected, the wood-based samples have higher loss-on-ignition (LOI) than the coal-based samples. Compared to the coal-based samples, all wood-based samples have a lower starting point for weight loss (180-300°C vs. 200-400°C), and their thermal reaction is more complex. Under Task 2 “Preparation and characterization of coal char sorbents”, selected samples were activated using the protocol previously developed by the authors. In addition, a cleanability study of one char was conducted to generate an enriched carbon sample that can be used to produce mercury sorbents and to study the effect of the carbon content in its mercury capture capacity. The enriched carbon sample has an ash content of around 3.6% and its surface area and pore volume are 53 m^2/g and 0.04 ml/g, respectively. This suggests that the some porosity was generated while in the pulverized coal (PC) combustor. Compared to the parent sample, the one-step steam activation process successfully increased the surface area and pore volume (53 vs. 863m^2/g and 0.040 vs. 0.490ml/g, respectively). Furthermore, two selected samples, one biomass-based sample from a gasifier and one coal-based sample from a boiler, were activated by steam and the porous textures of the resultant samples were analyzed. Under Task 3, "Mercury capture by the prepared char sorbents", the mercury content in selected raw char samples was tested using CVAA. The mercury contents were very low, mainly below 0.1 ppm. Selected char and activated char samples were tested with mercury capacity using a fix-bed protocol. Interestingly, the activated sample has lower mercury capacity (0.23mg/g) than its precursor fly ash carbon, although its surface area is around 15 times larger than its precursor, 863m^2/g vs. 53m^2/g. The pore size of the sorbent seems to play a role in the mercury capacity of the sorbents. However, the very different mercury capacity of the samples studied here cannot only be ascribed to differences in their porous structures. Other properties, especially surface functionality, are also important to determine their mercury capacity.

FINAL TECHNICAL PROGRESS REPORT

March 1, 2003 – June 30, 2004

Table of contents

1. Introduction

1.1. Rationale

On December 15, 2003 the U.S. Environmental Protection Agency (EPA) proposed for the first time to permanently cap and reduce mercury emissions from power plants. EPA is proposing two alternatives for controlling emissions of mercury from utilities. One alternative proposes to require utilities to install controls known as “maximum achievable control technologies” (MACT), which would reduce nationwide emissions of mercury by 14 tons (29%) by the end of 2007. The second alternative proposes to establish “standards of performance” limiting mercury emissions for new and existing utilities. If implemented, the nationwide utility emissions of mercury would be reduced in two distinct phases. In the first phase, due by 2010, emissions will be reduced by taking advantage “co-benefit” controls – that is mercury reductions achieved by reducing SO_2, and NO_x emissions. When fully implemented in 2018, mercury emissions will be reduced by 33 tons (69%).

Mercury is a naturally occurring element that can accumulate in the water and especially in the larger fish and pose the greatest risk to people who eat them regularly. According to a report of the U.S. Environmental Protection Agency (EPA), coal-fired utility boilers are the largest source of anthropogenic mercury, accounting for 33% of the total (EPA, 2002). Therefore, mercury emissions from coal-fired utility boilers have been identified as a hazardous air pollutant of greatest potential public health concern by EPA. Accordingly, there is a growing interest to develop technologies for mercury capture (EPA, 2002). The injection of commercial activated carbons is a promising technology to control mercury emissions from coal-fired combustion systems. However, due to the very low concentration of mercury in the flue gas (1 ppb vol), the complexity of the flue gas composition, the very short residence time (~6s) of the carbon sorbent in flue gas, and the poor selectivity of the carbon sorbent towards mercury, excess carbon adsorbent needs to be injected into the flue gas, resulting in carbon-to-mercury ratios around 1000:1 to 100,000:1 for commercially available activated carbons. Therefore, novel sorbents are being sought for mercury capture (Brown et al., 2000). Previous studies have shown that the reaction of mercury with the carbon sorbent is mass-transfer limited and, therefore, activated carbons with high mesopore and macropore volume, as well as high mercury selectivity and low particle size, will be superior candidates for mercury sobents (Sjostrom et al., 2002).

Due to the increasing restricted use of landfills, the coal industry needs to find uses for high carbon chars from coal-fired combustors or gasifiers instead of their current disposal practice. Following this demand, a one-step activation protocol was developed by the proposers to produce activated carbons from coal chars. Compared to the conventional two-step process that includes devolatilization of the raw materials followed by an activation step, chars only require a one-step activation process (Maroto-Valer et al., 2000, 2001; Zhang et al., 2003a) since they have already undergone devolatilization process while in the combustor or gasifier. The char-produced activated carbons have a fine particle size, are rich in micropores, and also present a high content of mesopores, which leads to good mass transfer properties during the adsorption process. Activated coal chars, therefore, can be a superior mercury sorbent candidate. Accordingly, the overall objective of the proposed research program is to develop activated carbon sorbents from coal chars for mercury capture and to determine their mercury capacity and compare them to commercial carbons.

1.2. Program objective

The objective of this research program was to develop activated carbon sorbents from coal chars for mercury capture. This research program included the selection and characterization of a suite of coal combustion and gasification chars provided by Southern Company and Penn State University. The characterization of the suite of samples collected was conducted at Penn State University using a battery of tests developed previously by the proposers. These samples were then activated following the protocols developed in previous CPCPC projects (See Section 1.3). Finally, the mercury capacity of the activated samples were tested and compared to commercial carbons.

1.3. Research design and tasks

This research program can be divided into the following three tasks described below.

- Task 1 “Procurement and characterization of coal gasification and combustion chars”. This task included the procurement and characterization of coal chars from different combustor and gasification units, and it was conducted in collaboration with Southern Company and Penn State University. The samples were characterized using a battery of tests, previously developed by the proposers, that includes thermogravimetric profiles, particle size distribution studies, and proximate and elemental analyses. Furthermore, the properties of these chars towards their use as precursors for activated carbons were also investigated, particularly their porous structure.

- Task 2 “Preparation and characterization of coal char sorbents”. The selected samples were activated using the protocol previously developed by the proposers (Maroto-Valer et al, 2001). The samples were heated under nitrogen flow to the desired temperature, and then steam was introduced in the reactor, while the reactor was kept isothermally for 0.5-2 hours. The properties of the activated carbons that have been synthesized under controlled conditions were systematically characterized. This study included a detailed description of the porous structure (micro-, meso- and macroporous) using conventional adsorption techniques, like N_2 adsorption isotherms at 77K. Finally, a cleanability study of the selected chars was conducted to generate enriched carbon samples that can be used for the produce mercury sorbents and to study the effect of the carbon content in their mercury capture capacity.
- Task 3 “Mercury capture by the prepared char sorbents”. This task investigated the ability of the prepared activated chars to capture mercury using a reactor developed by the proposers. The observed mercury sorption capacities were compared to those of commercial activated carbons.

2. Experimental

2.1. Task 1: Procurement and characterization of coal gasification and combustion chars

2.1.1. Study samples

Eleven char samples together with two commercial activated carbon samples, which are used typically as the benchmark for mercury capture study and field tests, were collected. Five char samples were provided by Southern Company, including three samples collected from a boiler at Plant Miller (Georgia) burning PRB coal (DarkAsh 99, DarkAsh00, and F9830) and two samples collected from a gasifier feeding lignite (Gasif-1 and Gasif-2). CPC-Filter and CPC-Knockout were collected from a gasifier fed with wood and provided by Community Power Corporation. GTI-Woodchar was also a wood-based sample and wasprovided by Gas Technologies Institute. The final sample, Tra-Woodchar, was provided by Tractebel Electricity & Gas International cogeneration facility in Northumberland, Pennsylvania, which is burning wood. Two lignite-based commercial activated carbon samples, Darco FGD and FGL, were provided by Norit Americas Inc.

2.1.2. LOI of the samples

The loss-on-ignition (LOI) contents of the char samples were determined according to the ASTM C311 procedure. Around 1 g of sample was oxidized in air for 3 hours at 800^{o}C to constant weight in a muffle furnace. The LOI content was then calculated from the weight loss of the sample after oxidation. The LOI analyses were conducted in duplicate.

2.1.3. Porosity studies

The porous texture of the char samples was characterized by conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The pore volume was calculated as the volume measured in the nitrogen adsorption isotherm at a relative pressure of 0.95 ($V_{0.95}$). The total specific surface area, S_t, was calculated using the multi-point BET equation in the relative pressure range 0.05-0.35. From the desorption branch, the micropore volume, V_{mi}, and external surface area, S_{ext}, were calculated using the α_S-method , where non-graphitized non-porous carbon black Cabot BP 280 (S_{BET}=40.2m^2/g) was used as a reference adsorbent. The mesopore volume (V_{me}) was calculated by subtracting the volume of V_{mi} from $V_{0.95}$. The micropore surface area, S_{mi}, was determined by subtracting the external surface area from the S_t. The pore sizes, 2nm and 50nm, were used as the limits between micro- and mesopores, and meso- and macropores, respectively, following the IUPAC nomenclature. The Barrett-Joyner-Halenda (BJH) method was used to calculate the mesopore size distributions. The desorption branch of the hysteresis loop in the isotherm was used for the mesopore size analysis.

2.1.4. TGA profiles

The thermogravimetric analyses were conducted on a Perkin Elmer TGA7. Typically around 10 mg of sample was heated under air flow (100ml/min) from room temperature to 100^{o}C then held for 10 minutes to remove moisture. The sample was heated to 900^{o}C at a heating rate of 10^{o}C/min.

2.2. Task 2: Preparation and characterization of coal char sorbents

The activation of the samples was performed in a horizontal activation reactor. The samples were heated under a nitrogen flow to the desired temperature, and then steam was introduced into the reactor for 1-3 hours, while the reactor was kept under isothermal conditions, as described elsewhere (Maroto-Valer et al., 2000, 2001; Zhang et al., 2003). In addition, the char sample

FA1 was subjected to physical separation by a sink/flotation technique using a liquid medium with density 1.6-2.5 g/ml and then followed by an acid digestion step of HCl/HNO_3/HF at 65°C to produce a carbon rich sample (FA1-Dem) that was used for the subsequent mercury capture studies. The FA1-Dem sample was steam activated at 850°C for 60 minutes using a horizontal furnace, under the conditions described above. The porous structure of the activated chars was characterized by N_2-77K isotherms, as described in Section 2.1.3.

2.3. Task 3: Mercury capture by the prepared char sorbents

2.3.1. Mercury capacity studies

The samples prior to the mercury adsorption tests were analyzed by a cold vapor atomic absorption spectrophotometer (CVAA) according to EPA 7470 method for inherent mercury content. A char sample and its activated counterpart, together with a commercial activated carbon, Darco Insul, were tested for mercury adsorption using a fixed-bed with a simulated flue gas at 138°C. A detailed description of the mercury capacity test protocol used in this work can be found elsewhere (Granite et al., 2000). The simulated flue gas used in the study contains 16% CO_2, 5% O_2, 2,000ppm SO_2, 270ppm Hg and balance nitrogen, and the length of exposure is 350 minutes.

2.3.2. XPS studies

The surface chemistry of the samples was investigated by X-ray photoelectron spectroscopy (XPS) using a Kratos Analytical Axis Ultra instrument and a monochromatic aluminum (1486.6eV) X-ray source. All data were charge corrected as C-C in carbon 1 s at 284.4 eV. The samples were mounted on double-sided adhesive tape and analyzed as received. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) of the Kratos instrument to the integrated peak areas. These RSFs take into consideration of the X-ray across section and the transmission function of the spectrometer. The approximate sampling depth under these conditions was 25 Å.

3. Results and Discussion

3.1. Task 1: Procurement and characterization of coal gasification and combustion chars

3.1.1. LOI of the samples

Eleven char samples and 2 commercial activated carbons, which are typically used as benchmarks for mercury capture studies, were collected. Among the char samples, 4 are biomass (wood) based and 7 are coal based (3 from PRB, 2 from subbituminous coal and 2 from lignite). Five samples were generated from gasifiers and 6 were generated from boilers, as listed in Table 1.

The LOI of the collected samples are widely distributed. Some samples contain more than 50% LOI. For instance, CPC-Knockout, which is a biomass-based sample collected from a gasifier, has a LOI as high as 89.6%, and contains only 10.4% ash. The other sample collected from the same facility, CPC-Filter, also has a high LOI, 70.6%. Another wood-based char sample, collected from the GTI gasifier, contains very small aluminum beads; however, they were separated from the char sample by sieving. The separated char sample, GTI-Woodchar, also has a high LOI (85.4%), as presented in Table 1. The other wood-based sample Tra-WoodFA, has a relatively low LOI, 22%, compared to the other wood-based samples.

Table 1. Summary of the samples collected in the present report.

Sample	Feed used	System	LOI, wt%	Ash,%
Gasif-1	Lignite	Gasifier	9.30	91.7
Gasif-2	Lignite	Gasifier	43.1	57.1
CPC-Filter	Wood	Gasifier	70.6	29.4
CPC-Knockout	Wood	Gasifier	89.6	10.4
GTI-Woodchar	Wood	Gasifier	85.4	14.6
Tra-WoodFA	Wood	Boiler	22	78
FA1	Subbit.	Boiler	62.7	37.3
FA2	Subbit.	Boiler	28.0	72.0
F9830	Subbit. (PRB)	Boiler	1.03	98.9
DarkAsh99	Subbit. (PRB)	Boiler	0.66	99.3
DarkAsh00	Subbit. (PRB)	Boiler	0.83	99.2
FGD	Lignite	Activation	63.8	36.2
FGL	Lignite	Activation	68.3	31.7

Some of the coal-based samples also have high LOI, such as FA1 and Gasif-2 (62.7% and 43.1%, respectively). The two Gasif-1 and Gasif-2 samples were collected from the same Southern Company's gasifier. Gasif-1 has an LOI of 9.3%, while Gasif-2 has a higher LOI of 43.1%. Gasif-2 is not a typical fly ash sample because it was collected from a vessel at the end of the run, and not collected during a steady-state operation conditions. However, there are some coal-based samples that have very low LOI, such as the samples collected from Southern Company boiler, DarkAsh99, DarkAsh00 and F9830, that have a LOI value as low as ~1%. The sample DarkAsh99 has the lowest LOI, 0.66%. Generally, the biomass-based samples collected have higher LOI than the coal-based samples.

Darco FGD and FGL are commercial activated carbons, which have been widely adopted as a baseline for mercury sorbent studies. Therefore, during this reporting period, they have been intensively characterized, including their LOI and detailed porous structure analysis. Darco FGD is a lignite-based commercial activated carbon, with very small particle size (less than 325 mesh), and is claimed as a free flowing powdered carbon. Its LOI value is 65% as listed in Table 1 (i.e., it contains 35% ash).

3.1.2. Porosity studies

3.1.2.1 Isotherms of coal-based char samples

The N_2-77K isotherms of seven coal-based samples are shown in Figure 1. The isotherms of two lignite-based samples (Gasif-1 and Gasif-2) are obviously different from those of subbituminous coal (FA1, FA2, F9830, DarkAsh99 and DarkAsh00). The former has a little increment in the range of micropore filling at low relative pressure, which keeps increasing with the relative pressure until the saturation pressure is reached. Additionally, there is a large hysteresis loop in the isotherms, which suggests that there are many mesopores in the samples. Additionally, Gasif-1 and Gasif-2, collected from a gasifier fed with lignite, have isotherms with similar shape, which suggests that although they have different carbon content, the pore volume distributions of the two samples are similar. In contrast, the isotherms of the subbituminous coal-based samples, especially FA1 and FA2, indicate that there are many micropores and macropores in the samples.

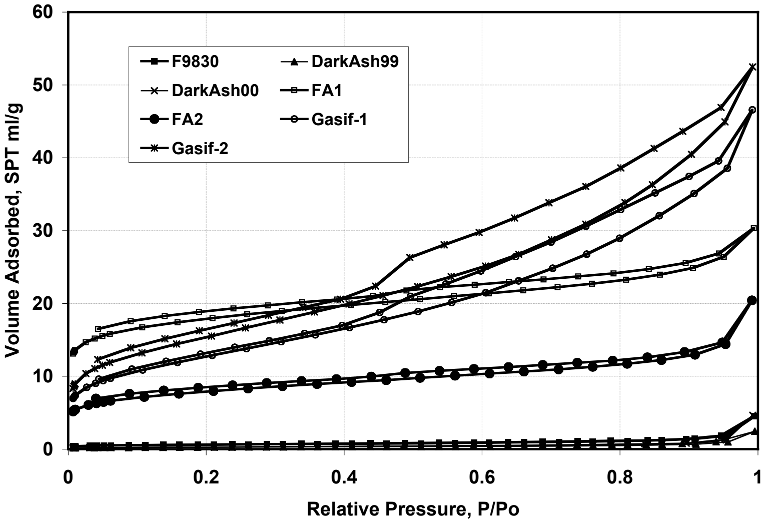


Figure 1. N_2-77K isotherms of coal-based char samples.

3.1.2.2. Isotherms of biomass-based char samples

The N_2-77K isotherms of the biomass-based samples are shown in Figure 2. Corresponding to its high carbon content of 89.6%, CPC-Knockout has the greatest adsorption, while Tra-WoodFA has the lowest adsorption among the wood-based samples. Two isotherms of samples from CPC gasifier, CPC-Knockout and CPC-Filter, exhibit an adsorption increasing trend in the entire relative pressure range, especially for CPC-Filter, which has a large increase when the pressure approaches saturation. Therefore, these two samples may have many mesopores and macropores, especially the CPC-Filter sample. In contrast, for the Tra-WoodFA sample collected from a boiler, its adsorption increases much less with increasing relative pressure, which suggests that the sample is dominated by micropores.

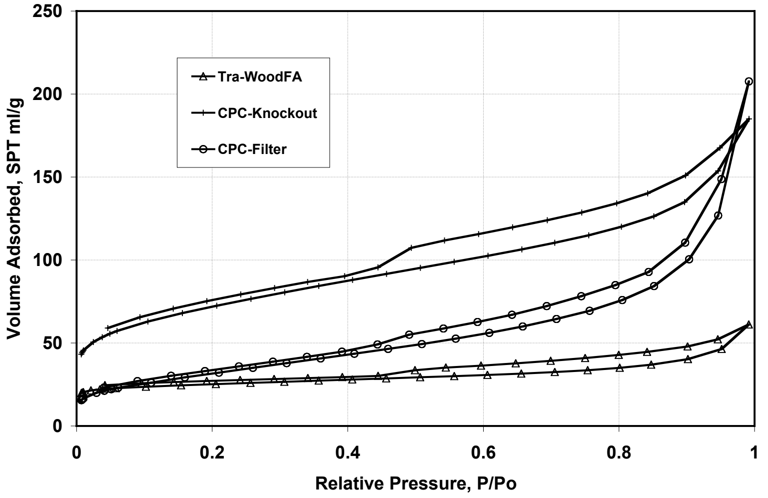


Figure 2. N_2-77K Isotherms of wood-based char samples.

3.1.2.3 Surface area and pore volume of the samples

Based on the isotherms shown in Figures 1 and 2, the surface area and pore volume of the char samples were calculated and are listed in Table 2. Corresponding to its high LOI and adsorption capability, CPC-Knockout has the highest surface area and pore volume, 243.2 m^2/g and 0.238 ml/g, respectively. It confirms our previous observation that the remaining carbon in fly ash has generated a certain porosity during the combustion/gasification process. The sample CPC-Knockout can be expected to have sorbent properties prior to any further treatment. Another sample collected from the sample facility, CPC-Filter, also has a high surface area and pore volume, 119.6 m^2/g and 0.196 ml/g, respectively.

Table 2. Porosity analysis results of the char samples.

Sample	S_{BET}, m^2/g	V_t, ml/g
Gasif-1	45.4	0.060
Gasif-2	54.5	0.070
CPC filter	120	0.196
CPC Knockout	243	0.238
Tra-WoodFA	77.4	0.072
FA1	53.1	0.040
FA2	25.5	0.020
F9830	2.10	0.003
DarkAsh99	0.90	0.002
DarkAsh00	1.10	0.002
FGD	526	0.473
FGL	476	0.411

The two samples collected from Southern Company's gasifier, Gasif-1 and Gasif-2, have similar surface areas of 45.4 and 54.5 m^2/g, respectively, although they have quite different LOI, 8.3 and 42.9%, respectively. Three low LOI samples collected from the Southern Company boiler, F9830, DarkAsh99 and DarkAsh00, as expected from their low LOI, have surface areas as low as 1~2 m^2/g. As expected, the commercial activated carbons have the highest surface areas and pore volumes of the studied samples.

3.1.3. TGA profiles

3.3.3.1. Coal-based char samples

The TGA curves of four samples from subbituminous coal are shown in Figure 3. All the samples began to loss weight at around 450°C and continue to lose weight at a constant rate until 650°C with one step change, except for sample Gasif-2, which began to lose weight as early as 200°C until it reached 480°C and it exhibited two step changes in weight loss. This suggests that the sample Gasif-2 may have a different reactivity rate during the activation process compared to other other samples, especially Gasif-1, although both Gasifi-1 and Gasif-2 were collected from the same facility and have similar surface area.

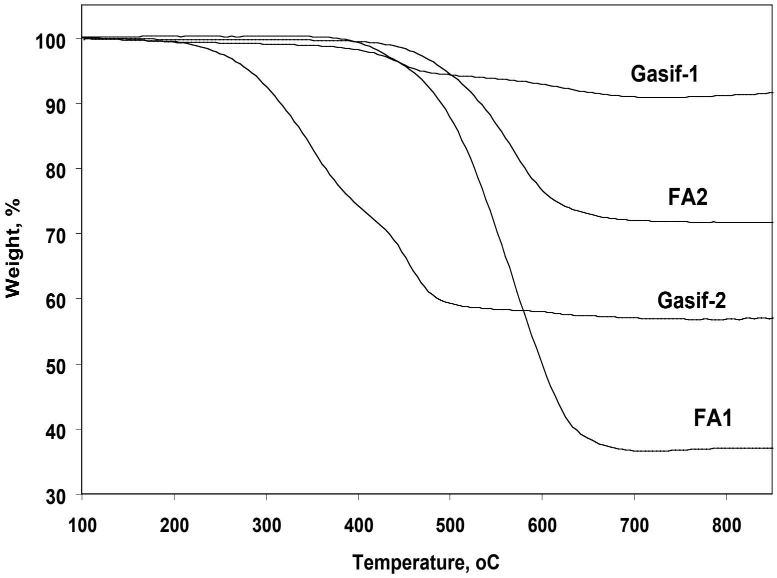


Figure 3. TGA curves of coal-based char samples.

3.1.3.2 Biomass-based char samples

The weight changes of wood-based char samples, when heated up to 850°C in air, are recorded and shown in Figure 4. Compared to the samples from coal, all wood-based samples have a lower starting point for the initiation of weight loss (180-300°C), and their thermal reaction is much more complex in the view of the TGA data, which have more than one weight loss step during a broader temperature range. For example, GTI-Woodchar lost around 80% of its weight in the temperature range 180 to 350°C, then lost another 2% weight at 550 to 700°C. While CPC-Knockout sample lost around 90% weight within 350-520°C with 7 different rates.

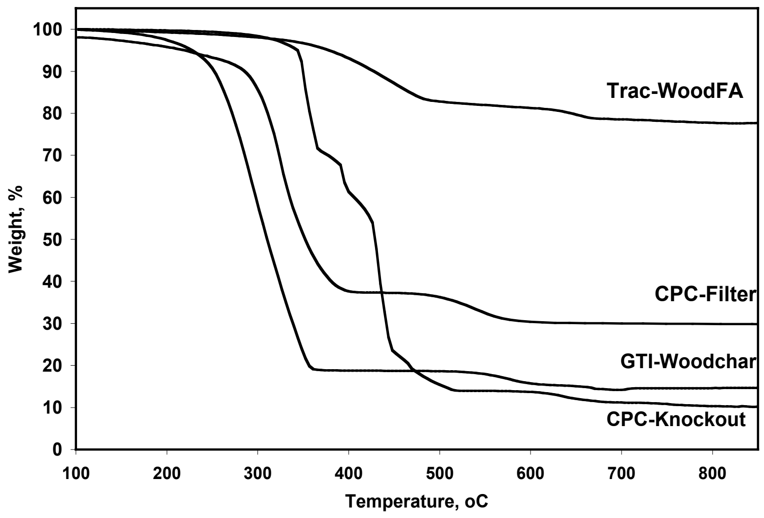


Figure 4. TGA curves of wood-based char samples.

3.2. Task 2: Preparation and characterization of coal char sorbents

3.2.1. Isotherms of activated chars

The char samples, GTI and FA1, were activated with steam at 850°C for 30 minutes. These two samples were selected for the activation studies because of their high LOI contents. The isotherms of the resultant activated carbons, FA1-30 and GTI-30, are shown in Figure 5. It should be noted that the isotherms of the activated chars shown in Figure 5 are on a carbon basis, while the isotherms of the parent chars (Figures 1 and 2) were presented on a total weight basis. The isotherms of the commercial activated carbons, FGD and FGL are also shown in Figure 5. It is obvious that the activated GTI char has a similar isotherm to that of the commercial activated carbon. All isotherms contain a hysteresis loop, which is usually associated with the filling and emptying of mesopores by capillary condensation. Besides the steep rise at the low relative pressure, which corresponds to micropore filling, the isotherm keeps increasing with the relative pressure, even near saturation pressure, which suggests there are mesopores and macropores in the sample. In contrast, activated coal-based char, FA1-30, has a type 1 isotherm, which features a steep increase at low relative pressure and levels off at higher relative pressure. However, compared to the raw char (FA1 and GTI-Woodchar, Figure 1), both activated char samples (FA1-30 and GTI-30) have much more developed porosity after the 30 minutes one-step activation process.

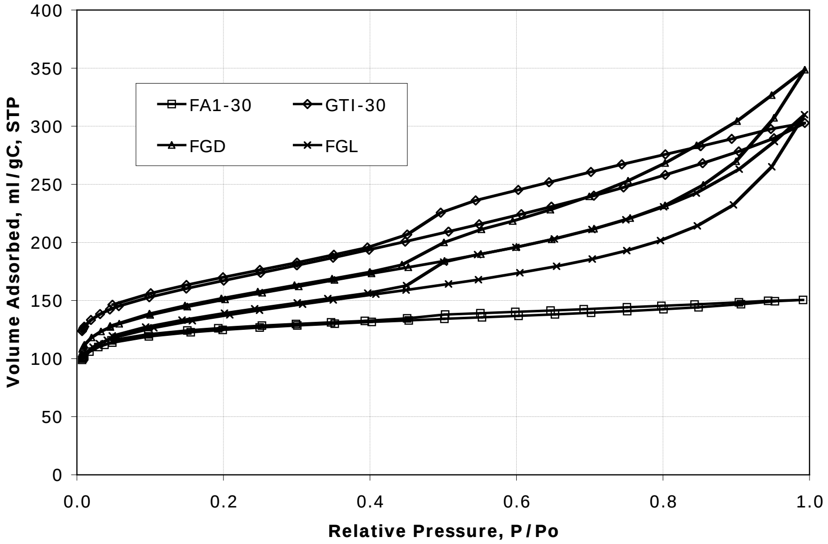


Figure 5. Isotherms of activated chars (FA1-30 and GTI-30) and commercial activated carbons (FGD and FGL).

3.2.2. Surface area and pore volume distribution of activated chars

The surface area and pore volume distribution of the samples were calculated from the isotherms in Figure 5 using the alpha-s method and the results are presented in Figures 6 and 7. The surface area and pore volume distribution of the activated chars are presented on a carbon basis.

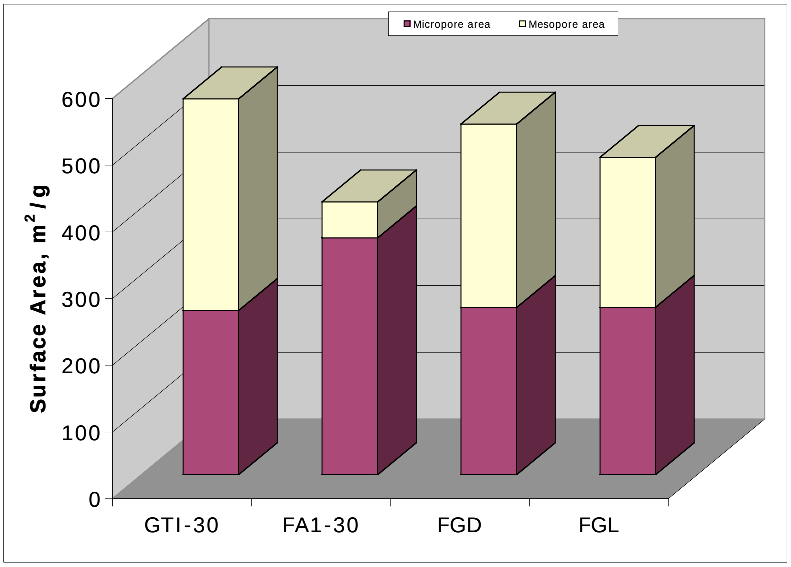


Figure 6. Surface area distribution of the activated chars (GTI-30 and FA-30) and commercial activated carbons (FGD and FGL).

The activated GTI sample has the greatest surface area ($564m^2/g$) on a carbon basis, and there is $317m^2/g$ contributed from mesopores, which accounts for ≈56% of the total. The commercial activated carbon FGD has a surface area of $526m^2/g$, and ≈53% ($275m^2/g$) is from mesopores. Corresponding to its different isotherm shape, activated FA1 has only 13% surface area that is contributed from mesopores (54 vs. $409m^2/g$).

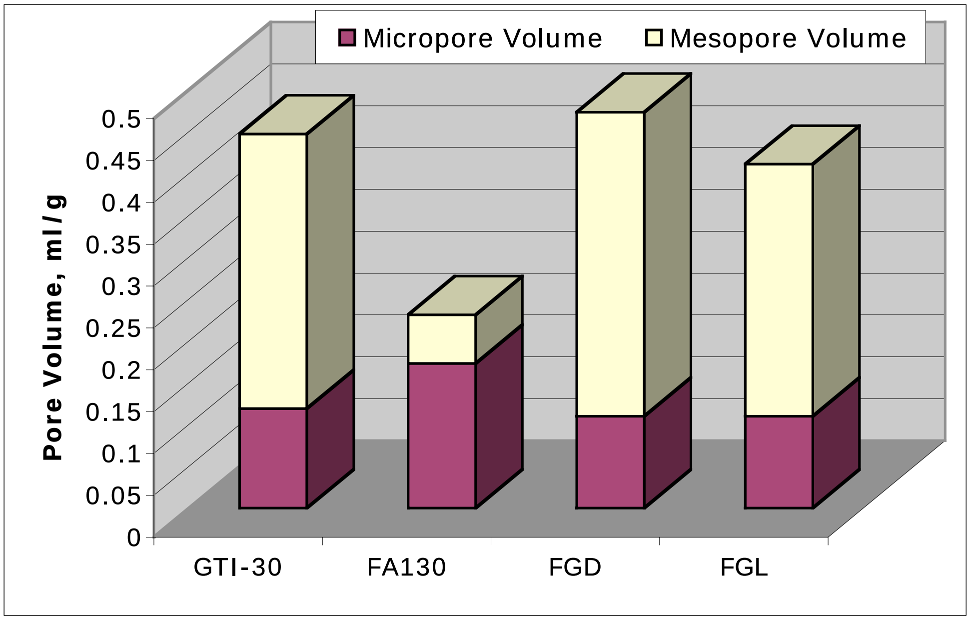


Figure 7. Pore volume distribution of the activated chars (GTI-30 and FA-30) and commercial activated carbons (FGD and FGL).

FGD has a total pore volume of 0.473 ml/g and 77% of the pore volume is from mesopores. GTI-30 has a similar pore volume distribution, with a total pore volume of 0.447ml/g of which ≈73% is from mesopores. Activated FA1 has more micropores and a larger mesopore volume, but the mesopores only account for 25% of the total pore volume.

Due to the small size of the micropores and overlapping of the fields of opposite walls of the micropores, the micropores are the major active site for most adsorbates. The mesopores act as adsorption sites for larger molecules and as transportation routes for small adsorbates. In certain cases, the transportation function of the mesopores are much more important than their adsorption function. For instance, for the carbon sorbent injection technology to control mercury emissions from coal-fired flue gas, the retention time of carbon in the flue gas is very short, on the order of several seconds; consequently, the reaction of the mercury and the carbon is mass transfer-limited (Sjostrom et al., 2002). Therefore, carbon sorbents for the mercury capture market should be those sorbents with good mass transfer properties. Darco FGD is a commercial activated carbon, which has been widely adopted as a baseline for mercury sorbent studies, and as expected, it presents a large amount of mesopores. The activated char sample, GTI-30, has a large quantity of mesopores and its surface area is comparable to the commercial activated carbon FGD (564 vs. 526m^2/g).

3.2.3. Cleanability and sample porosity

The sample FA1 was collected from a pulverized coal unit and has a carbon content around 58%, which is higher than those reported in previous studies that are typically ~15%. However, this work focuses on the utilization of high carbon fly ashes, and therefore, this high carbon content sample was intentionally selected. It is known that the mercury capacity of the inorganic fraction is very low compared to the carbon present in ash (Serre et al., 2000; Hassett et al, 1999). Therefore, the sample was subjected to physical separation by a sink/flotation technique using a liquid medium with density 1.6-2.5 g/ml and then followed by an acid digestion step of $HCl/HNO_3/HF$ at 65^oC to produce a carbon rich sample (FA1-Dem) that was used for the mercury capture studies. The ash content and porosity of the samples were characterized by TGA and nitrogen 77K isotherms, respectively. The ash content and porous structure, including total surface area, pore volume and average pore size (based on the cylinder pore model), for DEM-PCC1 are presented in Table 3.

Table 3. Porosity of the de-ashed char sample FA1-Dem, activated char AC-FA1 and Darco Insul.

Sample	Ash Content %	S_{BET} m^2/g	$V_{0.95}$ ml/g	D_a nm
FA1-Dem	3.6	53	0.040	3.0
AC-FA1	11.2	863	0.490	2.3
Darco Insul.	-	700	-	-

Note: Darco Insul is a byproduct of Darco FGD.

The cleanability process adopted in the present study can effectively remove the ash from the char sample, ash content 3.6% vs. 37.3% for FA1-Dem and FA1, respectively. The sample, FA1-Dem, has surface area and pore volume of 53 m^2/g and 0.04 ml/g, respectively. This suggests that the fly ash carbon has already generated certain porosity while in the PC combustor prior to the activation process, and the pores generated are mainly in the mesopore range with an average pore size about 3nm.

The porosity of the activated sample, AC-FA1, is also listed in Table 3. Compared to the parent char sample, the one-step steam activation process has successfully increased the surface area and pore volume of the char sample by creating new micropores or small mesopores. After activation the sample has a surface area of 863m^2/g, which is even higher than that of Darco Insul (700m^2/g, Table 4), that is a commercial activated carbon. Furthermore, the average pore size narrowed to 2.3nm compared to 3.0nm for the precursor char sample.

The mesopore size distribution curves of the de-ashed sample and the activated sample are shown in Figure 8. For the char sample, FA1-Dem, most of the mesopores are around 4.0nm, similar to other activated fly ash carbons and activated carbon fibers (Zhang et al, 1997). However, for the activated char, AC-FA1, besides the main peak at around 4.0 nm, another peak around 2.nm is observed, indicating some small mesopores have been generated during the activation process.

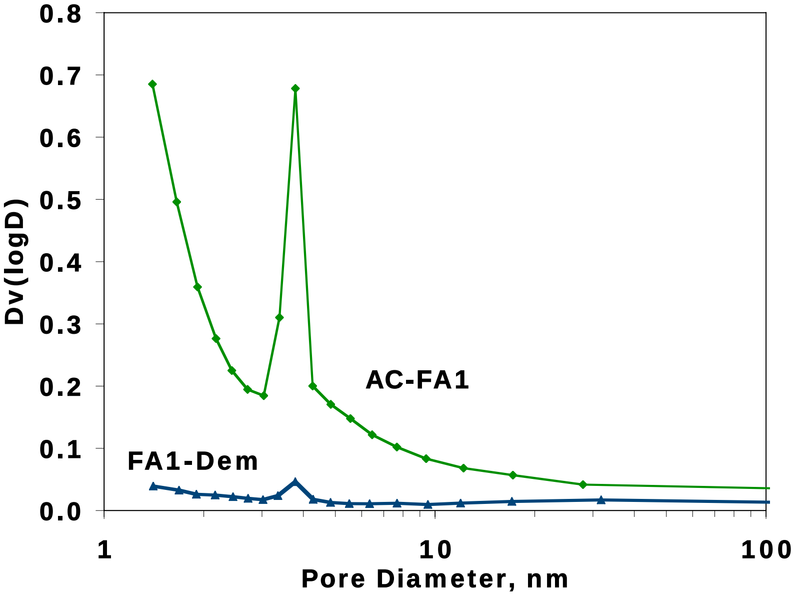


Figure 8. Mesopore size distribution of the demineralized fly ash carbon (FA1-Dem) and the activated fly ash carbon (AC-FA1).

3.3. Task 3: Mercury capture by the prepared char sorbents

3.3.1. Inherent mercury content of the char samples

The inherent mercury content of the char samples was analyzed by CVAA and the data is presented in Table 4. The mercury contents are very low, mainly below 0.1 ppm, and for two samples (FGD and Gasif-2), the mercury concentrations are below the instrument detection level (<0.01ppm). The sample from the GTI gasifier using wood as feedstock, GTI-Woodchar, has the highest mercury content (2.84 ppm). Darco FGD is a lignite-based commercial activated carbon, which has been widely adopted as a baseline for mercury sorbent studies. The FGD sample has a very small particle size (less than 325 mesh), and is claimed as a free flowing powdered carbon. Its mercury content is around 0.01ppm as listed in Table 4.

Table 4. Mercury content of selected samples collected in this study.

Sample	Coal Used	System	LOI, wt%	Mercury, ppm
Gasif-2	Lignite	Gasifier	43.1	0.11
CPC-Filter	Wood	Gasifier	70.6	0.03
CPC-Knockout	Wood	Gasifier	89.6	0.02
GTI-Woodchar	Wood	Gasifier	85.4	2.84
FA1	Subbit.	Boiler	62.7	0.20
FGD	Lignite	Activation	63.8	<0.01 [1]

[1] Below instrument detection level

3.3.3. Mercury capacity studies

Mercury adsorption test results are listed in Table 5, where the data obtained under the same conditions for the commercial activated carbon Darco Insul are also presented. The de-ashed char sample FA1-Dem has a mercury capacity as high as 1.85mg/g, which is somewhat comparable to the commercial activated carbon Darco Insul, whose mercury capacity is 2.77mg/g. Surprisingly, the activated char sample AC-FA1 has lower mercury capacity than its precursor fly ash carbon FA1-Dem, although its surface area is around 15 times larger than its precursor, 863m^2/g vs. 53m^2/g. However it should be noted that the precursor fly ash carbon has larger pore size than the activated sample (Table 4 and Figure 8), which suggests that the parent fly ash carbon has better mass transfer properties than its activated counterpart.

Table 5. Mercury capacity of selected samples.

Sample	Mercury Capacity, mg/g *
FA1-Dem	1.85
AC-FA1	0.23
Darco	2.77

Note: Tested using a fixed bed at 138°C and the simulated flue gas (Section 2.3.1).

Previous studies on a Thief sorbent, which is a semi-combusted coal extracted from a combustion chamber, have also shown that sorbents with modest surface areas yet exhibit good capacities for mercury from flue gas (Granite et al., 2000). Micropores (< 2nm) are the major active sites for most adsorbates, while mesopores (2-50nm) act as adsorption sites especially for larger molecules, and also as transportation routes for small adsorbates. In certain cases, the transportation function is more important than the adsorption site function. For instance, in the carbon sorbent injection technology to control mercury emissions, the retention time of carbon in flue gas is very short, and therefore, at most conditions, mass transfer rate is the determining factor and the adsorption of the mercury onto the carbon surface is mass-transfer-limited (Sjostrom et al, 2002). Therefore, a carbon sorbent selected for mercury capture should have good mass transfer properties. This is consistent with the date reported here, where in addition to the total surface area, the pore size also seems to play a role in the mercury capacity of the sorbents. However, the very different mercury capacity of the samples studied here cannot only be ascribed to differences in their porous structures. Other properties, especially surface functionality, are also important to determine their mercury capacity, as described in the Section below.

3.3.4. XPS studies

In order to investigate the surface properties of the samples, FA1-Dem and AC-FA1, XPS analyses were conducted using a Kratos Analytical Axis Ultra instrument, and the resultant survey spectra are shown in Figure 9. For FA1-Dem, in addition to the two major peaks C1s and O1s, there are also two small peaks at 690 KeV and 200 KeV, which are ascribed to F1s and Cl 2p, respectively. The presence of fluorine and chlorine in the FA1-Dem sample is probably a result of the acid digestion step, where HCl and HF acids were used. Furthermore, the comparison of the spectra for the two samples also shows that the O 1s peak for FA1-Dem is larger than that for AC-FA1. This indicates that the activation process may have caused the loss of certain oxygen functional groups. In addition, the activation process also removed almost all of F and Cl species from the surface of the sample, as shown by the lack of peaks at 690 Kev and 200 KeV for F 1s and Cl 2p, respectively, for AC-FA1 (Figure 9).

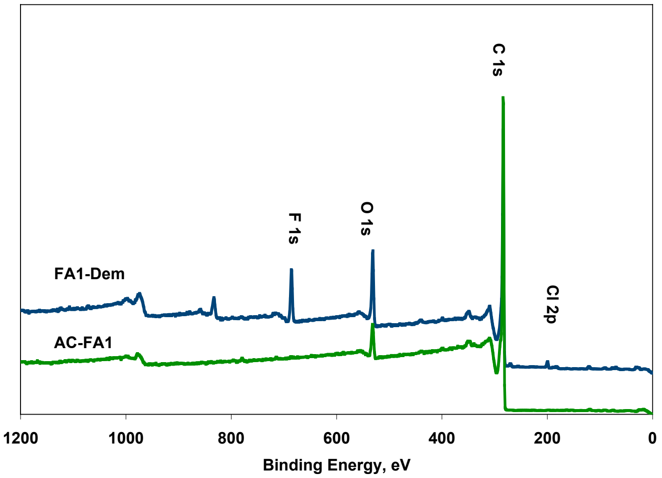


Figure 9. XPS survey spectra of the demineralized fly ash carbon (FA1-Dem) and the activated fly ash carbon (AC-FA1).

The high resolution scan data of O1s and C1s peaks for these two samples are shown in Figure 10 and 11, respectively. In Figure 10, the C 1s curve of DEM-PCC1 shows a shoulder at higher binding energy besides the main peak at 284 KeV, which is ascribed to oxidized carbon. This corresponds to the O 1s spectrum in Figure 11, which splits into two peaks at around 532 KeV and 531.5KeV that are assigned to single bond C-O and double bond C=O, respectively (Wang et al., 2000).

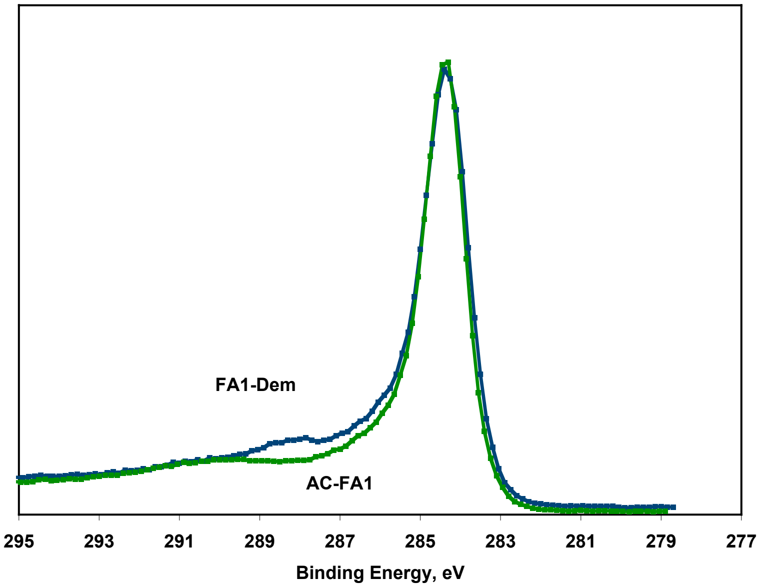


Figure 10. C 1s spectra of the demineralized fly ash carbon (FA1-Dem) and the activated fly ash carbon (AC-FA1).

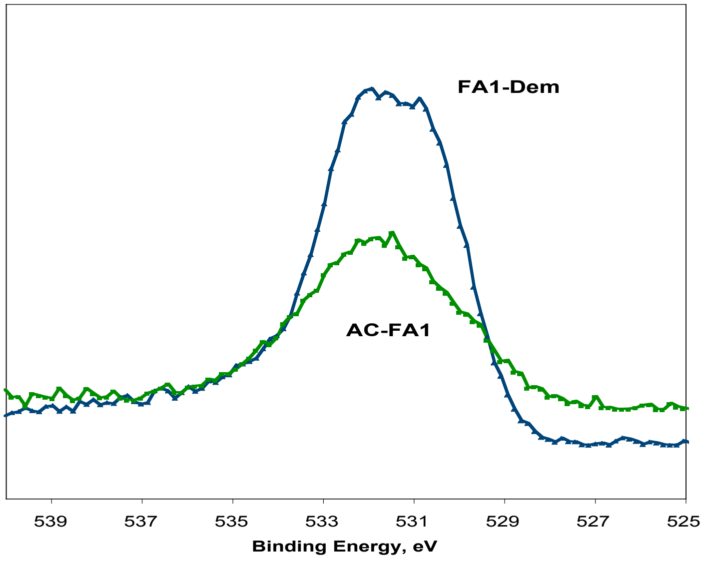


Figure 11. O 1s spectra of the demineralized fly ash carbon (FA1-Dem) and the activated fly ash carbon (AC-FA1).

Previous studies have focused on different adsorbents for mercury, including activated carbon, and also investigated the effect of several elements including F, Cl, I, S and O on mercury adsorption (Granite et al., 2000). EPA studies on the effect of activated carbon surface moisture on low temperature mercury adsorption indicated that surface oxygen complexes provide the active sites for mercury bonding (Li et al., 2002), where possibly lacton and carbonyl groups, are the active sites for Hg^0 capture (Li et al., 2003). However, other published work on the impact of surface heterogeneity on mercury uptake by carbonaceous sorbents under ultra high vacuum and atmospheric pressure concluded that in physisorption regime, oxygen functional groups decrease mercury adsorption due to their blocking of access for mercury to micropores, while in chemisorption regime, no significant impact of oxygen functionalities was observed (Won et al., 2002). The data discussed here supports the claim that the oxygen functionality and the presence of halogen species on the surface of fly ash carbons may promote mercury adsorption, while the surface area does not seem to have a significant impact on its mercury capacity (Table 5). Moreover, it has previously been reported that pre-treating activated carbon with HCl leads to higher capacity for Hg^0 adsorption in fixed bed capture tests (Ghorishi et al., 2002). Based on the above data, fly ash carbons from coal-fired power plant have the potential to capture mercury if they have mesoporous structure, and oxygen and halogen functional groups. It has been postulated that carbon sorbents have independent reaction sites that comprise at least an oxidation site and also a binding site for the oxidized Hg (Olson et al., 2000). Although this work cannot differentiate between the effect of oxygen functional groups, halogen species, and carbon sites, further studies on the modification of the surface properties of fly ash carbons and their mercury adsorption properties are underway to ascertain the effect of oxygen functionalities, halogen species and carbon sites.

4. Conclusions

Following the demand for mercury emission control and utilization of chars, this work focuses on developing sorbents from coal chars for mercury capture and to determine their mercury capacity under typical flue gas compositions. During this project, eleven char samples, including six samples from boiler systems (DarkAsh 99, DarkAsh00, F9830, Tra-WoodFA, FA1 and FA2) and five samples from gasifiers (Gasif-1, Gasif-2, CPC-Filter, CPC-Knockout and GTI-Woodchar) were collected and analyzed. These samples consisted of 4 biomass-based samples (CPC-Filter, CPC-Knockout, Tra-WoodFA and GTI-Woodchar) and 7 coal-based samples (including lignite- and sub-bituminous-based, Gasif-1, Gasif-2, FA1, FA2, DarkAsh 99, DarkAsh00 and F9830). In addition, two commercial activated carbons (Darco-FGD and FGL), which have been widely adopted as a baseline for mercury sorbent studies, were also analyzed. Furthermore, two selected samples, one biomass-based sample (GTI-Woodchar) from a gasifier and one coal-based sample (FA1) from a boiler, were activated by steam and the porous textures of the resultant samples were analyzed.

Of the samples collected, the wood-based samples have higher LOI than the coal-based samples. For example, wood-based sample CPC-Knockout has a LOI as high as 89.6%, although some coal-based samples also have high LOI, such as FA1 and Gasif-2 (62.7 and 43.1%, respectively).

The lignite-based commercial activated carbon, Darco FGD, contains 35% ash. Corresponding to its high LOI and adsorption amount, CPC-Knockout has the highest surface area and pore volume, 243.2 m^2/g and 0.238 ml/g, respectively. The sample CPC-Knockout can be expected to be a good sorbent prior to any further treatment. Compared to the coal-based samples, all wood-based samples have a lower starting point for weight loss (180-300^{o}C vs. 200-400^{o}C), and their thermal reaction is more complex.

Compared to the raw char (FA1 and GTI-Woodchar), both activated char samples (FA1-30 and GTI-30) have much more developed porosity after the 30 minutes one-step activation process. The activated GTI sample has surface area as high as 564m^2/g on a carbon basis, which is comparable to the commercial activated carbon FGD of 526m^2/g. The mesoporosity of activated GTI char is 56% on surface basis or 73% on volume basis. This is comparable to the commercial activated carbon FGD, which is 53% is on surface basis or 77% on volume basis. Both samples have a porous structure containing a large amount of mesopores, suggesting that they will have good mass transfer properties. A high mass transfer rate is a key factor in determining the mercury capture properties for mercury control in coal-combustion flue gas.

This work has studied the mercury capture capacity of fly ash carbon, and the effect of the properties of fly ash carbon and its activated product, including nano-pore structure and surface functionality. The fly ash carbon sample FA1-Dem has a mercury capacity as high as 1.85mg/g, which is comparable to the commercial activated carbon Darco Insul, whose mercury capacity is 2.77mg/g. Surprisingly, the activated fly ash carbon sample AC-FA1 has lower mercury capacity (0.23mg/g) than its precursor fly ash carbon FA1-Dem, although its surface area is around 15 times larger than its precursor, 863m^2/g vs. 53m^2/g. However, XPS data indicates that the demineralization using $HCl/HNO_3/HF$ not only removed most of ash from the sample, but it also changed the surface chemistry of the sample, leaving F, Cl elements and oxygen functional group on the surface of fly ash carbon. On the other hand, the activation process at 850^{o}C for 60 minutes may cause the loss of certain oxygen functional groups and almost all of F and Cl elements from the surface of the sample. The data in the present paper suggests that the oxygen functionality and the presence of halogen species on the surface of fly ash carbons may promote mercury adsorption, while the surface area does not seem to have a significant impact on its mercury capacity

Based on this work, fly ash carbons from coal-fired power plant have the potential to capture mercury if they have mesoporous structure, and oxygen and halogen functional groups. The studies presented here have shown that the chars investigated showed different mercury capacities. Although mercury capture technologies will be site specific, this work indicated that chars are a potential low-cost sorbent. Further studies on the modification of the surface properties of fly ash carbons and their mercury adsorption properties are underway to ascertain the effect of oxygen functionalities, halogen species and carbon sites.

5. Publications resulting of this project

1. M. M. Maroto-Valer, Y. Zhang, Z. Lu, E. Granite, and H. Pennline, Development of activated carbons from unburned carbon for mercury capture, *Proceedings International Ash Utilization Symposium*, CAER-University of Kentucky and U.S. DOE National Energy Technology Laboratory, Lexington, KY, October 20-22, 2003, Paper 90 (CD-ROM publication).
2. Y. Zhang, M. M. Maroto-Valer, E. Granite, Z. Tang, and H. Pennline, Understanding the properties of unburned carbon in fly ash towards its mercury capture capacity, *Proceedings of 20th Annual International Pittsburgh Coal Conference*, University of Pittsburgh, Pittsburgh, PA, September 15-18, 2003, Paper 240.pdf (CD-ROM publication).
3. Y. Zhang, E.J. Granite, M. M. Maroto-Valer, and Z. Tang, Activated carbons produced from unburned carbon in fly ash and their application for mercury capture *Prepr. Am. Chem. Soc. Div. Fuel Chem*., 2003, 48(1), 32-33.
4. M.M. Maroto-Valer, Y. Zhang, B.G. Miller, E. Granite, Z. Tang and H. Pennline, Mercury oxidation and capture by coal chars, *Proceedings Carbon 2004*, American Carbon Society, Providence, RI, July 11-16, 2004, Paper L035.pdf (CD-ROM publication).
5. M.M. Maroto-Valer, Y. Zhang, and B.G. Miller, Development of activated carbons from coal and biomass combustion and gasification chars, *Prepr. Am. Chem. Soc. Div. Fuel Chem.*, 2004, 49(2), 690-691.
6. M.M. Maroto-Valer, Y. Zhang, E. J. Granite, Z. Tang, H. W. Penline, Effect of porous structure and surface functionality on the mercury capacity of a fly ash carbon and its activated sample, *Fuel*, In Press.

6. Acknowledgements

The authors would like to acknowledge the Consortium for Premium Carbon Products from Coal (CPCPC) for support and Southern Company, Norit Americas Inc, Community Power Corporation, Tractebel Electricity & Gas International and Gas Technology Institute for providing the study samples. The authors would also like to thank DOE National Energy Technology Laboratory for the mercury capacity studies.

7. References

Brown, T.D., Smith, D.N., O'Dow, W.J., and Hargis, R.A., 2000, Fuel Proc. Tech, 65, 311.

EPA mercury web site, 2002, http:// www.epa.gov/mercury/information.htm#fact_sheets.

Ghorishi SB, Keeney RM, Serre SD, Gullett BK, Jozewicz WS. Environmental Sc. & Tech. 2002; 36(20):4454

Granite, E.J., Pennline, H.W. and Hargis, R. A. Ind. Eng. Chem. Res. 2000*, 39*, 1020.

Hassett D.J. and Eylands K.E. Fuel 1999:78:243.

Kwon S., Borguet, E. and Vidic, R.D., Environ. Sci. Technol., 2002, 36, 4162-4169

Li, Y.H., Lee, C.W. and Gullet, B.K., Carbon 40(2002)

Li, Y.H., Lee, C.W. and Gullet, B.K., Carbon 40(2002) 65-72

Maroto-Valer, M.M, Andrésen, J., and Morrison, J., 2000, DOE Conf. on Unburned Carbon, 21.

Maroto-Valer, M.M., Zhang, Y., Lu, Z., Andrésen, J. M., and Schobert, H.H., 2001, Proc. 18th Intern. Pittsburgh Coal Conf., CD publication, 52-01.pdf.

Olson, E.S., Dunham, G.E., Sharma, R.K., Miller, S.J. Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem. 2000; 45 (4): 886.

Serre S.D., and Silcox G.D. Ind. Eng. Chem. Res. 2000;39:1723

Sjostrom, S., Ebner, T., Ley, T., Slye, R., Richardson, C., Machalek, T., Richardson, M., and Chang, R., 2002, J. Air & Waste Manage. Assoc., 52, 902.

Wang Y., Viswanathan H., Audi A.A., Sherwood P.M.A. Chem Mater. 2000;12:1100

Zhang, Y.; Wang, M.; He, F. and Zhang, B. J. Mater. Sci. *1997, 32*, 6009

Zhang, Y., Lu Z., Maroto-Valer, M.M, Andrésen, J.M. and Schobert H.H., Energy and Fuel, 2003a, 17, 369-377.

Zhang, Y., Maroto-Valer, M.M, Granite, E., Tang, Z., Pennline, H., Proceedings of 20^{th} annual international Pittsburgh coal conference, 2003b, CD-Rom, paper 240.pdf.