An Industrial-Based Consortium to Develop Premium Carbon Products from Coal

Annual Technical Progress Report
for the period
October 1, 2004 through September 30, 2005

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Abstract

Since 1998, The Pennsylvania State University (PSU) has been successfully operating the Consortium for Premium Carbon Products from Coal (CPCPC), which is a vehicle for industry-driven research on the promotion, development, and transfer of innovative technology on premium carbon products from coal to the U.S. industry. The CPCPC is an initiative being led by PSU, its co-charter member West Virginia University (WVU), and the U.S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL), who also provides the base funding for the program, with PSU responsible for consortium management. CPCPC began in 1998 under DOE Cooperative Agreement No. DE-FC26-98FT40350. This agreement ended November 2004 but the CPCPC activity has continued under the present cooperative agreement, No. DE-FC26-03NT41874, which started October 1, 2003.

The objective of the second agreement is to continue the successful operation of the CPCPC. The CPCPC has enjoyed tremendous success with its organizational structure, that includes PSU and WVU as charter members, numerous industrial affiliate members, and strategic university affiliate members together with NETL, forming a vibrant and creative team for innovative research in the area of transforming coal to carbon products. The key aspect of CPCPC is its industry-led council that selects proposals submitted by CPCPC members to ensure CPCPC target areas have strong industrial support.

A second contract was executed with DOE NETL starting in October 2003 to continue the activities of CPCPC. An annual funding meeting was held in October 2003 and the council selected ten projects for funding. Base funding for the projects is provided by NETL with matching funds from industry. Subcontracts were let from Penn State to the subcontractors on March 1, 2004. Nine of the ten projects have been completed and the final reports for these 2004 projects are attached.

An annual funding meeting was held in November 2004 and the council selected eleven projects for funding. Subcontracts were let from Penn State to the subcontractors on March 1, 2005. Three additional projects were selected for funding during the April 2005 tutorial/funding meeting. Subcontracts were let from Penn State to the subcontractors on July 1, 2005.

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Introduction

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The objective of the second agreement is to continue the successful operation of the CPCPC. The CPCPC has enjoyed tremendous success with its organizational structure, that includes PSU and WVU as charter members, numerous industrial affiliate members, and strategic university affiliate members together with NETL, forming a vibrant and creative team for innovative research in the area of transforming coal to carbon products. The key aspect of CPCPC is its industry-led council that selects proposals submitted by CPCPC members to ensure CPCPC target areas have strong industrial support.

CPCPC is promoting the use of secure, domestic coal resources to produce environmentally benign, high-value carbon products, such as carbon fibers, activated carbons, binder pitches, cokes for baked anodes and graphite, carbon foams, and carbon nanotubes. Although coal is the largest domestic fossil fuel hydrocarbon resource of the U.S., estimated to last over 200 years at the present consumption rate, most of the premium carbon products developed and manufactured in the U.S. derive mainly from petroleum, thus creating dependence on foreign imports to manufacture essential carbon products for the domestic market. To ensure sustainable development of the carbon product, the inherent potential of the great abundance of coal in the U.S. must be pursued to supply and introduce environmentally benign and affordable premium carbon products to the general public. The CPCPC has, since 1998, strived for the recognition of coal as a valuable resource for producing premium carbon products. Several success stories have been funded so far including low-cost carbon fibers from coal for lighter vehicles, large production of inexpensive activated carbon for water and air treatment, and high-quality binder pitches and cokes from coal. Through its continuation, the industrial-driven consortium is committed to further promote projects that use coal to ensure a sustainable development of the U.S. carbon industry.

The scope of PSU's activities includes managing the process of attracting and maintaining consortium members, soliciting proposal, providing the forum for the CPCPC council in selecting proposals from members for technical work in the subject area, awarding and monitoring subcontracts to members to accomplish the selected technical work, and disseminating the results of the technical work via meetings of the consortium.

Executive Summary

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Experimental

No experimental work was performed. The project requires management activities from PSU.

Results and Discussion

During this budget period, an annual funding meeting was held at the Radisson Hotel at Waterfront Place in Morgantown, West Virginia on November 17-18, 2004. Eleven projects were selected by the council and subcontracts were let by PSU on March 1, 2005. The project funding periods are March 1, 2004 to February 28, 2005. The projects, principal investigators, and proposing organizations are:

“Design of Nanoporous Carbon Derived from Coal Tar Pitch/ Polymer Blends for Ultracapacitors,” Ramakrishnana Rajagopalan, The Pennsylvania State University

“Continued Development of Pitch/Nanotube and Fiber Composites,” Rodney Andrews, University of Kentucky

“Feasibility Study of Commercial Coal Gasifier Gases to form Carbon Nanofibers,” Thomas W. Hughes, Applied Sciences, Inc.

“Nanocarbons from Anthracite Coal,” Caroline Burgess Clifford, The Pennsylvania State University

“Adapting Anthracite Coal and Stockpiled Anthracite Fines to Green Sand Iron Foundaries,” Fred Cannon, The Pennsylvania State University

“Mild Coal Extraction for Production of Anode Coke,” Rodney Andrews, University of Kentucky

“Premium Carbon Products from Coal: A Sulfur-Based Approach,” Paul Painter, The Pennsylvania State University

“TiO₂ – Coated Activated Carbon,” David W. Mazyck, University of Florida

“Coal-Derived Nanofiber Sheet Development,” David W. Firsich, Inorganic Specialists

“Coal-Derived Composites using Pitch and Fly Ash,” Alfred H. Stiller, West Virginia University

“Needle Coke from Coal-Derived Feedstock, Doug J. Miller, GrafTech International, Ltd

A meeting was held at GrafTech International, Ltd., in Parma, Ohio on May 18-19, 2005 to review proposals, perform technology transfer by providing updates on 2004 projects, and participate in tours at GrafTech’s facilities. Three projects were selected by the council for funding and subcontracts were let by PSU on July 1, 2005. The project funding periods are July 1, 2005 to June 30, 2006. The projects, principal investigators, and proposing organizations are:

“Activated Carbons for CO₂ Capture from Coal-Derived Pitch/Polymer Blends,” Rodney Andrews, University of Kentucky

“Mechano-Thermal Method to Produce Carbon Nanotubes from Anthracite Coal,” Caroline Burgess Clifford, The Pennsylvania State University

Carbon Foam Production through Plasticization of Coal Tar Binder Pitch with Supercritical CO₂,” Joseph M. Stoffa, Premium Carbon Products LLC

A tutorial was held August 4-5, 2005 with the theme ‘Coal Measures of Pennsylvania’. The tutorial started at PSU with an overview of regional geology, then stops were made at a railroad cut exposure of the Lower Kittanning seam of the Allegheny Formation at the Curwensville Dam and a road cut along Interstate-80 where the Upper Freeport seam and several rider coals were exposed. The group then spent the night in Pottsville, Pennsylvania. The following day the group observed the Pottsville Formation along Route 61, Reading Anthracite’s Wadesville surface anthracite mine, and the Bear Valley Mine whale back anticline before ending at PSU.

One recruiting trip was made by attending the 2005 World of Coal Ash Conference held April 11-15, 2005 in Lexington, Kentucky.

Conclusions

A second contract was executed with DOE NETL starting in October 2003 to continue the activities of CPCPC. An annual funding meeting was held in October 2003 and the council selected ten projects for funding. Nine of these ten 2005 projects have been completed and the final reports are appended to this report.

An annual funding meeting was held in November 2004 and the council selected eleven projects for funding. Subcontracts were let from Penn State to the subcontractors on March 1, 2005. Three additional projects were selected for funding during the April 2005 tutorial/funding meeting. Subcontracts were let from Penn State to the subcontractors on July 1, 2005.

References

None.

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COAL DERIVED NANOFIBER SHEETS

CONSORTIUM FOR PREMIUM CARBON PRODUCTS FROM COAL FINAL REPORT

Performance Period March 1, 2004 – February 28, 2005
Principal Author: Dr. David W. Firsich

Submitted March 31, 2005

Subcontract No. 2674-ISI-DOE-1874
“Coal Derived Nanofiber Sheets”

Inorganic Specialists, Inc.
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Miamisburg, Ohio

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Abstract

This project is focused on the creation of improved strength in paper sheets made from coal-derived carbon nanofibers from the company Applied Sciences, Inc. (ASI). The ultimate goal is to develop a higher-value form of these coal nanofibers by finding ways to make them into papers or monoliths. Applied Sciences produces the coal nanofibers from a gasified coal feedstock in place of the hydrocarbon gas that they normally use to make nanofibers. The reaction conditions are similar to those which produce one of ASI's nanofiber products (PR-19). Our SEM characterization of the coal-derived nanofibers found that they were similar (but not exactly the same) as hydrocarbon-derived PR-19.

This study shows that coal-derived nanofiber paper has a strength comparable to its hydrocarbon analog PR-19. However, PR-19 is not the variety of nanofiber that makes the strongest nanofiber paper. In fact, their PR-24 fiber makes a paper more than twice as strong. Thus a better strength will be had when a coal analog of the PR-24 fiber becomes available, probably by mid-2005. But even with the modest strength of the current type of coal nanofibers, it was possible to fabricate a number of demonstration papers of coal-derived nanofibers, even one sheet that was 10"x10", which was exhibited at a CPCPC conference.

During this program we successfully scaled up sheet size from 4" diameter circles to square sheets as large as 12"x12". A number of aspects of nanofiber papermaking were investigated, including experiments with binders to add strength, studies designed to improve paper conductivity, screening of filter membranes to move the project in the direction of continuous papermaking, and an initial study of flexibility vs. conductivity. Since coal-derived nanofiber starting material was in short supply, most of this development work has been done on hydrocarbon-nanofibers; our approach is to first develop successful papermaking processes with hydrocarbon nanofiber, and then apply them to the coal-derived nanofibers we have on hand. Next year, when Applied Sciences produces a coal-derived analog of PR-24, we will be able to work with coal fibers exclusively. A larger supply will also make it possible for us to make monoliths out of the coal-derived nanofibers that can be made into composites.

The advances during this project include a doubling of sheet strength, the ability to make larger sheet samples, the development of procedures to enhance conductivity, and a better understanding of the morphology of coal-derived nanofibers.

In short, we achieved our goal of being able to make nanofiber paper samples with sufficient strength and size that they could be offered as demonstration samples to prospective customers in government and private industry. Some of these samples were actually sold to customers during the project's duration.

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Introduction

A method for the bulk preparation of carbon nanofibers from gasified coal has recently been developed by Applied Sciences Inc. (ASI) in Cedarville Ohio. The synthetic technique produces coal-derived nanofibers in the form of low-density, spongy clumps, similar to other carbon nanofiber products made by ASI. This raw material has the potential for use in high-value products, but only after suitable processing.

ASI nanofibers can be made into pure sheet form using a method created by Inorganic Specialists in Miamisburg Ohio. Freestanding sheets between 2 and 20 mils thick have been produced. It is thought that sheet form will add value and make the product marketable for applications such as membranes, electrodes, composite pre-forms, fuel cell components, etc. The sheet fabrication method is currently a laboratory process similar to papermaking; it needs to be improved so that the resulting nanofiber paper is tougher and stronger. Such a development effort is the focus of this project, which tests changes in nanofiber surface chemistry, dispersion methods, and solution composition to seek a stronger coal-derived nanofiber sheet product. The preparation of pure nanofiber sheets will principally be studied, although a lesser effort will examine the incorporation of binders. Imparting improved toughness to these sheets will increase their commercial appeal and improve the prospects for mechanical scale-up of sheet fabrication. The improved-strength sheets developed in this program are being furnished to Applied Sciences for marketing purposes.

Applied Sciences Nanofibers and Coal-Derived Nanofibers

Applied Sciences “nanofibers” are actually large diameter nanotubes with an uncommon morphology. In contrast to conventional nanotubes that consist of concentric tubes of graphite sheets (**A**), the ASI nanofibers consist of stacked cups of graphite sheets (**B**), with edge sites along their length.

ASI produces two types of nanofibers in bulk. One is a 60 nm diameter nanofiber with structure **B**, and the second consists of structure **B** coated with a thick layer of turbostratic carbon (**C**), giving it a much larger diameter (200 nm). This distinction is noted because to date, the nanotubes ASI has made from coal have been produced with the recipe that produces structure **C**, and structure **C** makes a paper with different properties than structure **B**.

C

As synthesized by Applied Sciences, the coal-derived nanofiber contains more contaminants (metal, soot, sulfur) than its hydrocarbon-derived analog. These can be reduced with processing, but our study was not overly concerned with this- we did not want to add extra processing steps to make a very pure paper, we simply wanted to explore the basics of sheet preparation and strength. Happily, during the course of this program, the coal-derived nanofibers made by ASI became cleaner, less contaminated with carbon soot, as shown below.

Early batch of coal-derived nanotubes

Cleaner coal nanotubes from later batch

The sheets we are producing with our papermaking procedure can vary significantly in density, depending on the fiber used and the way it is dispersed in its stock solution. We have observed paper densities over the range of 0.12 g/cc to 0.37 g/cc. Since the density of an individual ASI nanotube has been calculated as ~ 1.5 g/cc, this corresponds to a volume packing density of 8% to 25%.

EXECUTIVE SUMMARY

This project is focused on the creation of improved strength in paper sheets made from coal-derived carbon nanofibers from the company Applied Sciences, Inc. (ASI). The ultimate goal is to develop a higher-value form of these coal nanofibers by finding ways to make them into papers or monoliths. Applied Sciences produces the coal nanofibers from a gasified coal feedstock instead of the hydrocarbon gas that they normally use to make nanofibers. The reaction conditions used to date are similar to those which produce one of ASI's standard nanofiber products (PR-19). Our SEM characterization of the coal-derived nanofibers found that they were similar (but not exactly the same) as hydrocarbon-derived PR-19.

We have found that coal-derived nanofiber paper has a strength comparable to its hydrocarbon analog PR-19. These papers are about half as strong as the paper made from a different ASI nanofiber product (PR-24). Binders improve the strength of coal-derived nanofiber papers, allowing the preparation of thick papers or monoliths of the material. When new varieties of coal nanofiber that mimic PR-24 become available, strength should improve dramatically, and thin flexible sheets of the material can be made. Our expectation is that ASI will be making such materials by mid-2005. But even with the modest strength of the current type of coal nanofibers, it was possible to fabricate a number of demonstration papers of coal-derived nanofibers; one sheet was 10"x10", and was displayed at a CPCPC conference.

Much of this project's development work on enhancing strength, flexibility, and conductivity in nanofiber papers was performed on hydrocarbon-derived nanofiber, simply because we had a lot of it, and not much coal nanofiber. Advances from this work were then applied to the preparation of coal-nanofiber papers. These advances included a near doubling of tensile strength through the application of small amounts of binders to the finished papers. After screening a few binders, one was examined in more detail, preparing enhanced-strength papers with 2-7% binder content. It was found that heat-treating the paper after binder application further enhanced tensile strength. SEM showed clear evidence of binder incorporation in a sample with 6% binder content.

While tensile strength improved with binder incorporation, conductivity suffered. It was found that even small levels of binders caused serious electrical resistance increases, in some cases a 100-fold increase. It is hypothesized that the swelling that the nanofiber paper undergoes when wetted with water allows the non-conductive binder to settle between formerly touching nanofiber strands, reducing conductivity. This problem is considered manageable, and can be addressed by either making a paper that does not swell upon water wetting, or by using an organic-based binder.

Many nanofiber applications seek maximized conductivity, and so a number of experiments were performed to enhance the conductivity of nanofiber papers. Papers made from mixtures of regular- and partially-graphitized nanofibers showed modest improvements, while heat treated papers showed huge conductivity improvements (as much as a factor of 300); however, heat treatment introduced brittleness into the material.

To make nanofiber paper user-friendly, the goal is to make it both strong and flexible. It was found that denser nanofiber papers were more brittle and actually less strong, and it was also found that density could be influenced with additives to the nanofiber dispersion feedstock used to make the papers. Heat treatment made the material more brittle, and the addition of certain binders increased brittleness as well. Finally, a series of bending tests were performed on various samples with the goal of evaluating the best combination of flexibility and conductivity. This showed that the most bendable paper (74 degrees) was also the least conductive paper of the series.

During the performance period, an apparatus was built to scale-up nanotube sheet making from 4" circular sheets to larger squares of material. This has allowed us to make demonstration papers (as big as 12"x12") suitable for evaluation, and some of these samples have actually been sold. We also began to evaluate the larger filter membranes which will be needed to scale up the process to a continuous operation. Our goal is to develop both a nanofiber product and the elements of continuous papermaking such that the process can be ultimately transferred to a papermaking company.

General Experimental

All starting materials were purified with acid before making them into paper. This way, the resulting papers could be further modified and tested without a concern that contaminants were harming the results. After removal of contaminants, nanotube samples were further treated to make them suitable for papermaking, and then our basic proprietary papermaking process was applied. The samples prepared for this project were generally 5-15 mil in thickness. Pure nanofiber papers and papers with additives (vide infra) were prepared, analyzed, and sometimes post-treated to assess the treatment impact on strength or conductivity.

Strength tests were performed by a tensile test procedure on a "dogbone" shaped nanofiber paper sample that was tape-reinforced on either end. The apparatus shown below was used, and the procedure was to suspend one end of the dogbone from the underside of an analytical balance, while the other end was attached to a lab jack. The sample was gradually stretched by lowering the lab jack, and the force applied to the dogbone measured by the analytical balance. The balance was interfaced to a computer to collect 5 points per second until sample rupture.

Explanation of Strength Values

The strength values presented in this report correspond to the force necessary to pull apart a dogbone sample of a constant size, and they are normalized for the weight of the dogbone. Thus the values are irrespective of the density of the nanopaper, and they are dimensionless (grams of force/grams of sample). This procedure gives a weight-based comparative measure of strengths for different nanofiber paper samples.

To give the reader a feel for what the reported strength values represent, note that a material with a strength value of 0.5 can be handled, but only with care. A value of 2.5 is enough to impart a robust character to a thick sample (10 mils), while a thinner sample (5 mils) is more fragile. A strength value of >5.0 is sufficient for commercialization in our opinion. A 5 mil sample with a strength value of 5 can be moderately tugged and flexed without tearing. It is still not as strong as plastic film (or single-wall nanotube paper), but it exhibits a handling strength that might be expected for facile processing into a composite pre-form, or for use as an electrode.

Results and Discussion

During the course of this project we were supplied with relatively small samples of coal-derived nanotubes (there is simply not much of this material available, as the production of coal nanotubes is a development effort at Applied Sciences). At the same time, we had available large quantities of Applied Sciences' bulk-produced nanotubes made from hydrocarbon gas, and so we frequently used these materials to develop techniques for improving nanopaper strength. What we learned from working with the bulk-produced nanotubes was then tested in experiments with coal-derived nanotubes.

For the first half of this project, we were under the mistaken impression that the coal-derived nanofiber furnished to us was analogous to the hydrocarbon-derived nanofiber depicted in **B** below. We were frustrated because the coal-derived nanofiber made a far weaker sheet than its hydrocarbon-derived analog. We later learned that in fact, the coal-derived nanofiber was actually analogous to nanofiber **C**, having been prepared with the recipe for **C**. This was confirmed via SEM, which showed the diameter of the coal derived nanofibers was closer to **C**'s diameter of 100-200 nm rather than the 50 nm of nanofiber **B**.

Now the data made sense. Our work with ASI hydrocarbon-derived fibers showed that **C** always made a weaker sheet than **B**. When we compared the coal-derived nanofiber paper with a paper made from hydrocarbon-derived **C**, the strengths were comparable. We view this as good news, because when Applied Sciences does more work on developing coal-derived nanofibers and uses recipe **B**, our expectation is the resulting **B**-like coal nanofiber will create a much stronger nanofiber paper.

A) Development of Improved Strength

Improved nanotube sheet strength was found to depend on three main factors. The first was the choice of nanofiber used to make the mat (as already described in the introduction), the second had to do with how the nanotube solution was prepared and filtered, and the third was choice and application of binders or other post-treatments.

Nanotube Preparation and Filtration

At first we did not realize how the preparation of the nanofiber solution impacted the nature of the paper produced. The concentration of the nanotubes in solution, their dispersion, and solution additives all affected the nanofiber paper's strength, density, and flexibility. We found it desirable to disperse the nanofibers in the gentlest way possible; extensive, high-shear processing produced a weaker paper, presumably due to chopping of the nanofibers in solution. Sample-to-sample variations were puzzling until every step of nanofiber processing was reproduced exactly from sample to sample.

It was generally found that denser papers were more brittle, and counterintuitively, had less tensile strength. In fact, the highest density paper seen to date was a coal-derived nanofiber paper, with a density of .37 g/cc; it was very brittle and weak (a tensile value of 0.5). Coal-derived papers of lower density were more flexible and stronger, and it was found that solution composition could influence this density. It was even observed that some solution compositions would create a paper that would shrink upon drying, while others would maintain their original dimensions. Suffice it to say that we are learning how certain additives and procedures impact density and strength.

Nanofiber papers made from the scrap pieces of earlier papers always had a reduced strength and conductivity. This could be due to one or two reasons: It may be that once the fibers are formed into a mat, forces between fibers make re-dispersion more difficult. Or it could be that the nanofibers become increasingly chopped when they are mechanically dispersed more than once, shortening them and reducing the strength due to hydroentanglement of high-aspect-ratio fibers.

Our experience with using binders is discussed below. These binders were added after the paper was made. When binders were added to the nanofiber starting material before preparation of the paper, we often observed a poor nanofiber dispersion, and so a poor-quality paper resulted.

The Use of Binders for Enhanced Tensile Strength in Nanofiber Papers

We principally examined two water-based binders in this year's project, zeroing in on the optimum amounts to add, and how to apply them to the paper. Two additional binders were briefly examined; they showed little benefit, and were set aside in favor of the original two. Depending on the nanofiber used to make the paper and the paper's binder content, the observed relative tensile strength values ranged from 0.5 to 8.2

Binder 1.

We found that Binder 1 worked best if the sample was heat-treated following its application. For example, in one material heat treatment increased tensile strength from 2.12 to 3.43, while in another it increased from 4.3 to 5.3, and in another from 3.92 to >4.45. Thus in the series of nanofiber papers below, each binder-containing paper was heat treated following binder application. Regardless of the strength of the starting nanofiber paper, it is seen that Binder 1 enhances tensile strength when added in amounts between 1% and 7%.

Sample	Binder Content	Weight-Normalized Tensile Value
Nanofiber 1	0	1.26
Nanofiber 1 + Binder1	~7%	2.09
Coal Nanofiber, plain	0	1.29
Coal Sample + Binder1	~5%	2.43
Plain PR-24	0	3.2
PR-24 + Binder1	2%	5.3
PR-24 + Binder1	6%	5.13
PR-24 + Binder1	5%	>5.37
PR-24 + Binder1	6%	5.80
PR-24 + Binder1	30%	3.92

Note that the sample with a very high binder content (30%) actually goes down in strength. We can only speculate that this has to do with the way it is deposited in the structure. There may be precipitates of the binder in the structure that only add weight and provide no strength enhancement.

Binder 2.

Fewer experiments were done with Binder 2, because it produced samples that were noticeably brittle, even though some good tensile strengths were seen.

The table below also shows an example of how a paper re-made from an earlier paper has reduced strength. It also lists the tensile strength for a paper prepared with a sequential application of Binders 1 and 2.

Sample	Binder Content	Weight-Normalized Tensile Value
Plain PR-24 + Binder	0%	3.2
PR-24 + Binder 2	5%	5.85
PR-24 + Binder 2	25%	> 8.2
PR-24 + Binder 2, remade	5%	3.33
PR-24 + Binders 1 and 2	7%	7.43

Other Binder Observations

The way that the binder is applied makes a difference. When a paper was wetted with a binder solution, it would often become weak, warp, or even tear. A gentle method of application was eventually developed, but this technique doesn't appear suitable for a continuous process. This is an area we will continue to pursue, as there are many options yet to test.

In samples with relatively high binder contents (above 5%), evidence of the binder's presence could be seen with SEM. In the image below, no binder particulates are evident, but thick webbed areas are seen where a number of nanofibers touch. This image clearly contrasts with an SEM of a binderless nanofiber paper, the boundaries between neighboring nanofibers are far more distinct in the binderless paper.

SEM image of nanofiber paper sample containing a relatively high (~6%) binder content.

The information gleaned in these series of experiments was used to prepare a large (10"x10") sheet out of coal-derived nanotubes as a demonstration sample to display at the 2004 Fall CPCPC Meeting. This sample was made relatively thick (10 mils) with ~5% Binder 1 in order to give it reasonable handling strength and good flexibility.

B) Scale-Up to Larger Sheet Size

At the beginning of this program, the largest paper samples we could make were circular sheets 4" in diameter. During the program we built and tested a scaled-up filtration apparatus to create larger sheets, and began preparing papers that were typically 10"x10" and as thin as 2.5 mils (but generally 6-15 mils thick). The key to success here was to make the filter plate as homogenous and uniform as possible, so that the flow through the plate is very even. Two large size filter plates were made out of different materials; one produces a more uniform nanofiber paper than the other.

The filter plate was not the only limiting factor for creating larger sized papers. The filter membrane that rests on the plate has to be of sufficient size. The membranes we prefer for this application are not always available in large sheets. For example, the local Air Force base wanted to see if we could make a 12.5"x12.5" sheet demo for a potential application. We did succeed in making it (this is the largest sheet we have ever made, 50% larger than a 10"x10" sheet); however, to do so we used a membrane that was not our preferred membrane, simply because it came in a sufficient size. The search for large dimension membrane material for scale-up is discussed in the next section.

Only one large (10"x10") sheets of coal-derived nanofiber paper has been prepared in this work; until Applied Sciences makes more of the coal-derived fiber, we don't have a large supply of starting material to work with. We can re-make sheets out of sheets already prepared, but we find that the paper is weaker when we do this, and it throws another variable into the research. But as the coal-nanofiber supply improves, we will not only be able to make large demonstration paper samples from coal, we will also be able to create porous coal-nanofiber monoliths. Blocks of uniformly dispersed nanofibers can be made with a modification of the papermaking process, and such blocks can be made to net shape (no shrinkage upon drying). Such blocks could be pre-forms for high-performance composite materials.

Finally, we note that one of the initial objections to this project was a concern that nanofiber paper would have little commercial interest. During the first six months of 2004 we have sold 3 organizations a total of \$10K worth of samples, and this year we have an order for \$9K more.

C) Filter Membrane Testing

A series of filter membranes were tested with the goal of finding one that has this combination of properties: 1) A porosity small enough so that our dispersed nanofibers do not pass through. 2) Commercially available in sufficient widths and lengths that it can be used as an element of a continuous papermaking process. 3) A membrane surface that releases the nanofiber paper once it is formed (this is critical for continuous papermaking).

We have selected and tested eight membranes thusfar, and none have been entirely suitable. The best of the lot has sufficient size and strength, releases fairly well, and allows a negligible fraction of the nanotubes to pass- its drawback is that it is slightly non-uniform, which results in a nanofiber paper that is not completely smooth. The irregularity that it introduces into the paper is not noticeable when thick papers are produced, but is noticeable when 5-mil thick papers are made.

Searching for a suitable filter membrane will continue into next year. From the tests done to date, we know the size and porosity and other attributes we are looking for, so we can limit our search fairly effectively. New porous polymeric sheets made from polymer microfibers (and electrostatically spun nanofibers) are becoming increasingly available, and it is likely that some these new materials will be good candidates for our purposes.

D) Development of Improved Conductivity

Most of the nanofiber paper applications envisioned by Applied Sciences or the Air Force benefit from an maximized conductivity. We have experimented with a variety of strategies to enhance conductivity, and in general we find that there is a trade-off between strength, conductivity, and flexibility. In most cases, the relative conductivity within a series of samples was measured by a simple two-probe conductivity meter, although in one series of heat-treated papers a 4-point probe was also used. These are the approaches we have tried to date, and their results:

1) Paper from a mixture of carbon nanofibers and partially graphitized nanofibers.

In this approach we made papers from mixtures of ordinary nanofibers and partially graphitized nanofibers (denoted as LHT). This is an attempt to get a blend of strength and conductivity, and the results were as expected. The samples showed improved conductivities compared to ordinary nanofibers, but the strengths were so low that we did not attempt to measure them. It was possible to make 5-mil sheets that were 10"x10" from these nanofiber mixes, but they had to be handled gingerly.

<u>Sample</u>	<u>Resistance of 4" diam. sheet, ~7 mils thick.</u>
PR-24 Nanofiber	320 ohm
33% PR-24, 67% PR-24LHT	168 ohm
50% PR-24, 50% PR-24LHT	220 ohm
20% PR-24, 80% PR-19LHT	180 ohm
35% PR-24, 40% PR-19LHT, 25% PR-24LHT	170 ohm

2) The effect of binders.

We found that binders enhanced tensile strength, as discussed earlier, but the ones that we tried produced a reduced conductivity. The reason may have to do with the way the binders are applied. We have been using water-soluble binders up to now, and we find that when we wet the nanofiber paper with water it swells the paper, which presumably allows polymeric binder to deposit between the junction points of fibers within the paper, reducing conductivity.

As one might expect, miniscule amounts of binder show little influence on conductivity, while significant amounts make the nanofiber paper very resistive. This is illustrated in the data below on a series of 4" diameter papers that are each ~7 mils thick. During the next phase of this project we will experiment with strategies such that the paper does not swell when binders are added; it will be interesting to determine whether this mitigates this problem.

Sample	Binder Content	2-probe Resistance across a 4" sample
Plain PR-24 paper	0	320 ohm
Paper + binder	.5%	4000 ohm
Paper + binder	1.5%	18,000 ohm
Paper + binder	7%	33,000 ohm

3) Heat Treatment of Papers for Enhanced Conductivity

A group of disparate nanofiber paper samples of the same size were heated together in a vacuum furnace at 1500° C. The samples were close in weight, but each had a different composition, either pure nanotubes or mixtures of nanotubes, with a range of conductivities and bulk densities. Surprisingly, after firing, every sample was close in conductivity, although none had noticeably changed in dimension or weight. Conductivities were measured with both a 2-point probe and a 4-point probe to verify the results. These heat-treated papers were also brittle, as might be expected from such a partial graphitization.

Sample	Wt.	Thickness	Density	Resistance (2-pt. probe)	
				<u>Before firing</u>	<u>After 1500C</u>
Mix of 3 nanotubes	.485g	13.5 mils	.166g/cc	2200 ohm	7.8 ohm
Duplicate expt.	.527g	15.0 mils	.163g/cc	2040 ohm	6.4 ohm
Nanotube 1	.497g	16.8 mils	.137g/cc	460 ohm	6.4 ohm
Nanotube 1, purified	.508g	10.0 mils	.236g/cc	137 ohm	7.1 ohm
Duplicate expt.	.478g	8.8 mils	.252g/cc	128 ohm	7.4 ohm

4) Conductivity vs. Flexibility

The persistent problem in making conductive nanofiber papers has been the brittleness that the most conductive papers exhibited. In order to get somewhat quantitative about this issue, an apparatus was set up to measure the maximum bending angle before paper rupture. This made it possible to fabricate a number of samples in different ways, with

the goal of obtaining the best combination of conductivity and flexibility. In the plot below, the resistances of equivalent-size samples ranges from 11 ohms to 1640 ohms, with the most conductive sample showing the least flexibility, and the most flexible sample (with a flex angle of 74 degrees) the least conductive. In this series, the sample with a flex angle of 60 degrees gives the best combination of the two properties.

E) Coal-Derived Nanofiber Characterization

Elliot Kennel of West Virginia University was kind enough to arrange for some SEM/EDAX work on an early sample of coal-derived nanofiber paper (made with the first batch of coal-nanofiber furnished to us by ASI). Liviu Magean and Steve Carpenter performed the analyses.

The SEMs below show an overall view of the sample. Among the features noted are nanofibers of different diameters and morphologies; ball shaped objects and irregularly shaped objects. The EDAX measurements indicate the presence of carbon, as well as trace amounts of oxygen, sulfur, silicon, iron and chlorine. We hypothesize that sulfur and iron might be present from the coal or catalyst; silicon dioxide might be derived from mineral matter in the coal. Chlorine was not expected, and might be an artifact from washing the materials in city water.

SEMs of paper made with the first batch of coal-derived nanofibers from ASI, showing ball features and clusters of ball features.

C:\Steve\Elliott Kennel\Nanofiber Paper 15kV.spc

Label A: Nanofiber Paper 15kV

15kV EDAX overall view spectrum of the sample above.

The SEM of a nanofiber paper made from a cleaner sample of coal-derived nanofiber is shown below. The coal-derived nanofibers are of comparable dimension to the PR-19 hydrocarbon nanofiber, but the tubes often show a surface is a bit more lumpy- one analyst dubbed this “caterpillar”-like nanofibers. The ball-like features and the “caterpillar” appearance distinguish the coal material slightly from its hydrocarbon analog.

SEM and EDAX analysis of the balls and lumps within the early coal-derived nanofiber sample showed that the ball features are largely composed of carbon. If one end of this fiber type is examined under high resolution, it is seen that the fiber terminates in a ball-shaped growth with a visible bright spot on it. EDAX shows that this bright spot is iron, likely the iron catalyst particle that nucleated the nanofiber growth. A picture of these ball features and the bright spots in them is shown below.

Possible nucleated catalysts. The light spots give the EDAX signature below

EDAX measurement on the light spots at the fiber end, showing a high content of iron.

F) Other Activities for this Program

CPCPC Conference

A presentation on the work-to-date on coal-derived carbon nanofiber sheet development was given at the fall CPCPC conference in Morgantown, West Virginia in October. Samples of both coal-derived and hydrocarbon-derived nanofiber papers were shown, and the direction of proposed research was discussed. It has since transpired that Applied Sciences Inc. has been funded to continue their production of coal-derived nanofibers, which means that an ample supply for papermaking development is forthcoming. With this new support, ASI can use more than one recipe to make coal-derived nanofibers with different diameters and different morphologies. This will help us, as we can use the nanofiber type that makes the strongest paper in our work.

Attempt at Electrochemical Characterization

Two types of coal-derived nanofiber paper were prepared for electrochemical analysis as an electrochemical capacitor material. One was made of pure coal nanofiber alone, the other a mixture of coal-nanofiber and a high-surface-area mesoporous carbon. Disks of each material were punched out and assembled into sealed coin cells, where the electrodes were wetted with 6M sulfuric acid.

A number of attempts to evaluate these cells with electrochemical impedance kept giving high-current error messages from our instrument. New cells were prepared, and the same error messages were seen. Then a check of the instrument using a standard test cell showed that our problem was instrumental in nature, so the cells could not be evaluated. Our impedance instrument is being sent away for repair, and we can revisit this experiment during our next phase of this project.

Nanofiber Paper Applications Detailed

A white paper describing the uses for nanofiber papers and nanofiber monoliths was prepared for the CPCPC.

Conclusion

This modest effort has produced a lot of insight into the variables surrounding the art of nanofiber paper production. Strengths have been enhanced, larger size papers have been produced, and we have learned much about the interplay of variables that control strength, conductivity, flexibility, and density.

Coal-derived nanofiber paper sheets can now be made with a comparable strength to their hydrocarbon analogs. This strength is sufficient that coal-derived nanofiber monoliths or thick nanofiber papers from coal can presently be made. However, the exciting prospects lie ahead, for when ASI produces coal-nanofiber with their PR-24 recipe, our expectation is that coal-nanofiber paper strength will jump, and that thin, flexible coal nanofiber sheets with an optimized conductivity will be forthcoming. We also expect an increased supply of coal nanofiber starting material in the coming year, so that further development work can be done exclusively on coal.

This project is a developmental process, and it is still in progress. The work done this year has put us on the path towards developing a high-value-added product from coal. There is more work to do on scale-up and on the creation of an optimized combination of paper properties. On the other hand, the prospects for this technology to move in diverse directions are very encouraging. Coal-nanofiber monoliths for composites could be made with this technique. Nanofiber papers with modified surface chemistries (perhaps for biological use) are even possible. However, the first goal has to remain the creation of a process that can make a basic form of strong, conductive, and flexible coal-derived nanofiber paper on a continuous basis.

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Anthracite Coal as a Feedstock for Activated Carbon

Final Report

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Abstract

Progress has been made in the characterization of anthracite coal as a possible feedstock for activated carbon. Elemental and proximate analyses were conducted for samples of LCNN and Jeddo anthracite coal. A specially designed rotating activation reactor was constructed to activate anthracite coal in a carbon dioxide environment. The reaction was started and stopped at will by changing the gas atmosphere environment from carbon dioxide to nitrogen. The change in anthracite weight was followed over time, allowing a study of the overall kinetics of the reaction. Samples from the reactor were taken and surface area measurements were made. Intrinsic kinetics were also investigated utilizing a TGA over the temperature range from 900 to 1000°C.

Upon surface area characterization for LCNN anthracite coal, it was determined that BET and micropore surface areas were a function of both conversion and activation temperature. Likewise, for each of the activation temperatures tested, a good degree of repeatability was displayed for surface area measurements, and good control of BET to micropore surface area ratios was demonstrated. Thus, by carefully controlling the activation time and temperature, specific pore characteristics can be produced.

A sample was prepared and sent to David Firsich for evaluation as a possible carbon for use in the ultra capacitor. This carbon had a surface area of approximately 800 m²/g and was composed predominately of mesopores. De-ashing was attempted via HCl/NaOH washing, but this treatment showed no effect on the ash concentration. A similar sample was then treated with HF and resulted in a decrease in ash to less than 2%. Capacitance tests were conducted on this activated sample, and were found to produce encouraging results. The activated sample exhibited a capacitance of 175 F/g, comparable in energy storage to the best commercial capacitor carbons available. Due to the high mesoporosity of this sample, it is expected to exhibit good power properties as well.

Nomenclature

a = relative surface area

C_{CO_2} = concentration of carbon dioxide, mol/cm³

E_a = activation energy, kcal/mol

f = total fraction conversion due to pyrolysis

k, k_0 = reaction rate constants (cm³/mol·s)

R = gas constant, cal/mol·K

SA = measured surface area, m²/g

T = temperature, K, °C

t = time, s

v, β = physical parameters of the coal samples

w_{ash} = weight of ash for a given anthracite sample, mg

w_0 = initial weight of anthracite sample, mg

$w(t)$ = calculated weight of anthracite sample at any time t , mg

x_c = fraction conversion due to activation reaction

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Introduction

Activated carbons are characterized as having a large internal surface area and a specific pore structure. Activated carbons are noteworthy for their ability to selectively absorb molecules from both liquids and gases. They can be produced from a number of raw feedstock including wood, coconut shells and coal. Activated carbons are typically produced by thermal activation at elevated temperatures whereby carbon is treated in an oxidizing atmosphere (i.e. steam or carbon dioxide). The resulting burn off leads to a highly porous structure. Some uses of activated carbon include water purification, gas/liquid separation, catalyst production and in the area of the electric double layer capacitor. For most applications, activated carbon is exploited for its ability to selectively remove certain molecular constituents, while leaving other constituents behind. In the case of the electric double layer capacitor, the high surface area and controlled porosity of the activated carbon are exploited for its ability to store charge.

The problem addressed in this fundamental study is focused on the thermal activation of anthracite coal in a carbon dioxide atmosphere. The kinetics of the activation will be studied in detail and the development of surface area will be carefully assessed. Specific applications for the resulting activated carbons in the areas of separation processes and the electric double layer capacitor will be evaluated. If successful, the project may lead the way to the use of anthracite coal as a feedstock for activated carbons in specialized applications.

The use of anthracite coal as a possible source of activated carbons has been evaluated by Andréßen et al. [1]. Anthracite coal possesses an inherently ultra-fine porosity within the coal structure and utilizes the activation process to gain access to the fine porosity. Previous work using anthracite coal as a feedstock for activated carbons had been conducted by Bessant and Walker [2]. A two-stage process was developed: first, a devolatilization step in a N_2 atmosphere at $950^\circ C$. Secondly, the activation stage occurred at $950^\circ C$ in a CO_2 environment. In addition, the reactivity of numerous types of coal and coal char samples in a CO_2 environment was evaluated by Dutta et al. [3].

Experimental Results and Discussion

Six tasks were specified under the original proposal to be completed. Each of the six tasks had a timeline for completion. A list of these tasks is as follows:

Task 1: Acquisition of samples and analysis.

Three carbon samples were received and analyzed for composition. Two anthracite coal samples were received from LCNN and Jeddo Coal Co., and both were ground to 50-100 mesh prior to being subjected to proximate and elemental analyses. The sample from Jeddo was courtesy of James Pagnotti. Table 1 depicts the results of these analyses for each of the respective anthracite samples. A third sample, received from the Department of Energy courtesy of Todd Gardner of NETL, was a carbon sample that was previously activated. The composition of this previously activated sample is also depicted through Table 1.

Table 1. Elemental and proximate results for the three carbon samples studied for activation.

<u>Element % (daf basis)</u>	LCNN	Jeddo	DOE Activated Carbon
Nitrogen	1.30	1.30	1.20
Carbon	92.87	90.83	99.41
Hydrogen	2.16	2.58	0.50
Sulfur	0.48	0.48	0.00
Oxygen (by difference)	3.20	4.81	-1.11
<u>Proximate % (as received)</u>			
Moisture	3.54	3.18	6.13
Volatile Matter	4.60	5.72	6.04
Ash	6.28	3.64	0.88
Fixed Carbon	85.58	87.46	86.95

The previously activated carbon is being studied by the DOE as a possible catalyst for the conversion of hydrogen sulfide gas to elemental sulfur. To be effective, the catalyst requires a predominance of mesopores rather than micropores as it now has. The further activation was to be accomplished via the activation reactor to create more mesopores. The high carbon content for this sample was expected, as activated carbons from shell or wood precursors exhibit higher percent carbon when compared to amounts measured for the raw anthracite coal samples. The oxygen content was calculated, and a negative value was found when calculating it by difference. This value can be attributed to experimental error.

Task 2: Thermogravimetric analysis studies

TGA studies were performed in a Thermo-Cahn microbalance on the LCNN samples. The purpose of the study was to better understand the intrinsic kinetics of the coal-carbon dioxide activation reaction. The reaction occurred at temperatures of 900, 950, 975 and 1000°C, and the change in weight from the initial sample was tracked with time. Upon heating the apparatus, the reactor was maintained in a nitrogen environment to prevent the activation reaction from occurring. During this heating period an initial reaction, the pyrolysis reaction of the volatile matter, occurred. The purpose of this study was to examine the activation reaction of the coal in carbon dioxide; therefore, the pyrolysis reaction was considered, but no analysis was conducted.

TGA experiments were conducted, and a rate law expression for the activation reaction was developed. Results of TGA tests are displayed in Figure 1. The conversion, x_c , of anthracite coal in a CO_2 environment is described by Dutta et al. [3] as:

$$x_c = \frac{w_o - w_o f - w(t)}{w_o - w_o f - w_{ash}} \quad (1)$$

where w_o is the initial weight of the anthracite sample at the time when the activation in CO_2 begins, $w(t)$ is the weight of the sample at any time, t . Conversion for the pyrolysis reaction, f , was considered zero due to the fact that the pyrolysis reaction goes to completion in the nitrogen environment prior to activation in carbon dioxide. Likewise, the data displayed via Figure 1 are on a dry basis; therefore the weight of the ash was included with the conversion calculation.

Figure 1. TGA results for the activation of LCNN anthracite in a carbon dioxide atmosphere.

From the data collected via the TGA studies, activation reaction in carbon dioxide was assumed to follow 0th order reaction rate due to the linear change in conversion with respect to time. The reaction rate was assumed to be 1st order in CO₂ but since it was in excess, the CO₂ concentration is taken as constant. This behavior yielded the rate equation

$$\frac{dx_c}{dt} = k C_{CO_2} (1 - x_c)^0 \quad (2)$$

where k is the rate constant (cm³/mol·s), and C_{CO₂} is the concentration of carbon dioxide (mol/cm³), calculated with the ideal gas law. From the linear trend lines superimposed on the data in Figure 1 the values of k were calculated for each of the respective temperatures. Assuming Arrhenius-type temperature dependence according to Equation 3,

$$k = k_o e^{-\left(\frac{E_a}{RT}\right)} \quad (3)$$

an Arrhenius plot was constructed and the activation energy, E_a, and specific rate constant, k_o, were determined. Table 2 displays the reaction rate constants k for the temperatures examined through TGA studies; Figure 2 depicts the Arrhenius plot for the activation reaction in the TGA. The activation energy was found to be 56.8 kcal/mol, which is comparable to results found by Dutta et al. [3] for the reactivity of coal in carbon dioxide environment. Likewise, the specific reaction rate was 1.77 x 10¹⁰ cm³/mol·s.

Table 2. Activation reaction rate constants at varying temperatures for LCNN anthracite in CO₂ for the TGA.

Temperature (°K)	Rate Constant, k (cm³/mol·s)
1173	0.488
1223	1.217
1248	2.162
1273	3.221

Figure 2. Arrhenius plot for the activation of LCNN anthracite in a carbon dioxide environment, taken from the TGA studies.

Task 3: Anthracite activation

Activation of larger LCNN anthracite coal samples was conducted in the specially designed rotating activation reactor. The reactor consisted of a glass flask with a porous frit which is capable of containing approximately 20 to 50 grams of sample. Anthracite was loaded into the reactor, which was then inserted into a furnace. The glass flask was fitted to a rotating motor in which the entire assembly rotated at a constant speed. This rotation ensured adequate gas-solid contact as well as thorough mixing and uniform activation. Through the rotating assembly, gas was injected and gas phase products were passed through the porous frit and out of the reactor. Nitrogen was introduced to quench the reaction during heat-up and cool-down, and the reactant gas, carbon dioxide, was added once the desired reaction temperature is achieved. A schematic of this apparatus is depicted in Figure 3; likewise a picture of the rotating reactor is shown in Figure 4 with the flask outside of the oven to better illustrate operation of the reactor. Another benefit of this reactor design was the ability to remove the glass flask once room temperature was achieved, allowing the flask and its contents to be weighed while samples from the flask were taken at predetermined times. By following the weight change of the sample with time, the global kinetics of the activation process was followed. In addition, grab samples at each stage of activation were taken and further analyzed for surface area.

Figure 3. Schematic of the operation of the rotating activation reactor.

Figure 4. Picture of rotating activation reaction.

Activation studies on samples of LCNN anthracite coal were conducted for temperatures ranging from 900°C to 975°C. Figure 5 displays the results of activation. The temperatures are indicated in the legend, and the letters correspond to replications. For instance, 975B represents the second run for 975°C. The duplications performed display a good degree of reproducibility for the conversion calculations, as 900 and 975°C replication runs exhibit nearly identical trends.

It should be noted that 900A, 900B and 950A were run at CO₂ flowrates of 200 ml/min. However, 975A and 975B were both run with flowrates alternating between 200 ml/min and 400 ml/min. The purpose of alternating flows was to ensure that the activation reaction was not being limited at higher temperatures due to an insufficient amount of CO₂. Changing rates of conversion corresponding with the changing CO₂ flows would indicate the suppression of the reaction due to CO₂ starvation. As it is shown, there appears to be no significant deviation from conversion rates at the differing CO₂ flowrates. Hence, all subsequent runs were done at 200 ml/min CO₂ flow.

Figure 5. Activation for LCN anthracite in carbon dioxide at different temperatures. Results are on a dry basis.

The kinetic expressions for LCN anthracite in the activation reactor were evaluated as previously specified with the TGA studies. Table 3 displays the reaction rate constants k for the temperatures examined through the rotating activation reactor. The Arrhenius plot used to determine the kinetic expressions for data from the rotating reactor is depicted via Figure 6. The activation energy for the activation reaction in a carbon dioxide environment for the rotating reactor was 35.7 kcal/mol; likewise, the specific reaction rate constant was $1.99 \times 10^6 \text{ cm}^3/\text{mol}\cdot\text{s}$. The observed difference between the activation energies calculated for the TGA studies and the rotating activation reactor is believed to be attributed to a possible combination of heat and mass transfer effects within the rotating reactor. Further studies will be necessary to help elucidate the factors contributing to the lower activation energy and reaction rate constant witnessed in the activation reactor. Nonetheless, the kinetic data from the activation reactor can themselves be used to model the behavior of the reaction for the specific reaction system herein.

Table 3. Activation reaction rate constants at varying temperatures for LCNN anthracite in CO₂ rotating activation reactor.

<u>Temperature (°K)</u>	<u>Rate Constant, k (cm³/mol-s)</u>
1173	0.457
1223	0.807
1248	1.162

Figure 6. Arrhenius plot for the activation of LCNN anthracite in a carbon dioxide environment, taken from the rotating activation reactor.

Figure 7 displays the results of activation for the Jeddo anthracite. The activation reaction appears to be similar for both types of coal tested, although the LCNN anthracite sample exhibited a slightly greater reaction rate. As previously displayed for the LCNN anthracite, the activation reaction exhibits a good degree of reproducibility for cases run at the same temperature. This same trend appears for the Jeddo coal, as replicated test cases at 975°C display no significant deviation.

Figure 7. Activation for Jeddo anthracite in carbon dioxide at different temperatures. Results are on a dry basis.

Task 4: Surface area analysis

Surface area analysis was conducted for the LCNN samples activated at their respective temperatures. A Micromeritics Accelerated Surface Area and Porosimetry System (ASAP) 2020 was utilized to measure total BET surface area, as well as t-plot micropore surface area. Figure 8 displays the surface area trends for LCNN samples activated at 900°C. BET surface area appears to reach a maximum value of approximately 1300 m²/g. Likewise, the micropore surface area reaches a maximum at 560 m²/g. The data displayed in Figure 8 represent two separate test runs in which samples were removed from the rotating reactor at different time intervals for each run. This data support the belief that BET and micropore surface area can be controlled by monitoring the conversion, in which the conversion has been proven to be a reproducible function of time at the respective temperatures.

Figure 9 displays the BET and micropore surface area measurements for the LCNN anthracite coal activated at 950°C, and Figure 10 displays the same measurements for the 975°C activation. At 950°C, BET surface area reaches a maximum at approximately 900 m²/g, and micropore exhibits a maximum at 360 m²/g. Likewise, at an activation temperature of 975°C, values of 700 and 200 m²/g for the maximum BET and micropore surface area, respectively, are observed.

Figure 8. BET and micropore surface area measurements as a function of conversion for LCN anthracite at 900°C.

Figure 9. BET and micropore surface area measurements as a function of conversion for LCN anthracite at 950°C.

Figure 10. BET and micropore surface area measurements as a function of conversion for LCNN anthracite at 975°C.

As shown in Figures 8-10, surface area is not only a function of conversion, but is also a function of activation temperature. As temperature increases, the maximum BET and micropore surface area that can be achieved decreases. Micropore formation on the surface of individual anthracite particles is governed by the burn-off at the surface. At higher activation temperatures, the rate of burn-off increases, thereby increasing the rate of micropore production. However, it is believed that increases in temperature cause uneven burn-off at the surface, leading to faster degradation of the micropore walls, and the formation of mesopores with diameters between 20 and 500 Å.

Figure 10 displays a well-defined maximum of BET surface area for anthracite activated at 975°C. The decrease in total surface area coincides with the degradation of mesopore walls at the higher temperatures, similar to the degradation witnessed for the micropore walls at the lower conversion.

Surface area measurements were also completed for the activated Jeddo coal samples. Results have displayed similar trends compared to the LCNN activated carbons. At 975°C, the micropore surface area exhibits a maximum of approximately 230 m²/g. The rapid decrease in micropore surface area at higher activation temperatures coincides with the micropore wall degradation displayed for the LCNN anthracite. Figure 11 depicts the BET and micropore surface areas for the Jeddo anthracite at an activation temperature of 950°C. Likewise, Figure 12 shows the surface area measurements for the Jeddo anthracite at 975°C. Comparable to results found for LCNN coal, the maximum BET and micropore surface areas for activated Jeddo samples increase with decreasing temperature.

Figure 11. BET and micropore surface area measurements as a function of conversion for Jeddo anthracite at 950°C.

Figure 12. BET and micropore surface area measurements as a function of conversion for Jeddo anthracite at 975°C.

In an attempt to model surface area behavior for the LCNN and Jeddo coals, a correlation was used by Dutta et al. in which relative surface area, a , was determined as a function of coal conversion. According to Dutta [3], a is defined as:

$$a = \frac{\text{available pore surface area per unit weight at any stage of conversion (SA)}}{\text{initial available pore surface area per unit weight (SA}_0\text{)}} \quad (4)$$

According to this definition of a , the relative surface area calculated is applicable when there is a measurable value for the initial surface area. The raw anthracite coal examined through this study did not exhibit any initial available surface area, thereby causing the value of a to approach infinity. As a result, the initial surface area was extrapolated from measured values of total surface at the point where $x_c = 0.10$, denoting the initial surface area from Equation 4 as SA_1 .

The function relating relative surface area to conversion as previously studied by Dutta et al. is shown in Equation 5:

$$a = 1 + 100x_c^{\nu\beta} e^{-\beta x_c} \quad (0 \leq \nu \leq 1) \quad (5)$$

From this equation, the values of ν and β are physical parameters characteristic of a given coal. The value of ν represents the conversion x_c at which a reaches a maximum. However, this function is valid when the value of a can be determined by taking the initial surface area. As previously established, the anthracite coal samples exhibited no measurable surface area prior to activation and SA_1 was then assumed as the initial surface area at $x_c = 0.10$. Therefore, Equation 6 was utilized as the function to relate relative surface area to conversion x_c :

$$a = 1 + 100(x_c - 0.10)^{\nu\beta} e^{-\beta(x_c - 0.10)} \quad (0 \leq \nu \leq 1) \quad (6)$$

To determine the correct values of the physical parameters, ν and β were iterated until a function was achieved that was the best fit for the experimental data. These calculated values of the parameters are depicted in Table 4. When the experimental values of a were compared with the theoretical model using the physical parameters outlined in Table 4, accurate representations of the surface area behavior were established. Figures 13 and 14 depict this comparison between the experimental data and theoretical calculations for LCNN and Jeddo coal, respectively.

Table 4. Physical parameters used for mathematical model of surface area behavior.

Coal Sample	Temperature(°C)	SA₁ (m²/g)	ν	β
LCNN	900	65	0.90	1.65
	950	65	0.60	2.30
	975	65	0.55	2.70
Jeddo	950	104	0.75	2.55
	975	104	0.60	3.10

Figure 13. Comparison between experimental values for LCNN coal of relative surface area a and theoretical values (—) of surface area behavior.

Figure 14. Comparison between experimental values for Jeddo coal of relative surface area a and theoretical values (—) of surface area behavior.

The previously activated carbon sample received from the DOE was successfully activated at a temperature of 950°C in a CO₂ environment. Two samples were activated for different durations of times, and the surface area measured increased as the time was progressively increased. The initial sample consisted of approximately 1100 m²/g BET surface area and 833 m²/g micropore surface area. A BET surface area of 2500 m²/g was achieved upon activating the sample for a three hour duration. Figure 15 depicts the measured values of BET and micropore surface area for these activated carbon samples. As can be seen, there was a large increase in the total surface along with an increased amount of mesopores as requested by the DOE. These samples have been submitted to the DOE for testing in their hydrogen sulfide reaction system.

Figure 15. BET and micropore surface area measurements as a function of conversion for DOE activated carbon sample at 950°C.

Task 5 : Scanning Electron Microscope

Use of the SEM to further characterize selected samples of activated carbon was attempted. However, due to the very small pore sizes, the SEM was not able to provide any useful information about the pore structure of the carbon.

Task 6: Acid Wash

A sample of activated LCNN anthracite coal was prepared for acid wash in an attempt to prepare a low-ash carbon. The sample was activated at 975°C for 15 hours, giving a conversion of approximately 0.70. The wash consisted of heated 6 M NaOH, followed by a washing with distilled water. A final wash with 6 M HCl was administered. The ash percentage in both the original and de-ashed sample was measured so that the efficiency of the acid wash can be ascertained. Upon washing with HCl, it was determined that the ash content was not decreased.

A second acid wash was conducted utilizing HF. A sample of LCNN anthracite coal was activated for 16 hours at 975°C, giving a conversion of approximately 0.75. The surface area was measured prior to the acid wash, and exhibited a BET surface area of 638.4 m^2/g and a micropore surface area of 74.0 m^2/g . The activated sample was then subjected to 100 mL of 48 weight % HF for the duration of one hour. The sample was then washed with copious amounts of deionized water. Surface area measurements were taken again, as well as an ash analysis to determine the success of the wash. The BET surface area was 734.5 m^2/g and the micropore surface area was 79.7 m^2/g . The ash content was decreased to approximately 2% ash.

Upon submitting this low-ash sample to Dave Firsich for testing in the use of a electric double layer capacitor, it was determined that the anthracite coal sample exhibited characteristics comparable to capacitor carbons. First, a 6/4 ratio of coal nanofibers to activated LCNN coal was used to make an all-coal capacitor electrode. The capacitance of this electrode was determined to be about 105 F/g through a comparison of the integrated area of its cyclic voltammogram relative to a standard. It had been previously determined that the coal nanofiber exhibited 29 F/g, and so the capacitance of the activated LCNN coal could be calculated by accounting for the weights of the components and the overall electrode capacitance.

The capacitance of the activated LCNN coal was conservatively determined to be around 175 F/g. This is comparable in energy storage to the best commercial capacitor carbons available. With the high mesoporosity of the sample, it is expected that it will display good power properties as well. Further testing of the activated LCNN sample is expected; however, this initial result is very encouraging.

Conclusions

The activation reaction occurring between anthracite coal samples and carbon dioxide was studied over a range of temperatures. The kinetics of the activation reaction was studied via two apparatuses: TGA and a specially designed rotating activation reactor. At the conversions examined, the reaction displayed 0th order reaction kinetics for both apparatuses. The conversion measured for several anthracite coal samples using the rotating activation reactor exhibited linear trends that displayed a high degree of repeatability.

Upon surface area characterization for the anthracite coal samples, it was determined that BET and micropore surface area were a function of both conversion and activation temperature. Likewise, for each of the activation temperatures tested, a good degree of repeatability was displayed for surface area measurements, and good control of BET to micropore surface area ratios was demonstrated. Surface area behavior was modeled by relating coal conversion to relative surface area. Thus, by carefully controlling the activation time and temperature, specific pore characteristics can be produced.

A sample that was specially tailored with high mesoporosity, low micropore surface area, and low ash was submitted to Dave Firsich for testing in the electric double layer capacitor. The BET surface area was 734.5 m²/g and the micropore surface area was 79.7 m²/g. The ash content was decreased to approximately 2% ash through an acid wash. It was found that the activated LCNN coal exhibited a capacitance of 175 F/g, comparable in energy storage to the best commercial capacitor carbons available. Due to the high mesoporosity of this sample, it is expected to exhibit good power properties as well. Further testing of the activated LCNN sample is expected; however, this initial result is very encouraging in the development of anthracite coal as a feedstock for activated carbons for the use as ultracapacitors.

Finally, a specially-tailored carbon sample was provided to the DOE/NETL lab for evaluation as a catalyst in the direct oxidation of hydrogen sulfide to elemental sulfur in synthesis gas. Results were not available at the time of this writing.

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FINAL REPORT**SUBMITTED TO****CONSORTIUM FOR PREMIUM CARBON PRODUCTS FROM COAL**

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**UNDERSTANDING ANTHRACITE PROPERTIES
TOWARDS ITS USE AS INTUMESCENT MATERIAL FOR
POLYURETHANE FOAMS**

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ABSTRACT

Recent work has shown that expandable graphite can be used as an intumescent material to improve the thermal resistance of polyurethane foams. Moreover, previous studies conducted at Penn State have already shown that anthracites can be used to produce specialty graphites. Accordingly, the objective of this research program is to gain a fundamental understanding of the possible use of expandable anthracite as an intumescent material for polyurethane foams by investigating the thermal degradation of foams produced using expandable anthracites with various properties.

This Final Report summarizes the work conducted during the period March 1, 2004 – August 31, 2005 and focuses on the development and characterization of chemically modified anthracites by chemical impregnation.

Samples of rigid polyurethane foams were prepared at APCI with various levels of expandable graphite (EG) 3772 (EG with best expansion) in them such that the isocyanate (ISO) index was approximately 200-300. Thermal stability was best for a loading of 5% EG in the foam. For foams of an ISO index 300, the EG in the foam did not contribute to the thermal stability of the foam. However, for foams with an ISO index of less than 200 and 5% EG loading, there was increased thermal stability.

Raw coals and heat-treated anthracites were subjected to acid-pretreatments. Two high volatile anthracites were tested: the Vietnamese anthracite Hongay and the American anthracite Summit; one low volatile coal, Buck Mountain, was tested. There was reaction of the two high volatile coals with the acid-pretreatments, but not really an expansion. Buck Mountain showed no interaction with the acid/heat-treatment. Summit and Hongay coals were heat-treated to 3000°C to graphitize the coals, with Hongay the most graphitic. Both heat-treated coals were subjected to acid-pretreatment. From SEM, it is apparent that heat-treated/acid-pretreated Hongay expanded but Summit did not. TMA of Hongay did not indicate an expansion, but the vapor intercalated into the sample was released at a much higher temperature than when using raw coal acid-pretreatment. TMA of heat-treated acid-pretreated Summit indicated that acid was not intercalated into the structure. Even though heat-treated Hongay expanded after acid-pretreatment, the expansion was not enough to warrant testing the expandable anthracite in intumescent foam.

As expandable anthracite could not be used in the specified application, raw and acid-pretreated coals were activated using steam at 850°C for 2 h. After activation, the Summit surface area is ~500 m²/g, the Buck Mountain anthracite 760-1000 m²/g, and Hongay anthracite 900-1270 m²/g. Interestingly, the acid-pretreatment had a positive effect on Hongay anthracite, increasing the surface area from 900 to 1270 m²/g, while for Buck Mountain and Summit anthracites the acid-pretreatment had a null or negative effect. It appears the acid-pretreatment at 500°C was better for activation than the acid-pretreatment at 700°C. At the 500°C, some of the sulfate ion still remained in the sample, possibly creating additional spaces or links in the coal for the steam to interact with during activation. The lower surface areas of the Summit coal could possibly be due to the large amount of mineral matter inherent in the coal.

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March 1, 2004 – August 31, 2005

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FINAL REPORT
March 1, 2004 – August 31, 2005

1. INTRODUCTION

Recent research has shown that expandable graphite can be used as an intumescent material to improve the thermal resistance of polyurethane foams. [1] Moreover, previous studies conducted at Penn State have already shown that anthracites can be used to produce specialty graphites. [2] Accordingly, the objective of this research program is to gain a fundamental understanding of the possible use of anthracite as an intumescent material for polyurethane foams by investigating the thermal degradation of foams produced using expandable anthracites with various properties.

The principal objective was to monitor the properties of expandable and expanded carbon from raw and heat-treated anthracites for comparison to expandable graphites. If expansion were achieved with any of the anthracite materials, the expandable anthracite would be tested in intumescent foams.

During the project, several different methods were used to produce anthracite intercalation compounds from raw and heat-treated samples. [3-9] Several analytical techniques were used to characterize the properties of the raw samples and reacted samples, including proximate and ultimate analysis, thermomechanical analysis (TMA), particle size distribution, scanning electron microscopy (SEM), and porous structure analysis (N_2 adsorption isotherms for surface area measurement). Several coals were tested, both raw and heat-treated to 2500°C (HT2500) or 3000°C (HT3000). Two methods of intercalation were developed and applied to different Jeddo size fractions in an attempt to understand the possible effect of the particle size on the sulfur uptake. In addition, X-ray diffraction (XRD) studies were conducted to compare the crystalline structure of the anthracites with that of commercial expandable graphite (EG). EGs were added to foams and tested. The tests were used on foams that were formulated using commercial EG, to see the thermal stability effect on the foams before and after added EG.

2. EXPERIMENTAL

2.1 Study samples and Materials

For one sample, a Pennsylvania anthracite (Jeddo Coal Co.), and its heat-treated counterpart were selected initially. Three different particle size samples were selected: -200 mesh, 200-50 mesh and +50 mesh, respectively. In addition, four commercial expandable graphite samples (EG-3577, EG-3772, EG-3494 and EG-3538), produced from natural graphite, were provided by Anthracite Industries, Inc./Asbury Graphite Mills, Inc. and selected as benchmark samples.

Additional coal samples have been investigated: a Pennsylvania coal, Summit semi-anthracite, a Vietnamese coal, Hongay anthracite, and PSOC 1468 (Penn State Coal Sample Bank), an anthracite coal from the Buck Mountain seam. Information on these coals will be included in the Results and Discussion section.

Concentrated acids used in the pretreatments were purchased from Sigma-Aldrich.

2.2 Treatment of anthracites

2.2.1 Acid/Heat Treatments for Expansion

Two methods reported in the literature to exfoliate/expand natural graphite and anthracite were used as the basis for the method of expansion. [6-8] Modifications of these methods were selected to treat the graphitized anthracite, as described in the 3rd quarter progress report. [3-5].

Method 1: For this method, 10g of heated anthracite, 20g of sulfuric acid, 10g of nitric acid, 15g of perchloric acid and 0.3g of ethylene glycol were placed into a dry flask. The mixture in the flask was then stirred in an ice bath for 2 hours. After that, it was washed with deionized water to neutrality and dried at a temperature of 80°C for overnight.

Method 2: For this method, 10g of heated anthracite, 20g of sulfuric acid, 10g of nitric acid, 15g of perchloric acid and 0.5g of potassium permanganate were placed into a dry flask. The mixture in the flask was then stirred in an ice bath for 2 hours. After that, it was washed with deionized water to neutrality and dried at a temperature of 80°C for overnight.

As these methods did not prove successful for intercalation and expansion of JED HT2500-AT, other methods were explored. [5] Recent research has shown that sulfuric and nitric acids can react with anthracite and exfoliate graphite nanofibers, so long as the carbon pretreated with acid is processed as a paste. [9-11] This third method was explored to pretreat with sulfuric acid.

Method 3: 5g of raw anthracite (60 mesh), 15g of sulfuric acid, and 5g of nitric acid, were placed into a dry flask. One variation was added to determine the factors that would most affect acid interaction with coal.

Method 3A: The mixture in the flask was then stirred in an ice bath for various lengths of time. After that, it was washed with deionized water to neutrality and dried at a temperature of 80°C for overnight.

Method 3B: The mixture in the flask was then stirred at room temperature for various lengths of time. The sample was filtered without washing and was heated as a paste.

To determine expansion of the intercalated anthracite samples, they were rapidly heated by inserting into a muffle furnace at 500, 700, 900, and 1000°C.

2.2.2 Heat treatment of samples

Two sets of samples were heat-treated in order to graphitize the anthracite structure. Jeddo coal was heat-treated to 2500°C and is labeled as JED-HT2500. Summit and Hongay coals were heat-treated by GrafTech by baking the material using a heating rate of 60 °C/hr up to 1000°C with a 2 h hold, then graphitizing the material at a rate so that 3000°C is obtained in 3-3.5 h and held at 3000°C for 30 min. Henceforth, these samples are labeled SUM-HT3000 and HONG-HT3000.

2.3 Characterization

2.3.1 Proximate and ultimate analysis

Proximate and ultimate analyses were conducted for all the samples selected. Proximate analysis (moisture, volatile matter, ash and fixed carbon) was conducted using a LECO MAC. A LECO CHN 600 was used to determine the ultimate analysis (total carbon, hydrogen and nitrogen) and a LECO SC 132 was used to determine the total sulfur content.

2.2.2 Particle size distribution

The particle size distribution of JED-HT2500 (-200 mesh and 200-50 mesh) were analyzed using a Malvern Mastersizer “S” particle analyzer. This instrument provides the opportunity for wet and dry measurements, and the light source operates at a wavelength of 633 nm. Utilizing the wet technique, the operator can measure particle sizes throughout a dynamic size range of 0.05 μm to 900 μm . The solution used for the analysis was methanol. The maximum particle size determined by this analyzer is 900 μm (16 mesh), and therefore, it could not be used to analyze the top particle size sample (+50 mesh, $\sim 300 \mu\text{m}$). Therefore, to characterize the particle size distribution of this sample a series of standard sieves from 70-6 mesh (210 – 3360 μm) was used.

2.2.3 Thermomechanical analysis (TMA)

At APCI, TMA was conducted under air to characterize the thermal behavior (expansion) of the expandable graphite samples. The experiments were performed with a heating rate 5°C/min from ambient to 400°C. The flow rate of air was 100 mL/min, and a Hermetic Al DSC pan with inverted lid was used for the analysis. Several samples were analyzed by a TMA at GrafTech, Inc., in Parma, Ohio. The TMA used was an Universal Instrument, Model 2940 TMA V2.4E, with the heating rate set at 10°C/min up to 600°C.

2.2.4 Porous structure

N₂ adsorption isotherms at 77 K were used to characterize the porosity of the samples using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT and a Micromeritics ASAP 2000. The pore sizes 2 nm and 50 nm were taken as the limits between micro- and mesopores and meso- and macropores, respectively, following the IUPAC nomenclature. [12]

2.3.4 X-ray Diffraction

XRD analyses were conducted to investigate the crystal structure of the parent anthracites, and also the expandable graphite samples made from both natural graphite and the heat treated anthracites. XRD measurements were taken with a Scintag Model X2 θ/θ goniometer with Cu radiation Ka1/Ka2 with Si (Li) Peltier detector operated at 30 kV and 50 mA.

2.3.5 Foam Preparation – General

Samples of rigid polyurethane foams were prepared at APCI with various levels of EG in them. The polyurethane foam samples were formulated with a mixture of polyol, MDI, surfactant, pentane, water, and catalysts such that the isocyanate (ISO) index was approximately 200-300. EG was stirred into the polyol side such that the weight percent of the EG in the total formulation was 0, 1, or 5 wt%.

2.3.6 Butler Chimney Test

The procedure for this test is based on ASTM method D 3014-4a. [13] Briefly, the chimney apparatus is 12 in. x 2.5 in x 2.5 in., with three walls and a glass plate placed in front of the apparatus. The apparatus is elevated 6.5 inches from the base to allow a Bunsen burner to be placed beneath it. The samples are cut to 10 in. x 0.75 in. x 0.75 in. pieces and impaled by a holder, which is then hung from the back wall of the apparatus. The burner is lit and placed beneath the sample for 10 seconds. The following parameters are measured: flame burn out time, flame height, flame temperature, and mass loss.

2.3.7 Break-Through Tests

Figure 1 is a schematic of the break-through test. Small panels of rigid foam were prepared for the break-through test. The foam samples were formulated as described in 2.3.2 and poured into a plaque mold that had 26 gauge metal facers (8 in. x 8 in.) loosely attached to the top and bottom faces of the mold, such that when demolded, a panel with metal facers on both sides would be produced. A 700-1000°C gas flame (Bunsen burner) is applied to the outside of the metal facer on a foam panel. Thermocouples are inserted at 7, 20, and 35 mm into the foam core to record the temperature. The panels were heated for 5-20 minutes, and the temperatures and mass loss recorded.

3. RESULTS AND DISCUSSION

3.1 Characterization of Raw Coal, Intercalated Graphite, and Intercalated Anthracite

3.1.1 Proximate and Ultimate Analysis of Raw Samples

Table 1 lists the proximate and ultimate analysis results of raw and heat-treated anthracites. The coals range from high volatile to low volatile anthracites, with ash contents varying from 4-20%. The heat-treated anthracites have low ash, oxygen, hydrogen, nitrogen, and moisture, as expected from a heat-treated sample.

3.1.2. Proximate and Ultimate Analysis of Intercalated and Expanded Samples

Table 2 lists the proximate and ultimate analysis results of the expandable graphite samples, and Table 3 lists how some of the properties relate to the pH and expansion ratio of the samples. The expandable graphite samples were obtained from Asbury Graphite, samples already intercalated with sulfuric acid. The expandable graphite samples have higher percentages of volatile matter and sulfur content, probably coming from sulfuric acid typically used for the intercalation. There seems to be a relationship between the expansion ratio and the sulfur or volatile content of these samples, where the higher the sulfur or volatile matter, the larger the expansion ratio of the expandable graphite. This is probably due to a higher concentration of intercalated compound can produce more gas products and helps to increase the expansion of the graphite upon heat treatment.

Table 4 lists the proximate analysis results of some of the intercalated raw anthracites and heat-treated anthracites. Similar observations can be made, with an increased sulfur content an indication of possible expansion. The sulfur and volatile content of the Hongay coal is comparable to the EGs with lower expansion ratios.

3.1.3. Particle size distribution of JED-HT2500

Figure 2 shows the particle size distribution of the separated fractions of JED-HT2500 samples. It can be seen that the particle size distribution of the sample less than 200 mesh has the wider distribution compared to the other two samples. The average particle size for these three samples, (-200 mesh, 200-50 mesh and +50 mesh) was 9.9, 65.6 and 721.8 μm . The wavy distribution observed for the top fraction sample (+50 mesh) may be due to the sieving method used and not enough time being allowed to separate the different particle size fraction.

3.1.4. XRD of Graphitized Anthracites

Figures 3 and 4 show the X-ray diffractograms of the JED-RAW and JED-HT2500 samples. It can be seen that JED-RAW has wide peaks at 26° and 45° (Figure 3), while these peaks are much narrower, particularly the peak at 26° , for the heat-treated sample (Figure 4). This indicates that the raw anthracite presents a disordered structure, while the heat-treated anthracite has a more ordered crystalline structure (Figure 4). The narrow peak appearing at 35° is probably associated with inorganic crystals. Similar XRD results were obtained for HONG-HT3000 and SUM-HT3000, so figures were not included. Table 5 lists the d-spacing ($\text{\AA}$) and the L_c calculated from the XRD diffractograms. While all three coals became much more ordered due to the high temperature of the heat treatments, it appears the coal producing the highest order was Hongay.

3.2 Expansion of Expandable Graphite, Anthracite, and Heat-treated Anthracite

3.2.1 Expansion of EG

3.2.1.1 Relationship of Fraction Size, Sulfur Uptake, and Volatile Matter to Expansion

A relationship between the expansion ratio and the sulfur or volatile content of the EG samples was identified, where the higher the sulfur and volatile matter content, the larger the expansion ratio of the expandable graphite. This is probably due to a higher concentration of intercalated compound, which would produce more gas products and increase the expansion of the graphite upon heat treatment. Accordingly, methods 1 and 2 were applied to different anthracite size fractions (+50 mesh and -200 mesh) in an attempt to maximize the sulfur uptake. This is discussed in section 3.2.2.1.

3.2.1.2 TMA

Four expandable graphite samples were submitted for characterization of intumescence by TMA, and the test results are presented in Figure 5. All the four samples expand in volume on heating in air. Two of the samples (EG-3772 and EG-3577) expand abruptly and at moderately low temperatures. The other two samples (EG-3494 and EG-3538) begin their expansion at higher temperatures, expand at lower rates, and have a lower degree of overall expansion.

Table 6 lists the extrapolated onset temperatures for the expansion, which are somewhat higher than the temperatures where expansion is first observed, especially for samples EG-3494 and EG-3538. For this series of samples, the onset temperatures increase in the following order: EG-3538>EG-3494>EG-3577>EG-3772. Three of the samples (EG-3494, EG-3538 and EG-3577) were tested in duplicate using different sample sizes, with little effect on the onset temperature.

3.2.1.3 Effect of Expansion of Intercalated Graphite, as Noted by XRD

XRD studies were also conducted on EG-3772, JED-HT2500-AT, and JED-HT2500-AT-HT900. The XRD diffractogram of EG-3772 presents very narrow peaks, indicating a highly developed ordered crystalline structure (Figure 6), although less ordered than JED-HT2500 or a typical graphite. In contrast to the chemically treated anthracites (Figures 7 and 8), the peak at 35° disappears, indicating a very low content of inorganics.

The JED-HT2500-AT-HT900 was generated after applying method 1 to JED-RAW (200-50 mesh). JED-HT2500-AT900 was generated by rapidly heat-treating JED-HT2500-AT by inserting the sample into a muffle furnace at 900°C. When comparing the XRD of JED-HT2500-AT and JED-HT2500-AT900 samples (Figures 7 and 8) with JED-HT2500 (Figure 4), it can be seen that the peaks around 26° and 45° are very similar. However, some differences appear for the peak around 35°. For the heat-treated anthracite, there was a sharp peak around 35°, while for the JED-HT2500-AT and JED-HT2500-AT900 samples, this peak becomes smaller or even disappears. This is probably due to the oxidization effect of the acids used during the treatment process and the removal of some inorganic compounds.

Table 7 lists the crystal structure parameters (d-spacing and L_c) calculated from the XRD diffractograms. It can be seen that the d-spacing and L_c increased from 3.4351 and 29 Å for JED-RAW to 3.3589 and 309 Å for JED-HT2500, indicating a larger crystalline structure present after heating.

After chemical treatment, the d-spacing values did not change significantly (3.3589 vs. 3.3598), while the L_c decreased (309 vs. 176). This is probably due to the chemicals use for the treatment that may have destroyed the crystal structure of the heat-treated anthracite. The JED-HT2500-AT900 sample has higher d-spacing and L_c values than those reported for JED-HT2500-AT, probably due to the heating process used to generate JED-HT2500-AT900. Finally, it can be seen that the commercial sample has the smallest d-spacing and largest L_c compared to the anthracite samples. These differences in the crystalline structure between the commercial expandable graphite and the treated anthracites may be responsible for their different expansion behavior. XRD spectra of HONG-HT3000-AT and SUM-HT3000-AT were not obtained.

3.2.2 Expansion of Acid-treated and Heat-treated/acid-treated Anthracites

Anthracites, raw and after high temperature heat treatment, were acid-pretreated. Several methods were tested in order to expand the coals before and after heat treatment. Initially, only heat-treated Jeddo anthracite was tested, JED-HT2500, and with some very strong acids and oxidizing agents (methods 1 and 2). The acids used in these two methods are very strong and explosive (perchloric acid), and as no expansion was noted with either of the two methods and this coal, it was decided to try different acid-pretreatments and coal. The new method was to use sulfuric/nitric acids, both rinsed from the sample and as a paste (methods 3A and 3B), on different raw (Hongay, Summit, and Buck Mountain) and heat-treated coals. Previous work has shown a reaction between the coal and acids, particularly in Hongay anthracite coal. [9, 10]

For our initial tests, the raw samples were treated with sulfuric/nitric acids, rinsed, and heated to 900°C (Method 3A). This method is similar to expansion of graphite. [9-11, 14] For the samples intercalated by method 3A, sulfur uptake was low and expansion did not take place. However,

for method 3B, leaving the acid in the sample as a paste, increased the sulfur content and also expanded the samples slightly when heated to 900°C.

3.2.2.1 Relationship of Fraction Size, Sulfur Uptake, and Volatile Matter to Expansion

Figure 9 shows the sulfur content of the three size fractions of JED-HT2500 (–200 mesh, 200-50 mesh and +50 mesh) after applying method 1 or 2. All the treated anthracites have higher sulfur content than the parent sample, whose sulfur content was 0.3 wt%. There does not seem to be any clear relationship between fraction size and sulfur content. However, the +50 mesh fraction samples present higher sulfur uptakes than the other two fractions (0.6 wt% vs. ~0.4-0.5 wt%). Both methods seem to result in similar sulfur uptakes. The produced samples did not report any significant volume increase when rapidly heated. Previous research has reported that larger particles tend to expand better than smaller particles. [14]

HONG-AT and HONG-HT3000-AT had an increased sulfur content relative to the other coals samples (greater than 2 %, while other coals had less than 1.5%), and comparable to the EGs with a lower expansion ratio (Tables 3 and 4). This is an indicator as to why Hongay expanded and the other coals did not.

3.2.2.2 TMA of Anthracite Coals, raw, acid treated, and intercalated heat-treated.

For the EG made from natural graphite, the volume of the EG increases tens or even hundreds times upon rapid heating, due to the vaporization of intercalated substances that forces the graphite layers apart.

The JED-HT2500-AT did not show any appreciable expansion, so TMA was not done on this particular sample. As we were not successful with expanding JED-HT2500-AT, we decided to modify the method and to use coals that have been shown to expand in the literature. [6-10] HONG-AT700 and SUM-AT700 (method 3B, paste) appeared to expand a little in the crucible, but BUC-AT700 did not. HONG-HT3000-AT700 (method 3A) expanded (~ 3 times the original volume in crucible), but SUM-HT3000-AT700 did not. TMA was done on the three raw and acid-treated coals to see if expansion could be detected quantitatively. Figure 10 is the TMA expansion graph for BUC-RAW and BUC-AT. Figures 11 and 12 are the TMA expansion graphs for Hongay (HONG-RAW, HONG-AT, and HONG-HT3000-AT) and Summit (SUM-RAW, SUM-AT, and SUM-HT3000-AT).

As can be seen in Figure 10, BUC-RAW showed a slight increase in volume, about +1.5 %, probably due to slight thermoplastic properties, and then a loss at ~500°C when volatile matter is probably evolving. However, BUC-AT did not interact at all with the acid, and the change in dimension appears to be due to the acid vaporizing at 208°C and a loss of volume, again at ~500°C. For SUM-RAW (Figure 11), there is only a +0.5% increase in volume and then a loss at ~500°C when volatile matter is probably evolving. SUM-AT shows an interaction with the acid beginning at 133°C, with the peak at 198°C, and then loss in volume at ~480°C. For SUM-HT3000-AT, it is apparent that no acid was intercalated in the sample and therefore no opportunity for interaction with acid. For HONG-RAW (Figure 12), there is a +1.25% increase in volume and then a loss at ~450°C when volatile matter is probably evolving. HONG-AT shows an interaction with the acid beginning at 145°C, with the peak at 217°C, and then loss in dimension at ~450°C. For HONG-HT3000-AT, there was an interaction with acid, with the acid

vaporizing at 362°C and peaking at 412°C, although expansion is not observed in the sample with this method.

3.2.2.3 SEM of Acid-Treated Anthracite, and Heat-treated Acid-Treated Anthracite

As discussed in the previous section, the amount of sulfur and volatile matter in each sample is listed in Table 4, a possible indicator to determine how well these materials may expand. TMA indicated an interaction with the acids, but not much expansion. Figure 13 shows SEM micrographs of HONG-RAW, HONG-AT-HT700, and HONG-HT3000-AT700.

A slight expansion or reaction was achieved for Hongay and Summit coals, as can be seen in the SEM, but in subsequent discussions with APCI, it was decided that using the anthracite as an acid paste could not be used in the foam formulation as the acid may interfere with the catalyst used in the foaming process.

Both Hongay and Summit were heat-treated to 3000°C, intercalated with acids according to Method 3A, and expanded at 700 and 1000°C. SEM indicates expansion of HONG-HT3000-AT in particular and is shown in Figure 13(c) at 700°C and in Figure 13(d) at 1000°C. However, TMA indicated that HONG-HT3000-AT did not expand significantly, and since it should expand to at least 5 times its original size to keep generated foams from being too dense, it was determined that even the HONG-HT3000-AT would not be useful as an intumescent material. Therefore, while Section 3.3 describes the use of the commercial expandable graphites in the foams, acid-pretreated expandable anthracites were not added to foams and were not tested. However, several of the raw and acid-treated coals were activated to determine the usefulness of the samples as activated carbons.

3.3 Examination of Foams With and Without Expandable Graphites

3.3.1 Comparison of Foams With and Without Expandable Graphite- Butler Chimney Test

Foam of ISO index less than 200 was prepared with and without 5% loading of EG-3772 and evaluated using the Butler Chimney Test. For the sample with no EG-3772 added, the weight before the test was 3.70 g, and the weight after the test was 1.158 g, giving a PMR of 31.3 %. The exhaust time lasted for 25.8 seconds. However, when adding 5 wt % EG-3772 to the foam, the PMR was 65.9% and the exhaust time was reduced to 12.68 seconds.

3.3.2 Comparison of Foams When Varying Carbon Content Added to Foams – Butler Chimney Test

Samples of rigid polyurethane foams were prepared with various levels of expandable graphite in them and evaluated using the Butler Chimney Test (ASTM D3014-4a). [13] The polyurethane foam samples were formulated with a mixture of polyol, MDI, surfactant, pentane, water, and catalysts such that the isocyanate index was approximately 200. EG-3772 was stirred into the polyol side such that the weight percent of the expandable graphite in the total formulation was 0, 1, or 5% by weight. The density of the resulting polyurethane foam was approximately 40 kg/m³.

Figures 14 to Figure 16 show the percent mass retained (PMR), exhaust time and flame temperature results of Butler chimney tests, respectively. It can be seen that for a low amount of

EG-3772 (e.g., 1.0 wt% in the foam) there was not significant effect on the thermal stability of the foams. The PMR increased from 33.61 to 36.26%, while the flame temperature decreased from 442 to 367°C. With a higher amount of EG-3772 added in the foam (e.g., 5.0 wt% in present study), there was a significant effect on the thermal stability of the foam. The PMR increased from 36.28 to 64.4 %, while the exhaust time and flame temperature also showed a big reduction when the EG amount was 5.0 % in the foam.

Figure 17 shows the char of EG added foam. It can be seen that there were small worm-like structures on the outside of the char, probably due to the EG-3772 structure after expansion. There was no such worm like structure formed for the intumescent material added foam. This indicates that there was different mechanism of flame reduction for the foam with EG compared to the original intumescent foam during the burning process. It was determined that adding EG to the foams is an effective way to form a protective char layer in an open flame test, and thus reduce the amount of polymer burned.

3.3.3. Comparison of Different Foams When Varying Type of Foam Using the Break Through Test

Figure 18 shows the break through tests for foams with an ISO of 300, with and without 5% EG-3772. For the foam with the ISO 300, the loss of mass with carbon added was 10.6 g, while if no carbon was added the decomposition loss was 11.8 g, not a significant change. Figure 19 shows the break-through tests for foams with an ISO of less than 200, with and without 5 % EG-3772. For the foam with ISO index less than 200, after 20 minutes, the loss of mass to the with carbon added was 7.9 g, while the sample with no EG had a mass loss of 11 g after 5 minutes.

3.4 Other Possible applications

3.4.1 Porous structure studies

Figure 20 shows the N₂ isotherms at 77 K of JED-HT2500-AT and JED-HT2500-AT900-1 samples, as well as the untreated anthracite sample (200-50 mesh). All the isotherms are very similar, and JED-HT2500-AT900 presents the highest nitrogen adsorption at low relative pressures, indicating that this sample has the highest surface area (Table 8).

Table 8 lists the surface area and pore volume of Jeddo samples. The parent anthracite has very similar surface area and pore volume to the JED-HT2500 samples. The surface area and pore volume of the JED-HT2500-AT900 samples are larger than those of the JED-HT2500-AT samples, where the JED-HT2500-AT900-1 has the highest surface area and pore volume. This indicates that the two methods used here increase the surface area and pore volume of the anthracite after expansion, and it seems that method 1 is more effective than method 2 in terms of increasing the surface area and pore volume.

As mentioned in Section 3.2.2.2, the raw and acid-treated coals (Hongay, Summit, and Buck Mountain) were activated in steam at 850°C for 2 h. Table 9 lists the total surface area the average pore volume. In the future, these samples will be tested as activated carbons for mercury adsorption.

The surface areas and pore volumes of the raw anthracites, BUC-RAW, HONG-RAW, and SUM-RAW are quite low, $1 \text{ m}^2/\text{g}$ or less. Even after acid-pretreatment, for the most part, the surface areas and pore volumes are low, with the exception of SUM-AT700. Summit is quite high in ash content, so it may have been possible that the acid may have selectively removed some of the ash to open up the porosity of the coal slightly to $\sim 30 \text{ m}^2/\text{g}$. Overall, Summit anthracite has the lowest surface areas, even after activation. After activation, the activated Summit coal surface areas are $\sim 500 \text{ m}^2/\text{g}$, the activated Buck Mountain samples $760\text{--}1000 \text{ m}^2/\text{g}$, and Hongay samples $900\text{--}1270 \text{ m}^2/\text{g}$. Interestingly, the acid-pretreatment had a positive effect on Hongay samples, increasing the surface area from 900 to $1270 \text{ m}^2/\text{g}$, while for Buck Mountain and Summit samples the acid-pretreatment had a null or negative effect. It appears the acid-pretreatment at 500°C was better for activation than at 700°C . Thermogravimetric analysis, energy dispersion analysis, and sulfur analysis of the samples (data not shown) indicated that at the 500°C , some of the sulfate ion still remained in the sample, possibly creating additional spaces or links in the coal for the steam to interact with during activation. The lower surface areas of the Summit coal could possibly be due to the large amount of mineral matter inherent in the coal, thus limiting how well the coal could activate.

Past research has shown that an acid-pretreatment may increase the surface area compared to the raw coals. Most notably, Albiniak et al., Furdin, and Daulin et al. have shown increased surface area for activated carbons made from acid-pretreated anthracites. [6, 7, 15] However, they used perchloric acid, a material known to be explosive, creating an additional hazard, and little attention was paid to the coal chosen for the prepared activated carbons. Albiniak et al. showed similar results for Hongay anthracite with a perchloric/nitric acids acid-pretreatment, so our treatment is comparable using a less explosive material, sulfuric acid. More recently, Lyubchik et al. showed that anthracites with higher volatile matter pretreated with either perchloric or nitric increased the porosity relative to activation with no pretreatment, with nitric acid pretreatment increasing surface area of coals an additional $500\text{--}700 \text{ m}^2/\text{g}$ from the activated raw coals. [16]

4. CONCLUSIONS

The goal of this project was to use heat-treated (graphitized) anthracites to replace graphite in expandable graphites that, if used in intumescent foams, would improve the thermal stability of the foams. Four expandable graphites (EG, fairly pure graphites already intercalated with sulfuric acid) were obtained from Asbury Graphite, Inc. These EGs were characterized and expanded to determine the best material for use in intumescent foams (EG is used to retard ignition, flame propagation and thermal degradation in the foams), and would be the baseline for comparison for heat-treated expandable anthracites. The best EGs to use are those with a high expansion ratio, neutral pH (acidic materials could interfere with the catalyst used in foam preparation), and larger particle size. There was only one of the Asbury expandable graphites that best met these conditions; this was Sample No. EG-3772, as it has a nominal particle size + 50 Mesh, expansion ratio of 280 to 1, and a pH of 7.00.

Samples of rigid polyurethane foams were prepared at APCI with various levels of EG-3772 in them such that the isocyanate (ISO) index was approximately 200–300. The best loading of EG in the foam was at 5%. For foams of an ISO index 300, the EG in the foam did not contribute to

the thermal stability of the foam. However, for foams with an ISO index of less than 200 and 5% EG loading, there was significant effect as determined by the Butler Chimney Test and the Breakthrough tests.

In initial experiments, JED-HT2500 was tested. Two expansion methods were tested, based on literature, using nitric/perchloric acids as the intercalants. [5, 6] However, no significant expansion was noted. In previous CPCPC work it has been shown that slight expansion or reaction of anthracites occurs using a more common expansion method, using sulfuric and nitric acids, by heating the acid-treated anthracites as a paste and using anthracite coals that may be more amenable to expansion/reaction. [8, 9]

Two high volatile coals were tested, the Vietnamese anthracite Hongay and the American anthracite Summit, and one low volatile coal, Buck Mountain, was tested. Initially, they were tested by acid-pretreatment of raw coals. TMA, SEM, and surface area of the reacted coals indicated an interaction with the acid during heat treatments to 500-700°C, but not really an expansion. The acid-pretreatment actually had a negative effect on activated carbons from Buck Mountain, and TMA indicated Buck Mountain did not appear to react with the acids.

Summit and Hongay coals were heat-treated to 3000°C to graphitize the coals. XRD indicated these coals graphitized and the Hongay coal graphitized better than Jeddo or Summit. Both heat-treated coals were subjected to acid treatment, followed by rinsing, and heat-treated to 700-1000°C. From SEM, it is apparent that Hongay expanded but Summit did not. TMA of Hongay did not indicate expansion, but the vapor intercalated into the sample was released at a much higher temperature than when using raw coal as an acid paste. SEM showed that HONG-HT3000-AT700 expanded. TMA of Summit indicated that acid was not intercalated into the structure, and SEM confirmed this. Even though HONG-HT3000-AT700 expanded, the expansion was not enough to warrant testing the materials in an intumescent foam.

Since expandable heat-treated anthracite could not be used in the specified application, raw and acid/heat-treated coals were activated using steam at 850°C. Each sample was monitored by surface area and pore volume in order to see the effect of the acid-pretreatment on the activation. Overall, Summit anthracite has the lowest surface areas, even after activation. After activation, the Summit surface area is ~500 m²/g, the Buck Mountain anthracite 760-1000 m²/g, and Hongay anthracite 900-1270 m²/g. Interestingly, the acid/heat-treatment had a positive effect on Hongay anthracite, increasing the surface area from 900 to 1270 m²/g, while for Buck Mountain and Summit anthracites the acid/heat-treatment had a null or negative effect. It appears the acid/heat-treatment at 500°C was better for activation than the 700°C heat-treatment. Thermogravimetric analysis, energy dispersion analysis, and sulfur analysis of the samples indicated that at the 500°C, some of the sulfate ion still remained in the sample, possibly creating additional spaces or links in the coal for the steam to interact with during activation. The lower surface areas of the Summit coal could possibly be due to the large amount of mineral matter inherent in the coal, thus limiting how well the coal could activate.

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7. TABLES

Table 1: Ultimate and proximate analyses of coals that will be tested.

Sample	Moist. ^a %	Ash %	V.M. ^b %	F. C. ^c %	Carbon wt%	Hydrogen wt%	Nitrogen wt%	Sulfur wt%	Oxygen wt%
JED-HT2500 <200 mesh	0.34	9.43	n.d. ^d	n.d.	90.31	0.00	0.58	0.28	<0.01
JED-HT2500 50-200 mesh	0.10	8.57	n.d.	n.d.	91.02	0.00	0.67	0.33	<0.01
JED-HT2500 50 mesh	0.14	7.55	n.d.	n.d.	92.26	0.00	0.57	0.26	<0.01
SUM-RAW	1.50	20.2	12.7	67.2	73.26	1.59	1.42	0.64	3.62
SUM-HT3000	27.23	0.18	12.79	59.80	99.17	0.00	0.20	0.44	0.00
BUC-RAW	0.96	7.01	4.27	88.72	87.04	0.67	1.24	0.59	3.45
HONG-RAW	0.80	4.25	10.38	85.37	89.21	2.58	0.85	0.66	2.45
HONG-HT3000	22.56	0.34	10.23	66.86	99.30	0.00	0.22	0.14	0.00

a Moisture content, as determined by Leco MAC-400

b Volatile Matter content, as determined by Leco MAC-400

c Fixed Carbon content, as determined by Leco MAC-400

d not determined

Table 2: Ultimate and proximate analyses of expandable graphites.

Sample	Moist. ^a %	Ash %	V.M. ^b %	F. C. ^c %	Carbon wt%	Hydrogen wt%	Nitrogen wt%	Sulfur wt%	Oxygen wt%
EG-3494	0.94	10.66	16.60	72.74	77.37	0.41	0.11	2.46	8.98
EG-3538	1.85	11.20	15.05	73.76	82.37	0.00	0.07	2.36	3.99
EG-3577	0.82	4.32	29.96	65.72	80.24	0.58	0.07	2.70	12.09
EG-3772	0.52	0.26	38.10	61.64	80.96	0.85	0.00	3.08	14.86

a Moisture content, as determined by Leco MAC-400

b Volatile Matter content, as determined by Leco MAC-400

c Fixed Carbon content, as determined by Leco MAC-400

Table 3: Analysis data of the expandable graphite samples.

Sample name	Nominal ^a Size	Ash ^b Wt %	V.M. ^b Wt %	Sulfur ^c Wt %	Expansion ^a ratio, X to 1	pH ^a
EG-3494	-50mesh	10.66	16.60	2.46	130	3.22
EG-3538	-200mesh	11.20	15.05	2.36	30	7.23
EG-3577	+50mesh	4.32	29.96	2.70	290	2.88
EG-3772	+50mesh	0.26	38.10	3.08	280	7.00

a – As determined by Asbury Graphite

b – Volatile Matter, as determined by Leco MAC-400

c – As determined by Leco SC 100

Table 4: Ultimate and proximate analyses of Intercalated and Expanded Coals Buck Mountain, Hongay, and Summit.

Coal Name	Intercalation Method	Moist. ^a %	Ash %	V.M. ^b %	F.C. ^c %	Sulfur ^d Wt%	Exp
BMT-AT	Method 3A	47.14	6.47	18.92	74.61	1.33	No
BMT-AT	Method 3B	n.d. ^e	n.d.	n.d.	n.d.	n.d.	No
SUM-AT	Method 3A	29.99	14.91	24.60	60.49	1.32	No
SUM-AT	Method 3B	1.97	3.14	48.28	48.58	1.25	No
SUM-HT3000-AT	Method 3A	19.26	0.55	13.98	85.47	1.30	No
HONG-AT	Method 3A	2.06	3.23	33.11	63.66	0.87	No
HONG-AT	Method 3B	1.95	14.25	53.78	31.97	2.82	Slight
HONG-HT3000-AT	Method 3A	21.30	0.57	15.09	84.34	2.05	Yes

a Moisture content, as determined by Leco MAC-400

b Volatile Matter, as determined by Leco MAC-400

c Fixed Carbon content, as determined by Leco MAC-400

d As determined by Leco SC 100

Table 5: The crystal structure parameters calculated from XRD spectra of heat-treated coals Jeddo, Hongay, and Summit.

Sample name	d-spacing (Å)	L _c (Å)
JED-RAW	3.4351	29
JED-HT2500	3.3589	309
HONG-HT3000	3.3608	351
SUM-HT3000	3.3611	203

Table 6: Extrapolated temperature of the expandable graphite samples

Sample ID	Extrapolated Onset (°C)
EG-3494	217, 237
EG-3538	241, 238
EG-3577	162, 165
EG-3772	151

Table 7: The crystal structure parameters calculated from XRD spectra of heat-treated Jeddo and EG-3772.

Sample name	d-spacing (Å)	L _c (Å)
JED-HT2500	3.3589	309
JED-HT2500-AT-1	3.3598	176
JED-HT2500-AT900-1	3.3605	229
EG-3772	3.3575	389

Table 8: Surface area and pore volume of Jeddo coal and heat-treated Jeddo after acid-pretreatment and expansion.

Name	Surface area (m ² /g)	Pore volume (mL/g)
JED-RAW	4.16	0.0076
JED-HT2500-AT-1	4.13	0.0096
JED-HT2500-AT900-1	12.57	0.0189
JED-HT2500-AT-2	3.15	0.0086
JED-HT2500-AT900-2	5.60	0.0121

Table 9: Total surface area, pore volume, and pore size of raw coal, raw coals with acid-pretreatment, and heat-treated coals with acid-pretreatment, Buck Mountain, Hongay, and Summit.

Sample Name	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (Å)
BUC RAW	1	n.d.	n.d.
BUC AT500	1.57	0.002721	69.4
BUC AT-HT700	1.36	0.001730	50.9
BUC RAW-ACT	1013.15	0.495260	19.6
BUC AT500-ACT	916.26	0.453500	19.8
BUC AT700-ACT	761.73	0.371635	19.5
HONG RAW	0.64	0.000877	54.4
HONG AT500	0.74	0.000717	39.0
HONG AT700	0.65	0.000732	45.1
HONG RAW-ACT	904.84	0.470313	20.8
HONG AT500-ACT	1271.58	0.751552	23.6
HONG AT700-ACT	1264.06	0.778108	24.6
HONG HT3000	0.83	0.002317	112.2
HONG HT3000-AT700	7.19	0.014013	77.9
SUM RAW	0.54	n.d.	n.d.
SUM AT500	0.67	0.000936	53.2
SUM AT700	29.68	0.018004	24.3
SUM RAW-ACT	583.10	0.316979	21.7
SUM AT500-ACT	588.31	0.350076	23.8
SUM AT700-ACT	491.19	0.283376	23.1
SUM HT3000	5.78	0.019782	137.0
SUM HT3000-AT700	9.35	0.030797	131.8

n.d.- not determined

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Final Report

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Mesophase pitches, suitable for producing premium carbon products were prepared from a commercial coal tar distillate (CTD) using both the thermal and solvent extraction routes. Initially, a series of pressure heat treatments were carried out to convert the CTD to a thermal tar with an acceptable Modified Conradson Carbon Value (MCC). The tar was then distilled to an ~ 130 °C softening point (SP) pitch which was then used to produce a mesophase pitch by thermal heat treatment with inert gas sparging. Properties of the mesophase pitch, including softening point, mesophase content and viscosity vs. temperature data showed it to be suitable for fiber spinning and carbon foam production.

The 130 °C SP pitch was further distilled to produce isotropic pitches of higher softening points which were then solvent extracted with toluene to give a mesophase pitch. Extraction times and temperature were varied in order to ascertain the conditions which would produce a processable product. Mesophase pitches with 342 °C SP values from both the thermal and extraction routes were compared using mass spectroscopy to investigate the differences in molecular constitution. The results show that this CTD material can serve as a precursor for the production of high quality mesophase pitch.

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1.1. Program Background

Mesophase pitch is an important raw material for producing premium carbon products, such as high modulus carbon fibers, highly conductive carbon foams, matrices for carbon/carbon composites and meso-carbon microbeads (MCMB). In the U.S.A., mesophase pitch is mainly made from petroleum-based feedstocks and used only for internal consumption. There is no domestic commercial source of mesophase pitch. Both Cytec Corp. and Conoco/Phillips have produced mesophase pitch as a precursor for carbon fibers. However, Conoco/Phillips terminated their carbon fiber project in 2003. Currently, the only commercial source of mesophase pitch in the world is the AR pitch produced from naphthalene by Mitsubishi Gas Chemical Co.

The goal of this program was to demonstrate a process route for producing mesophase pitch from coal-derived distillates. GrafTech has an extensive background in the chemistry and processes involved in the production of mesophase pitch. It also has the equipment (high pressure/high temperature autoclaves) necessary for processing distillate materials to pitch and mesophase. Both solvent extraction and heat treatment procedures were to be used to effect final transformation to high quality mesophase pitch which would be suitable for producing premium carbon products such as carbon fibers and carbon foams. Detailed characterization of the mesophase pitches was to include: mesophase content and domain size, rheological behavior, reactivity and molecular weight distribution. A successful program could lead to the use of coal-derived feedstocks as precursors for high-value carbon products such as fiber, foams, C/C composites and anode carbons for Li ion batteries.

1.2. Program Concepts

Our basic concept was to obtain a commercial coal tar distillate material, which is free of solids and highly aromatic, and to demonstrate its suitability as a precursor for mesophase pitch for high performance carbon products. A key first step was to thermally transform the distillate into a tar which would provide an acceptable yield of pitch after distillation. Batch heat treatments under pressure were used to polymerize the polynuclear aromatic components of the distillate to potential mesophase-forming species. The goal was to obtain a tar with a high Modified Conradson Carbon (MCC) value while avoiding the formation of mesophase or coke. Simplistically, the goal of the batch heat treatments was to define the maximum heat treatment severity that could be employed in a classical continuous thermal treatment process carried out in a tubestill. The presence of mesophase in the product thermal tar from a tubestill thermal treatment process is not acceptable because it would cause premature coking on the walls of the tubestill. On the other hand, the highest feasible MCC coking value in the thermal tar is desired because this will provide an acceptable yield of pitch after distillation.

The simple batch heat treatment approach used here is really an approximation of a single-pass continuous thermal treatment process. In a true full-scale continuous production process, the distillate obtained from distillation of thermal tar to pitch would be recycled back to the continuous tubestill thermal treatment unit. This would increase the pitch yield (and subsequent mesophase pitch yield) significantly, perhaps doubling the yields from the single-pass process.

A main element of our program was to utilize solvent extraction concepts to produce the final mesophase pitch and to compare this approach to that of conventional thermal treatment.

The solvent extraction route was first reported by Riggs and Diefendorf⁽¹⁾ and was employed by Conoco/Phillips to transform petroleum pitch to mesophase.⁽²⁾ The thermal route, which involves heat treating pitch with inert gas sparging, was developed at Union Carbide for obtaining petroleum pitch-derived mesophase pitch for carbon fibers.⁽³⁾

The solvent extraction route requires preparation of a precursor pitch with a high concentration of high molecular weight species capable of forming mesophase. These components will transform to mesophase after they are separated from the lower molecular weight non-mesophase formers by extraction. The intricate phase behavior of the anisotropic and isotropic phases in a mesophase pitch and the interaction between high and low molecular weight components is highly complex and has recently been modeled by Hurt and co-workers.⁽⁴⁾

For mesophase pitch production by either the thermal or extraction route, precise control of the production process is critical. First, the mesophase pitch yield should be high. Second, both the mesophase content and the mesophase viscosity need to be acceptable for further processing. For example, for petroleum-derived mesophase pitch for fiber spinning, it was shown that near 100% mesophase could be achieved at a softening point of less than 350 °C.⁽⁵⁾ In this way, fiber spinning could be carried out below reaction temperatures. A schematic representation for transforming coal tar distillate to mesophase pitch by both the thermal and extraction routes is shown in Figure 1.

Two Routes to Mesophase Pitch

Figure 1: Schematic Representation of Mesophase Pitch Formation Using Thermal and Extraction Routes

The achievement of our program goals involved the successful completion of a number of interrelated steps. These included:

1. Selection and characterization of an appropriate coal tar distillate(CTD).
2. Determining suitable parameters (time, pressure, temperature) for converting the CTD to an acceptable thermal tar. This was done on both the laboratory and pilot scales.
3. Distillation of the thermal tar to a precursor isotropic pitch.
4. Conversion of the isotropic pitch to a high mesophase content mesophase pitch with acceptable viscosity characteristics using thermal treatment.
5. Preparation of a high softening point (SP) pitch which could be solvent extracted to give a mesophase pitch.
6. Determining extraction conditions (solvent, concentration, temperature) for obtaining an acceptable mesophase pitch.
7. Characterization of mesophase pitch properties and constitution.

The details for attaining these discrete objectives are the subjects for the remainder of this report.

2. EXECUTIVE SUMMARY

The purpose of this work is to demonstrate and explain the production of commercially useful mesophase pitch from coal tar distillate (CTD). In order for a mesophase pitch to be

acceptable for fiber spinning or other high performance applications it must have a high mesophase content, the mesophase must be the continuous phase, and the viscosity must be low enough to process below reaction temperature. This work shows how to correctly measure these parameters and gives numerical values for acceptable quality. 95

The experimental conditions and treatment of data presented in this work should be able to be applied to large-scale production. An operating window for the pressure heat treatment step was determined that maximizes yield without producing mesophase (mesophase formation is only desirable in the last step of the process). The “soaking volume factor” used in the pilot plant batch process can be directly applied to a large-scale continuous process.

Two processes for producing mesophase pitch were compared in this work. The first route was by thermal treatment; the second route was by extraction. The thermal treatment process gave pitch that was 85% mesophase with a softening point of 343 °C. The yield of mesophase from starting CTD was 18.7%. The extraction process produced 80% mesophase pitch with a softening point of 342 °C. The overall yield of mesophase pitch from CTD was 13.4%. These process yields could be higher in continuous processes with recycle of intermediate distillates.

There have been many previous studies on the preparation of mesophase pitch from a variety of precursors. However, to be commercially viable, the mesophase pitch must have demonstrated properties that meet the criteria for production of high performance carbon products such as carbon fibers. These properties are well recognized by manufacturers of mesophase-derived carbon products but are generally not described in the open literature. In this program, we have identified these criteria and attempted to demonstrate how they can be achieved using a coal-derived precursor. These studies have also provided some new insight into the physical and chemical processes involved in the transformation of coal-derived precursors to mesophase.

3. EXPERIMENTAL PROCEDURES

3.1 Material Selection

We contacted both Koppers Industries and Reilly Industries to obtain samples of commercially available high boiling coal tar distillates. Both companies kindly provided samples of candidate materials from their plant locations and we evaluated them in a preliminary screening program using several key tests. Since the initial materials received proved to be unsuitable, a second set of materials was received from each company for incorporation into the program.

3.2. Coal Tar Distillate Testing

3.2.1 Preliminary Testing

A special TGA method, which was adapted from ASTM method E 2008, was used to estimate the boiling range of the material. The method uses a pan/lid sample assembly with a nominal 35-micron hole in the lid. The heating rate is 5 °C/min to 500 °C in a low flow rate of argon gas through the TGA. The TGA measurements were made using a TA Instruments TGA, Model 2950.

A standard coking value test, Modified Conradson Carbon (ASTM D-2416), was used to estimate the amount of very high boiling material present in the material before heat treatment. Hot-stage microscopy⁽⁶⁾ was used to see how much crystalline material was present in a sample at room temperature and to assess the melting/dissolution temperature of the crystals in the bulk liquid. This temperature defines the minimum temperature that the sample must be heated to obtain a truly representative sample for various analytical tests and avoid segregation problems from settling of the crystals during quiescent storage.

3.2.2 Detailed Analytical Testing

Samples passing the preliminary testing were also evaluated by elemental analysis, density or specific gravity (ASTM D-71), and QI content (ASTM D-2318). The elemental analysis (C,H,N) was obtained using a Leco CHN instrument. A Leco SC132 instrument was used to measure the sulfur content.

3.3 Analytical Testing of Pitch and Mesophase Products

Mettler softening points and MCC values were determined for various pitch products. For the mesophase pitches, mesophase contents were estimated from polarized light photomicrographs on annealed samples or by hot-stage microscopy.⁽⁶⁾

Number average molecular weights for some tar and pitch samples were measured for pyridine solutions using vapor phase osmometry (VPO). Molecular weight distributions were measured for mesophase pitches using laser desorption ionization mass spectrometry. The data were obtained for us by Dr. M. Biers at the Carnegie Mellon University. The details of the technique are discussed in Section 4.9.

3.4 Lab-Scale Autoclave Assembly for Pressure Heat Treating

A one-liter Parr Model 4601 stainless steel autoclave was used to carry out the screening kinetics studies. It is equipped with a high-pressure nitrogen gas inlet, a manually controlled gas release valve and standard emergency pressure relief devices. Small samples (5-10 g) of the distillate materials were contained in several individual test tubes inserted into holes in a specially machined aluminum block fixture which was inserted into the autoclave. The temperature of the aluminum block, which maintains excellent temperature uniformity and conducts heat quickly, was monitored continuously with a thermocouple, along with other control thermocouples in the electrically heated furnace. The furnace set point temperature is controlled manually.

A nitrogen gas pressure of 100 psig was applied at room temperature and the autoclave was heated as rapidly as possible (approximately 2 hours) to the desired sample temperature. Gas pressure was controlled manually in the 95-105 psig range throughout the heating phase of the run. At the end of the hold period, the entire autoclave was removed from the furnace to quench the reactions as quickly as possible. The gas relief valve was closed during the cool-down period until the sample temperature reached approximately 200 °C where the residual gas pressure was vented very slowly to ambient pressure. This procedure avoids accidental foaming of the samples and ensures good yield measurements.

The pilot-scale pressure heat treatments were performed in an autoclave system with dimensions of 29.8 cm I.D. by 144.8 cm inside length. The autoclave is capable of 1500 psig pressure and up to 600 °C operating temperature. The temperature can be computer controlled for a pre-determined ramping rate, final hold temperature and hold time. Gas pressure was maintained during a run with an automatic pressure control system. The pressure heat treatments were carried out on material contained in a covered stainless steel can with a capacity of about 4 liters. The can was partially filled with approximately 1550 g of coal tar distillate.

3.6 Laboratory Distillation of Tar to Pitch

The pressure heat-treated coal tar distillates (CTD) were converted to pitches with different softening points by distillation. The distillation was performed in resin flasks using inert argon gas sparge. Final temperatures were kept below 350 °C to minimize further reaction. In the initial distillations, 1000 g of tar was converted to 120-130 °C SP pitch. This product was then used as a precursor for higher SP pitches for use in solvent extraction. The same gas sparging system was used to produce the higher SP pitches.

3.7 Preparation of Mesophase Pitch by Extraction

We initially used small-scale solvent extraction with toluene to determine the conditions for obtaining mesophase from the high SP pitches.

The extractions were carried out by stirring 25 g of the powdered pitch with 500 ml of toluene for a period of about 3 hours. The mixture was then filtered through a Buchner funnel using filter paper. The collected solid was dried at 75 °C under vacuum to effect removal of toluene solvent. The toluene insolubles were examined by hot-stage microscopy and annealed at 350-400 °C for examination by polarized light microscopy.

The extractions were performed using toluene at both room temperature and 75 °C. A single extraction was tried using toluene near its boiling point in a Soxhlet extractor to investigate the fusibility of the TI fraction.

Once these small-scale scoping studies were completed, larger-scale extractions were performed using 50 g of pitch in 1000 ml of toluene. Following extraction, the insolubles were heated under nitrogen with stirring to 350-360 °C to remove residual solvent and to homogenize the mesophase pitch.

3.8 Preparation of Mesophase Pitch by Thermal Conversion

The thermal transformations of isotropic pitch to mesophase were carried out in a specially designed lab-scale reactor using ~200 g quantity of starting material. The reactions were performed at temperatures of 390-400 °C with nitrogen gas sparging using published procedures.⁽³⁾

3.9 Exploratory Preparation of Mesophase-Derived Carbon Foam

About 10 g samples of mesophase pitch prepared from the solvent extraction method and by thermal conversion, as described in Section 3.7 and 3.8, were used to explore the preparation

of carbon foam. The foaming experiments were performed by first compressing the mesophase pitch into a dense pellet and then heating the pitch to 550 °C in a specially designed laboratory-scale container followed by a 30-minute hold at the 550 °C temperature. Argon was used before the heat up and at cool down to prevent oxidation.

4. RESULTS AND DISCUSSION

4.1 Analysis of Koppers and Reilly Coal Tar Distillate Samples

4.1.1 Results on Early Koppers and Reilly Samples

TGA results on the first set of samples showed that they contained a large amount of low boiling material and not enough of the desired high boiling material that is typical of heavy creosote oil. The MCC values were also very low and fairly large quantities of crystalline material were present in the samples at room temperature, probably mostly naphthalenes and anthracenes.

These results were reviewed with Koppers and Reilly representatives and both of them provided subsequent samples that came closer to the desired high boiling range typical of heavy creosote oil.

4.1.2 Results of Subsequent Koppers and Reilly Samples

(a) TGA and MCC Results

The pinhole TGA curve for the Koppers Heavy Creosote Oil from their Chicago plant is shown in Figure 2. The extrapolated onset and endset temperatures of 312° and 419 °C, respectively, are acceptable, although a higher onset temperature might be preferable to give a somewhat higher yield after heat treatment. Approximately 98% of the sample had volatilized by 450 °C. This is consistent with the 1.2% MCC value measured for this material.

Figure 2: TGA Koppers Heavy Creosote Oil

The pinhole TGA curve for the Reilly Heavy Oil sample from their Lone Star plant is shown in Figure 3. The extrapolated onset and endset temperatures are 258° and 365 °C, respectively, indicating that this material has considerably more low and intermediate boiling range material than the Koppers Heavy Creosote oil sample. Approximately 95% of this sample had volatilized by 450 °C, so it contains slightly more very high boiling material than the Koppers sample. The higher TGA residue is also consistent with the slightly higher MCC value of 1.5% for this Reilly material.

Both distillates were evaluated in the lab-scale heat treatment testing program described below.

Figure 3: TGA Reilly Heavy Oil

A pinhole TGA run was also made on a standard 110 °C Mettler SP coal tar binder pitch from Koppers for comparison. The TGA curve is shown in Figure 4. The extrapolated onset temperature of 329 °C is considerably higher than those for either of the distillate materials, as one would expect. The 63% residue yield after 500 °C is also consistent with expectations for a pitch under these conditions.

Figure 4: TGA Koppers 110 °C Coal Tar Binder Pitch

Elemental analyses were obtained for the second Koppers coal tar distillate material. The results were: C=92.3%, H=5.44%, S=0.58% and N=1.03%. The atomic C/H ratio was 1.42.

4.2 Soaking Volume Factor Calculations for Heat Treatment Severity

Finding a method or parameter to characterize the relative heat treatment severity of a given batch or continuous heat treatment is a long standing problem dating back to the original development of large-scale continuous thermal cracking processes in the early days of petroleum refining. One approach originally introduced to address this issue in gas-phase thermal cracking was the ‘Soaking Factor’ concept.⁽⁷⁾ Complete application of the method employs corrections for effect of pressure drop in the tubestill on the gas phase density, effects of temperature on both gas density and reaction rate as the feedstock passes through the tubestill, flow rate or residence time, etc. In essence, the method is a numerical summation of the extent of reaction experienced by the feedstock as it moves through each incremental element of the tubestill.

Our primary interest here is a considerably simpler problem where thermal reactions, both cracking and polymerization, are taking place in a batch process at a high enough pressure to keep most of the feedstock in a liquid state. Hence, there is no need to apply any gas or liquid phase density corrections because the entire sample volume experiences essentially identical heat treatment severity. This reduces the calculation to a numerical summation of the relative reaction rate at the sample temperature times a time increment for the entire run. The temperature dependence of the reaction rate was calculated from an Arrhenius equation fitting (assumes first

order kinetics) of the raw data given in the literature (Table 19-18 of reference 7). The resulting equation has an Arrhenius activation energy of 46.5 kcal/mole which is consistent with results for polymerization and cracking of various hydrocarbon feedstocks. Since we are only interested in a relative measure of heat treatment severity, we followed the literature approach and assigned the reaction rate at 800 °F (427 °C) a value of 1.0. We also adopted the literature approach and assigned a soaking factor value of 1.0 for hold period of 4.28 hours at 800 °F. We called the factor calculated on this basis for batch heat treatments a “Soaking Volume Factor” or SVF to differentiate it from the full-blown density corrected calculation used for a continuous thermal cracking process. The final mathematical equation used to calculate our SVF values is shown below.

$$SVF = \sum_i (kT / k800_i) \times \Delta t / 4.28$$

where $kT/k800_i$ is the relative reaction rate and Δt is the time interval in hours.

SVF calculations for “ideal” heat treatments, where the heat up and cool-down are infinitely fast, at 430-440 °C are summarized below in Table I.

Table I
Summary of SVF Calculations for Ideal Heat Treatments for 5 Hours

Sample Temperature °C	Calculated SVF
430	1.37
435	1.74
440	2.19

The SVF approach was applied to the two small-scale Parr autoclave heat treatments and some of the pilot-scale autoclave heat treatments which will be described in subsequent sections of this report.

4.3 Lab-Scale Pressure Heat Treatment of Koppers and Reilly Coal Tar Distillates

The first Parr autoclave run was carried out at 430 °C at 100 psig nitrogen for a nominal hold period of 5 hours with two test tube samples each of the Koppers Heavy Creosote Oil and Reilly Heavy Oil samples. The calculated SVF for this run from the sample temperature versus time data was 1.43. This is slightly higher than the value of 1.37 for the “ideal” heat treatment at 430°C; the difference in the SVF values of 0.06 reflects the small contribution from the relatively rapid heat-up and cool-down rates in this small-scale equipment. Product tar yields were 95.7% and 93.3% for the Koppers material and 83.7% and 82.2% for the Reilly material. The good agreement for the yield data for these small 5-7 g samples for a given feedstock indicates that the overall heat treatment severity and experimental procedure were well controlled. Average yield data and the screening characterization results for this Parr autoclave run are summarized in Table II below.

Table II
Summary of Yield and Characterization Results
on Products from 430 °C Parr Autoclave Run

Sample	Average Yield, %	MCC, %	Hot-Stage Microscopy
Koppers Heavy Creosote Oil	94.5	17.0	No mesophase
Reilly Heavy Oil	82.9	16.4	No mesophase

The results show that the MCCs of both coal tar distillates were increased substantially from their original values of 1-1.5% up to 16-17% by the heat treatment at 430 °C for 5 hours. Both heat-treated tars were also free of any mesophase. Therefore, a second heat treatment was carried out at a higher temperature to see if the MCC coking value could be increased further without making mesophase.

The second Parr autoclave run was carried out at 440 °C at 100 psig nitrogen pressure for a nominal hold period of 5 hours with two test tube samples of the Koppers material and 3 test-tube samples of the Reilly material. The calculated SVF from the temperature versus time data for this run was 2.40. This is somewhat higher than the value of 2.19 for the “ideal” run with 5 hours at 440 °C. Again, the difference of 0.21 reflects the contribution from the heat-up and cool-down portions of the overall heat treatment. Product tar yields were 93.5% and 91.9% for the Koppers material and 81.5%, 82.8%, and 80.5% for the Reilly material. The good agreement in the yield results for a given feedstock indicates that this Parr autoclave heat treatment experiment was also well controlled. Average yield data and limited characterization results are summarized below in Table III.

Table III
Summary of Yield and Characterization Data on Products
from 440 °C Parr Autoclave Run

Sample	Average Yield, %	MCC, %	Hot-Stage Microscopy
Koppers Heavy Creosote Oil	92.7	24.9	Some mesophase
Reilly Heavy Oil	81.6	23.2	Some mesophase

The results in Table III show that the increased heat treatment temperature did produce a greater increase in the MCC coking values of both materials, but both heat-treated tars were found to have a low concentration of mesophase in the hot-stage microscopy examinations. Hence, the heat treatment severity in the 440 °C-5 hour run was slightly too high for both of these coal tar distillates.

The coking value and mesophase formation response of both feedstocks were amazingly similar in both of the Parr heat treatment experiments, despite their somewhat different origins and boiling ranges. However, the yield of heat-treated tar was significantly lower for the Reilly Heavy Oil, almost certainly due to its higher concentration of low and medium boiling components. This was evident in the TGA curve for this material which was presented previously. Therefore, the Koppers Heavy Creosote Oil was selected for the pilot-scale work based on the anticipated higher product yield which would improve the overall process economics.

Based on the results of these Parr autoclave experiments, nominal heat treatment conditions of 430°-435 °C for 5 hours at 100 psig were selected as the initial target for the pilot-scale runs.

4.4 Pilot-Scale Pressure Heat Treatment of Koppers CTD

A typical pressure heat treatment temperature and pressure plot as a function of time is shown in Figure 5 for the first pilot-scale pressure heat treatment run.

Figure 5: Temperature and Pressure vs. Time for First Pilot-Scale Run

The first pilot-scale run at a nominal “external” temperature of 435 °C, where the thermocouple was located on the external skin of the can, was carried out with two loosely covered cans containing approximately 1500 g each of the Koppers Heavy Creosote Oil stacked vertically in the autoclave. The product tar yields were 92.3% for Can #1 which was on the top and 94.0% for Can #2 which was on the bottom. Surprisingly, the average MCC value for Can #1 was quite low, 11.9%, while that for Can #2 was 19.2% which is in the expected range. Subsequent investigation found that Can #1 was positioned partially out of the uniform temperature hot zone of this autoclave and did not receive the same heat treatment severity as Can #2. No further characterization work has been carried out on the Can #1 tar product, due to its ill-defined heat treatment conditions. The product tar from Can #2 was used for the pitch production experiments described in the next section. The temperature uniformity issue was avoided in subsequent runs by limiting the sample size to one can only located in the known hot zone of the autoclave.

Hot-stage microscopy examinations of the product tars from both Cans #1 and #2 from the first pilot-scale pressure heat treatment showed them to be free of mesophase when they were heated rapidly to 400 °C. This is consistent with the MCC values for these materials and the results obtained in the lab-scale heat treatments experiments described earlier.

The product tar yield was 84.5% for the single can used in the second pilot-scale pressure heat treatment run which was made at a higher nominal average external product temperature of 441 °C. This is considerably lower than the 94.5% yield for the first run made at the lower 435 °C temperature. The average MCC of the product tar was 24.5% which is considerably higher than that for the first run at 435 °C. As expected, hot-stage microscopy showed that the tar from the second run at 441 °C had a significant concentration (1-5%) of mesophase spheres. No additional work was carried out on this material.

The third run was carried out at a lower external product temperature (431 °C) to avoid mesophase formation. The product tar yield was 95.8% and the average MCC was 14.3%. A hot-stage microscopy examination of this material showed that it contained no mesophase. This material was deemed acceptable for further characterization and conversion to pitch.

Two additional pilot-scale pressure heat treatments, PHT-4 and PHT-5, were carried out on the CTD in order to provide more material for mesophase pitch preparations. MCC values were determined for the derived tar products and they were also examined by hot-stage microscopy for the presence of mesophase. The results for these five runs are summarized in Table IV.

Table IV
Summary of Pilot-Scale Pressure Heat Treatment Runs PHT-1 to PHT-5

Run No.	Estimated External Prod. Temp, °C	Yield, Wt %	MCC, Wt %	Mesophase Content, Vol. %
PHT-1, #2	435	94.0	19.2	0
PHT-2	441	84.5	24.5	1-5
PHT-3	431	95.8	14.3	0
PHT-4	434	92.7	20.4	0
PHT-5	432	90.5	22.1	0

The tar products from PHT-4 and 5 had MCC values of 20-22% which appear to be the maximum we can achieve with this CTD feedstock in our currently configured pressure treating system without developing mesophase. The results of examination of the treated materials for the presence of solids or mesophase will be discussed in a later section.

Two additional pilot-scale pressure heat treatment runs, PHT-6 and PHT-7, were carried out after relocating the product thermocouple to an interior location in the approximate middle of the liquid sample. This thermocouple location should be a much better measure of the actual average temperature of the bulk liquid sample in the can. These runs also provided additional material for production of pitches. The results from these runs are summarized below in Table V. SVF values were calculated from the temperature versus time data for these runs because the recorded temperatures were more representative of the actual sample temperature.

Summary of Pilot-Scale Pressure Heat Treatment Runs PHT-6 to PHT-7

Run No.	Internal Product Temp, °C	Yield, Wt %	MCC, Wt %	SVF	Mesophase Content, Vol. %
PHT-6	430-435 (7 hr. hold)	90.5	23.4	2.43	1-5
PHT-7	430-435 (5.25 hr. hold)	95.0	19.1	1.87	0

The overall heat treatment severity for run PHT-6 was too high, primarily due to the longer 7-hour hold period at 430-435 °C. The calculated total SVF was 2.43 which is comparable to the 2.40 value calculated for the 5 hour-440 °C Parr autoclave heat treatment. The high MCC value and the presence of a significant amount of mesophase are also consistent with this high level of heat treatment severity. Interestingly, examination of the details of the SVF calculations shows that the heat-up portion of this run contributed 0.18 to the total SVF and the cool-down period contributed 0.19. These values are much higher than those for the corresponding small-scale Parr autoclave heat treatments because the heat-up and cool-down rates are considerably slower for the larger scale pilot plant equipment. The SVF methodology gives us at least a semi-quantitative approach to assess the effects from the differences in the heat-up and cool-down rates in the small-scale and pilot-scale equipment.

Run PHT-7 had a similar heating and cooling schedule curve as PHT-6, except that the hold period was reduced to 5.25 hours in an attempt to reduce the total SVF to a target value of about 1.75. In fact, the sample temperature was a little bit higher than desired in a portion of the hold period, so the actual SVF of 1.87 was slightly high. However, the MCC value is acceptable and there was no mesophase in the product tar, so this tar should be acceptable for conversion to pitches.

It should be noted that the optimum batch heat treatment conditions, 5 hours at ~435 °C, give an SVF of about 1.8. This is significantly higher than the 1.2 value which has been reported for continuous thermal cracking of petroleum feedstocks.⁽⁷⁾ The extremely refractory nature of this high boiling CTD is the reason for the greater required heat treatment severity.

4.4.1 Filtration of Pressure Heat Treated Tars

In the course of examining some of the pitches prepared by distillation of the pressure treated coal tar distillate by hot-stage microscopy, the presence of some very small solid particulates was observed. These particles appeared as very small “pinpricks” which were not deformable at ~400 °C when observed by polarized light at 100X on the hot stage, suggesting that they were some type of birefringent carbonaceous solid.

A portion of a pitch prepared from PHT-1 was examined by the conventional metallographic method so that these particles could be examined at much higher magnification (750X) in both polarized light and bright field to obtain more information on their structure and origin. The particles were found to be 1-4 micron diameter birefringent spheres with multiple extinction contours within their boundaries. The concentration of these solids in this pitch was well below 1%. They can be described as

either undeformable mesophase or “semicoke” spheres. Unfortunately, they could affect spinnability and/or carbon fiber properties if they were still present as discrete particles after the isotropic pitch is converted to a mesophase pitch. It was not evident whether these particles originated in the original coal tar distillate or were generated during our processing. Therefore, small portions of several of the thermal tar products from both the lab-scale Parr autoclave and the pilot-scale pressure heat treatments were converted to “pitches” by heating to 350 °C in a ceramic boat in a tube furnace to remove the most volatile components. These pitches were then examined at high magnification by the conventional metallographic method in an attempt to identify the origin of these carbonaceous particles. Unfortunately, all of these pitches were too soft to be polished without considerable smearing and the concentration of the particles was too low to enable us to identify their origin with certainty.

Examination of the two annealed extract samples described later by conventional microscopy showed that they contained large “metallic” appearing particles with sizes on the order of several hundred microns. The same large metallic particles were also detected in the pitches from the conversion of the pilot-scale pressure heat treated tars, but they were absent in the pitch derived from the tar produced in the laboratory-scale Parr autoclave using glass test tubes. Observations using SEM-EDX identified these metallic particles as being high in both iron and sulfur, presumably some form of iron sulfide. It is most likely that they originate from a corrosive attack by the coal tar distillate on the standard carbon steel containers used in the pressure heat treatments. Coal tar products are known to have acidic components, as well as various sulfur-containing constituents, and such species could attack carbon steel at high temperatures. The problem can be avoided easily in any future work by using stainless steel cans instead of carbon steel containers.

Since both the large metallic and very small carbonaceous solids could adversely affect the mesophase quality, we decided to attempt to remove them by filtration. The tar products from PHT-2, PHT-4, PHT-5, PHT-6 and PHT-7 were filtered through a fritted glass funnel with a pore size of about 10-15 microns. The tars were heated to about 100-120 °C in order to reduce their viscosity prior to filtration and the filter funnel was heated using heating tape. After filtration, examination of the tars by hot-stage microscopy showed that the concentration of both carbonaceous and metallic solid contaminants had been reduced substantially. However, there was still a significant concentration of the small normal mesophase spheres in the tars from the more severe heat treatments. Apparently, the smallest mesophase spheres in these tars could pass through the pores in the glass frit. Filtration was employed prior to conversion of the tars to pitches for all of the later pilot-scale heat treatments.

4.5 Distillation of Tars to Isotropic Precursor Pitches

4.5.1 Pitches From Tar PHT-1

The tar obtained from the first pressure heat treatment (PHT-1), was initially distilled to a 128 °C SP pitch. This pitch was to be used as the precursor for higher SP pitches for scoping experiments for the solvent extraction route to mesophase. The objective was to establish the requirements for achieving an isotropic pitch which would provide an acceptable yield of mesophase using toluene as a solvent. Toluene was

deemed to be the most practical and economical of the solvents which can dissolve appreciable amounts of the polynuclear aromatic components of pitch. 108

Properties of this pitch (13-22) are presented in Table VI along with those obtained for the precursor CTD. As expected, the aromaticity and average molecular weight have increased considerably as a result of the pressure heat treatment and distillation processes.

Table VI
Properties of Koppers Coal Tar Distillate and Derived 128 °C SP Pitch

Test	Koppers Coal Tar Distillate	Pitch 684-13-22
C, %	92.3	92.7
H, %	5.44	4.59
Atomic C/H Ratio	1.43	1.70
N, %	1.03	1.13
S, %	0.58	0.44
MCC, %	1.2	61.4
RT Density, g/cc	1.16	NM
QI, %	0.0	NM
TI, %	NM	15.5
Number Average Molecular Wt. (VPO)	163	304

In a second distillation, the 128 °C SP pitch was used to prepare smaller quantities (~50 g) of higher SP pitches with softening points ranging up to 220 °C. The pitch yields and softening points for the various products are summarized in Table VII. The pitch yields are based on the original Koppers Coal Tar Distillate

Table VII
Pitches From Distillation of Pressure Treated CTD – PHT-1

Pitch ID Number	Overall Yield , Wt %	SP , °C
13-22	32.1	128.5
13-38	26.1	164.9
13-50	23.6	187.2
13-52	22.8	194.0
13-54	19.7	204.2
13-81	17.9	220.6

The pitch softening points are directly related to the amount of distillate removed. This conclusion is apparent from Figure 6, where the pitch softening point is plotted versus yield. The filled squares represent the data from Table VII.

Figure 6: SP vs. Yield for Pitches from Distillation of PHT-1 (Can #2)

4.5.2 Pitch From Tar PHT-3

In order to obtain more pitch material, we also performed a distillation on the tar product from PHT-3. As seen in Table IV, this material was less severely treated and had a lower MCC value than the tar from PHT-1. The tar was distilled to produce about 350 g of pitch (13-77) with a softening point of 132 °C. The pitch yield was 26.1%. The red diamond-shaped symbol in Figure 6 represents the data point for this pitch and, as can be seen, it deviates from the plot of the pitches derived from the PHT-1 (#2) tar. The pitch yield is evidently related to the severity of the thermal treatment in conversion of CTD to tar.

The 132 °C SP pitch (13-77) was used as a precursor for the thermal mesophase pitch and also used for assessing the potential mesophase domain size.

4.5.3 Pitches From Filtered Tar

The tars from PHT-4 and PHT-5 which had been filtered to remove any solids, were combined and distilled to produce a solids-free pitch (15-13) with an SP of 129 °C. The pitch obtained in a 38% yield (35% from the original CTD) was then used for larger scale preparation of thermal and extracted mesophase pitch..

A 420 g portion of the (15-13) pitch was further distilled to produce a high SP pitch with a softening point of 222 °C in a yield of 63% (22% based on the original CTD). This high SP pitch(15-29) was used to produce extracted mesophase pitch.

4.6 Mesophase Domain Size Determinations

We used the pitches produced by direct distillation of the pressure heat treated CTD to obtain measurements of the mesophase domain size. Our mesophase domain size procedure, which is described in a previous publication⁽⁸⁾, is designed to evaluate the potential mesophase domain size capability for a carbon precursor. The method involves heat treating the material to

produce ~30-50% mesophase, followed by an annealing step at 400 °C to coalesce and anneal the mesophase. After cooling to room temperature, the annealed pitch is encapsulated in epoxy and polished by standard metallographic procedures to enable measurements of its mesophase domain size using polarized light microscopy and an image analysis method.

This procedure was employed using the two pitches (13-77) and (15-13) as starting materials. These represent the ~130 °C SP products produced from unfiltered and filtered tar. The average domain size determined for the mesophase from (13-77, unfiltered) was 169 microns, while that for the mesophase from (15-13, filtered) was 188 microns. These values are consistent with those for a fiber quality mesophase⁽⁹⁾. The slightly lower value for the pitch from unfiltered tar probably reflects the effects of the small amount of solids inhibiting coalescence. Shown in Figure 7 are photomicrographs taken in bright field and polarized light for mesophase from (13-77). Similar photomicrographs for the mesophase from (15-13) are presented in Figure 8.

Figure 7a: Mesophase Derived from CTD (Unfiltered Tar), Polarized Light

Figure 7b: Mesophase from CTD (Unfiltered Tar), Bright Field.
Finely divided solids are concentrated at the mesophase-isotropic phase boundary

Figure 8a: Mesophase Derived from CTD (Filtered Tar), Polarized Light

Figure 8b: Mesophase Derived from CTD (Filtered Tar), Bright Field

4.7 Thermally Produced Mesophase Pitch

Mesophase pitches were prepared using direct thermal treatment of isotropic pitches from the distillation of the heat-treated coal tar distillate. The process involves heat treating at a high enough temperature to effect chemical polymerization while sparging with an inert gas to remove the low molecular weight species and reaction by-products.⁽³⁾ In a first trial, the unfiltered 132 °C SP pitch(13-77) was used as the starting material and heat treated in a reaction vessel for 24 hours at 390 °C to produce a product with a softening point of 338 °C. The mesophase pitch yield was 53%, based on the precursor isotropic pitch. Shown in Figure 9a is a polarized light photomicrograph of the annealed mesophase pitch (13-84). The anisotropic mesophase is the continuous phase with small spherical isotropic regions uniformly distributed throughout the bulk coalesced mesophase. The mesophase content is estimated at about 75%. This appearance is typical for pitches suitable for fiber spinning in that the rheology is controlled by the continuous mesophase and the material does not undergo significant phase separation at

spinning temperatures⁽⁵⁾. In contrast, Figure 9b shows the appearance of mesophase pitch with a lower mesophase content (~50%) which exhibits phase separation and is unsuitable for production of carbon fibers.

Figure 9a: Thermal Mesophase Pitch (13-84), 338 °C SP, 75% Mesophase

Figure 9b: Segregated 2-Phase Mesophase Pitch, ~50% Mesophase

A second thermal mesophase pitch was prepared using the 129 °C SP pitch obtained from distillation of the filtered thermal tar (Sect.4.5.3). The heat treatment was increased to 26 hours at 390 °C followed by 2 hours at 400 °C. About 180 g of mesophase pitch product (15-35) was obtained in a yield of 53%. The mesophase pitch softening point was 343 °C. From examination of the mesophase pitch by polarized light microscopy, the mesophase content was estimated as 85%. A polarized light photomicrograph of the annealed mesophase pitch is shown in Figure 10.

Figure 10: Thermal Mesophase Pitch (15-35), 343 °C, 85% Mesophase

This mesophase pitch appears to be an acceptable precursor for products such as high performance carbon fibers and carbon foam. In order to obtain more detailed information about the processability of the material, particularly for fiber spinning, we measured its viscosity versus temperature. Shown in Figure 11 is a plot of viscosity versus temperature for the (15-35) thermal mesophase pitch. An activation energy plot of log viscosity versus $1/T(K)$ is presented in Figure 12. An activation energy of 24.2 kcal/mole was calculated from this plot.

Figure 11: Viscosity vs. Temperature for Thermal Mesophase Pitch (15-35)

Figure 12: Viscosity vs. $1/T(K)$ for Thermal Mesophase Pitch (15-35)

4.8.1 Small-Scale Extractions of 204 °C SP Pitch (13-54)

We performed some initial small-scale toluene extractions with the 204 °C SP pitch (13-54) in order to determine the quantity of low molecular weight components that need to be removed in order to develop mesophase. Examination of the original pitch by hot-stage microscopy showed that it was completely isotropic. Extractions were performed with toluene at room temperature and with heated toluene at 75 °C. The room temperature extracted residue was re-extracted a second time with toluene at room temperature in order to determine if more material could be removed using the fixed ratio of 25 g solid to 500 ml of solvent. The extraction residues were screened initially by hot-stage microscopy to obtain a quick estimate of mesophase content and viscosity. They were also annealed by heating at 350 °C and examined by conventional optical microscopy to determine the amount of mesophase more accurately. The hot toluene extract residue was also annealed at 400 °C. The results are summarized in Table VIII.

Table VIII
Yields and Mesophase Contents from Toluene Extraction of Pitch (13-54)

Treatment	Yield, Wt. %	Estimated Mesophase Content, Vol.%
1x at 25 °C	64	10-20
2x at 25 °C	50	40-50
1x at 75 °C*	45	70-80
1x at 75 °C**	44	90-95

*Annealed at 350 °C, **Annealed at 400 °C

The results in Table VIII show how sensitive the mesophase concentration is to the amount of low molecular weight material removed. At least 45% removal is required in order to obtain > 80% mesophase from the 204 °C SP pitch. The hot toluene extraction residue gave an ~ 70-80% anisotropic phase content after being annealed at 350 °C. When the same material was annealed at 400 °C, the mesophase content increased to a value of over 90% as a result of only an additional 1% weight loss. The mesophase derived from the pitch extraction exhibited a very large average domain size. A polarized light photomicrograph for the mesophase from the 1X cold toluene extraction is shown in Figure 13. Figure 14 presents a photomicrograph of the mesophase from the pitch extracted with toluene at 75 °C. The insolubles from the hot toluene extraction, after annealing at 350 °C to remove any residual solvent, gave a Mettler softening point of 357 °C.

Figure 13: Polarized Light Photomicrograph of Mesophase from 1X Toluene Extraction of 204 °C SP Pitch(13-54)

Figure 14: Polarized Light Photomicrograph of (400 °C) Annealed Mesophase from Hot Toluene Extraction of 204 °C SP Pitch (13-54)

We also performed an exhaustive extraction of the (13-54) pitch with near boiling toluene using 1 g of pitch in a micro-Soxhlet apparatus. The objective was to see whether this material would still soften when heat treated. We were not able to obtain an accurate yield of the insolubles from this extraction, due to leaching of material into and out of the thimble. We could not detect softening of this toluene insoluble material when examined on by hot-stage microscopy, but when it was heat treated rapidly to 500 °C in an inert

atmosphere, it did fuse to give a coke-like product. A polarized light photomicrograph of the 500 °C residue is shown in Figure 15. As expected, it is 100% anisotropic. The large anisotropic domain size shows that this material would provide a needle coke.

Figure 15: Polarized Light Photomicrograph of Soxhlet Extracted TI Heated to 500 °C.

4.8.2 Toluene Extractions of 222 °C SP Pitch (15-29)

Following the initial work described previously, we continued the solvent extraction experiments using the 222 °C SP pitch (15-29) which had been prepared from the filtered tar. Some small-scale extractions similar to those presented above in Table VIII were performed. The insolubles were examined by both hot-stage microscopy and conventional optical microscopy and the results are summarized in Table IX.

Table IX
Toluene Extractions of 222 °C SP Pitch (15-29)

Treatment	Yield%	Microscopy Observations
1X Toluene, 25 °C	65	~50% mesophase, segregated isotropic
2X Toluene, 25 °C	61	80% mesophase determined on an annealed sample
Toluene, 75 °C	55	>90% mesophase, very viscous

We then extracted 150 g of the precursor (15-29) pitch two times with toluene at 25 °C in order to obtain sufficient extracted mesophase pitch for characterization and for foaming experiments. We obtained a 61% yield of product which was then heat treated with stirring in an inert atmosphere to remove residual solvent and effect homogenization. The Mettler softening point of the material was measured as 342 °C.

A conventional optical microscopy examination of the homogenized product showed that it was predominantly mesophase with a relatively uniform and very small domain size because the material had been stirred vigorously during the cool-down. Unfortunately, the high agitation level also precluded making a determination of the isotropic phase content in this sample because any isotropic phase regions would have been too small to be detected visually. However, small inclusions of material that was too viscous to be incorporated in the bulk mesophase during the homogenization were clearly evident. An example of a high viscosity inclusion particle is shown below in Figure 16.

Figure 16: Polarized Light Micrograph at 200X Showing Viscous Inclusion Particle in Bulk Mesophase in Homogenized 2X Toluene Extract Pitch

The presence of these high viscosity inclusions probably precludes spinning this pitch into fibers, but it should not be a significant problem for use as a carbon foam precursor.

Portions of the exudates from the Mettler Softening Point measurement of the 2X Toluene Extract pitch were also examined by conventional optical microscopy. Both transverse and longitudinal sections of the exudates were examined. In both sections, the mesophase domain size was somewhat larger than that in the homogenized sample because the mesophase in the exudates annealed to some extent during the cool-down. There was also more extensive separation of the isotropic and mesophase portions of this pitch during the cool-down and a low concentration of isotropic phase pockets could be seen dispersed in the bulk mesophase in some areas, as shown below in Figure 17.

Figure 17: Polarized Light Micrograph at 750X Showing a Region with a Significant Concentration of Very Small Isotropic Phase Pockets in the 2X Toluene Extract Pitch

The overall isotropic phase content in this pitch from examination of all of the partially annealed exudate particles appeared to be approximately 10%.

4.9 Molecular Weight Analysis For Precursor and Mesophase Pitches

We obtained molecular weight composition data for the thermal and solvent extracted mesophase pitches and their pitch precursors. The measurements were made using Laser Desorption Ionization Mass Spectrometry (LDIMS) and were performed for us by Dr. Mark Bier of Carnegie Mellon University. The equipment and procedures have been described by him in a previous publication⁽¹⁰⁾.

Shown in Figure 18 are the LDIMS results for the precursor 128 °C SP pitch (15-13) prepared by distillation of the tar from pressure heat-treated coal tar distillate. Molecular composition data cover the mass range of 200-1500 (Figure 18a) and in a separate plot in the narrower molecular weight range of 200-600 (Figure 18b). It is apparent that the largest number of components are concentrated in this latter lower molecular weight region. It should be emphasized however, that the mass spectrometry technique really presents a number average molecular composition. Therefore, very high molecular weight species which could constitute a significant weight fraction of the pitch, would represent a very small fraction in a number average measurement.

The molecular weights identified for the components in the 128 °C SP pitch represent aromatics containing from about 4-9 condensed rings. For example the 217 peak could be assigned to amino-pyrene while the largest peak at mass 252 could be assigned to benzo-pyrene. Other major peak assignments can be made to mass 376(C₃₀H₁₆), tribenzoperylene, and mass 426(C₃₄H₁₈), diperinaphthylene-anthracene⁽¹¹⁾.

Figure 18a: Mass Spectrum of 128 °C SP Pitch (15-13)
(Molecular Weight Range 100-1500 Daltons)

Figure 18b: Mass Spectrum of 128 °C SP Pitch (15-13)
(Molecular Weight Range 200-600 Daltons)

Shown in Figure 19 is the mass spectrum obtained for the 222 °C SP pitch (15-29) that was used to produce mesophase by solvent extraction. As can be seen, the 4 and 5 ring aromatics (MW 200-270) have all been removed in the distillation process used to transform the 128 °C SP pitch to this higher softening point material. It is now also apparent that after removal of these low molecular weight species, the very high molecular weight components with molecular weights up to ~1500 are becoming evident. These species which correspond to aromatics with up to 20 rings were evidently present in the thermal tar produced by pressure heat treatment of the CTD since all subsequent processing to the (15-29) pitch involved only physical distillation.

Figure 19: Mass Spectrum of 222 °C SP Pitch (15-29)
(Molecular Weight Range 200-1500 Daltons)

The mass spectrum obtained for the mesophase pitch produced by the thermal route is presented in Figure 20. The spectrum span includes the range from molecular weights 100 to 1500. When comparing the result with those in Figure 18 for the precursor isotropic pitch, it is evident that all of the components with molecular weights below 340 have been removed in the heat-treatment/sparging process used to produce mesophase. The spectra has the appearance of an oligomeric material with clusters of peaks corresponding to dimers, trimers, tetramers etc. of the monomeric species that were present in the precursor pitch. This result is more apparent in the condensed spectrum (MW 200-900) in Figure 21. Similar oligomeric molecular weight distributions have been reported in mesophase pitches prepared from model compounds⁽¹²⁾ and in petroleum-derived mesophase pitch.⁽¹³⁾

**Figure 20: Mass Spectrum of Thermally Produced Mesophase Pitch (15-35)
(Molecular Weight Range 100-1500 Daltons)**

**Figure 21: Mass Spectrum of Thermally Produced Mesophase Pitch (15-35)
(Molecular Weight Range 200-900 Daltons)**

In Figure 22, mass spectra data are presented for the mesophase pitch (15-68) prepared by solvent extraction. Again the oligomeric nature of the material is readily apparent. For the data in Figures 21 and 22, the mass spectra data have been normalized to the most intense peak at mass 426 which can be considered a dimer peak for the low molecular weight constituents in the precursor material. It thus might appear that the extracted pitch has more very high molecular weight components than the thermal mesophase pitch. However, when the spectra for the thermal and extracted mesophase pitches are both normalized to the 589 (trimer peak) as shown in Figure 23, this is not the case.

Figure 22a: Mass Spectrum for Solvent Extracted Mesophase Pitch (15-68)
(Molecular Weight Range 100-1500 Daltons)

Figure 22b: Mass Spectrum for Solvent Extracted Mesophase Pitch (15-68)
(Molecular Weight Range 200-900 Daltons)

**Figure 23a: Mass Spectrum for Thermal Mesophase Pitch (13-35)
Normalized to Mass 589 at Maximum Intensity**

**Figure 23b: Mass Spectrum of Solvent Extracted Mesophase Pitch (15-68)
Normalized to Mass 589 at Maximum Intensity**

The mass spectrometry data shed considerable light on the mesophase formation process. The solvent extracted mesophase pitch exhibits the presence of molecules with molecular weights ranging up to 1600. Since only physical processes of distillation and extraction were used to convert the CTD thermal tar to mesophase pitch, these high molecular weight species must have been formed during the pressure heat-treatment used to convert the original CTD to thermal tar. All the subsequent physical steps remove the low molecular weight “mesophase inhibiting” constituents to allow essentially complete mesophase development.

In the thermal process, additional chemical reaction is introduced during the prolonged heat treatment at 390-400 °C applied to the 128 °C SP pitch precursor. The largest difference in the molecular composition between the thermal and extracted mesophase pitches is the much higher prevalence of dimeric species (mass 400-500) in the thermal mesophase pitch. This confirms that the main reaction is the conversion of low molecular weight monomers to dimers during the thermal treatment. As seen by the results in Figure 23 the composition for the much higher molecular weight components is similar for the two pitches. These results are consistent with those published previously for molecular weight studies of mesophase pitch formation which showed that thermal reaction leads mainly to conversion of monomer to dimer components with significant further polymerization to higher molecular weight oligomers⁽¹⁴⁾.

The calculated mesophase pitch yield for the thermal pitch from the starting coal tar distillate was determined as 18.7% compared to only 13.4% for the extracted mesophase pitch. The reason for this significantly higher yield for the thermal mesophase is that only a portion of the low molecular weight monomer components are removed by the physical sparging process, while the remainder are transformed to dimers where they can become constituents of mesophase. In the extraction process, all these components are physically removed without any chance for reaction.

The procedures we used in the laboratory/pilot plant program to transform CTD to mesophase were all batch process steps which contributed to the over-all low yields. As stated earlier, it is obvious that in any commercial process a number of the unit steps would be done in a continuous mode where unreacted species could be recycled back into the process to maximize yield.

4.11 Preparation of Carbon Foam

We successfully produced some carbon foam material from both the extracted and thermal mesophase pitches. Due to the rapid heat up schedule used in the foam preparation, the resultant foams were low density <0.1 g/cc, and weak. Shown in Figure 24 are photographs of carbon foam products prepared from the thermal and solvent extracted mesophase pitches. Examination under polarized light (Figure 25) showed the foam cell wall structure to be completely anisotropic.

Figure 24a: Carbon Foam from Thermal CTD-Derived Mesophase Pitch

Figure 24b: Carbon Foam from Solvent Extracted CTD-Derived Mesophase Pitch

Figure 25: Polarized Light Photomicrograph of Foam from Thermal Mesophase Pitch

Coal tar distillate was shown to be an acceptable precursor for mesophase pitch suitable for producing high performance carbon products. The key initial step involves a pressure heat treatment for polymerizing the low molecular weight aromatic components to higher molecular weight oligomers capable of forming mesophase. For a commercial continuous process, it is necessary to carry out these reactions while maintaining a homogeneous liquid state free of solid mesophase and coke. Soaking volume factor calculations can be used to determine the best conditions for effecting these transformations.

Physical separation procedures of distillation and solvent extraction can then be used to concentrate the high molecular weight components and allow the formation of mesophase. Distillation to a high softening point pitch, followed by extraction with toluene, was shown to provide a route to mesophase which can be used to make conductive carbon foam. Mesophase content can be altered by choice of extraction conditions.

Higher mesophase pitch yields were obtained using the thermal route where an intermediate softening point pitch was heated treated at temperatures sufficient to effect thermal reaction. The thermal treatment can effectively polymerize low molecular weight monomeric components of the pitch into dimers capable of incorporating into the mesophase. Viscosity versus temperature measurements for the thermal mesophase pitch show that it is suitable for spinning fibers. It attains a viscosity which is suitable for spinning (~200 poise) below reaction temperature.⁽¹⁵⁾

The key requirements of large anisotropic domain size, continuous anisotropic phase, and acceptable viscosity were demonstrated for the coal tar distillate-derived mesophase pitches produced in this program. However, it is likely that mesophase properties can be improved even further by more careful selection of the CTD precursor. The CTD-derived mesophase pitch appears to be more thermally stable than petroleum-derived mesophase as evidenced by the very long heat treatment and sparge times for thermal conversion to >80% mesophase. This could be an advantage for carbon fibers where thermal stability is required to achieve long periods of continuous spinning. This factor likely results from the absence of activating side chains in the CTD derived mesophase. CTD mesophase is also expected to be somewhat more graphitizable than petroleum mesophase as a result of absence of side chains. However, other fiber processes such as rapid thermosetting could be more difficult. The coal tar distillate used in this program was a commercial heavy creosote oil with a rather wide boiling range. Narrowing the composition could remove more reactive components and lead to mesophase pitches with even lower viscosities than those achieved in this program. Our program was not designed to provide an optimum process but had the objective of demonstrating how coal-based feedstock can be transformed to high quality mesophase pitch. Further work is needed to demonstrate an economically viable continuous commercial process which would optimize both mesophase pitch quality and mesophase pitch yield.

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CONSORTIUM FOR PREMIUM CARBON PRODUCTS FROM COAL

Accelerated Processing of Isotropic Carbon Fibers from Coal

FINAL TECHNICAL REPORT

for period

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Rodney Andrews (PI) and Terry Rantell

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Abstract

The results of Laboratory and supporting technical assessments conducted under Subcontract No. 2672-UK-DOE-1874 are reported for the period March 1, 2004 to February 28, 2005. This contract is with the University of Kentucky Research Foundation, which supports work with the University of Kentucky Center for Applied Energy Research. This work was an investigation to find viable methods for significantly accelerating the stabilization process in the synthesis of carbon fibers from an isotropic pitch feedstock.

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Executive Summary

A number of avenues have been explored in an investigation to find viable methods for significantly accelerating the stabilization process in the synthesis of carbon fibers from an isotropic pitch feedstock. Stabilization is the rate limiting step in the process and for pitch derived fibers is usually accomplished by oxidation in air at a progressively increasing temperature to around 300°C. Two generalized approaches to tackling the problem were identified from a literature search that in theory offered significant scope for promoting the reactivity of the pitch and thereby substantially decreasing the time required for stabilization of the pitch fibers. In the first approach organometallic compounds were used that are known polymerization promoters for coke formation and for increasing carbon yield. These were added to a reference pitch in low concentrations (1wt%) and the products assessed for the synthesis of carbon fibers relative to the processing of the reference material.

In the second general approach the intention was again to increase pitch reactivity, this time by chemical modification of the polyaromatics in the pitch. The intent here was to add functional groups to the PAH species to promote polymerization. Lewis acids were used to catalyze the adduction of reactive pendant groups to the pitch. It is important that any such modifications to the structure of the pitch aimed at improving process economics do not adversely affect its beneficial properties. This could include process fundamentals such as the ability to convert the pitch into fiber by melt spinning or indeed to the properties of the resultant carbon fibers. In the event, the selected methods did not achieve the required result prompting a search for an alternative technique that could potentially accelerate polymerization reactions without drastically changing the desirable properties of the pitch. The addition of reactive heteroatom

containing functional groups in the form of selected polymers was identified as a possible route to this end.

The conversion of the resultant pitch/polymer blends into carbon fiber was achieved and the processing rate compared to the reference pitch. Unfortunately, no significant improvement in stabilization rate was found. However, the materials generated in the process of this investigation were converted into active carbons by carbonization and activation in steam. These new materials have been found to offer significant potential for CO₂ adsorption from waste gas streams.

Introduction

The conversion of coal into carbon fibers is a multi-stage process. In the first phase the coal is converted into pitch, usually by extraction with a high boiling aromatic solvent at a temperature in the range 400 to 430°C, followed by separation of the undissolved material and removal of most of the process solvent by vacuum distillation. The softening point of the pitch, typically 220 to 260°C, is controlled by adjusting the final distillation conditions, (temperature and absolute pressure). The selection of softening temperature is a compromise: a low softening point allows easier melt spinning of the pitch for conversion to fine filament, while a high softening point allows faster processing of the raw pitch fiber into carbon fiber via stabilization and carbonization stages. Thus the softening temperature needs to be as high as practicable without adversely affecting the fiber forming step.

Fiber stabilization is the rate-controlling step in the whole process, and is related to the softening temperature of the pitch and its chemical composition. Stabilization is also commonly dependent upon the diameter of the green fibers as the cross-linking reactions are usually initiated by diffusion of oxygen into the core of the fiber. The most practical and economic method of stabilization is by oxidation in air at a progressively increasing temperature to about 300°C. To avoid fiber deformation and sticking, the cross-linking reactions must be initiated below the glass transition temperature, T_g . As oxidative cross-linking reactions proceed, T_g and the softening temperature both increase, and the reaction temperature can be raised until the fibers are rendered infusible. At this stage they will not soften or melt as the temperature is raised further, Figure 1.

Figure 1 Oxidative stabilization regime for pitch derived carbon fibers

Practical methods to significantly accelerate the stabilization process without compromising other steps in the synthesis of the carbon fibers have been investigated. Thus, pitch softening point was not directly used as a means to this end, but rather chemical promotion to render the pitch fiber infusible was addressed. The methods employed needed to be both practical and cost effective. Thus, difficult and expensive methods such as the use of chlorine or bromine atmospheres have not been considered for increasing stabilization rate. Two different approaches were tested. In the first, organometallic compounds were used in low concentrations as additives to the pitch to enhance the rate of the cross-linking reactions. As an alternative, reactive functional groups were chemically attached to the pitch. The role of the functional groups was to promote polymerization of the polyaromatic compounds in the pitch. It was important that any chemical modification did not change the fundamental composition and properties of the pitch. Thus, the

pitch needs to be relatively stable during the melt spinning stage and the additives should only become reactive during subsequent processing, at a higher temperature for example. Ideally, it would have been better if an accelerating agent could have been found that was sensitive to an external stimulus, such as UV light, that could be used to initiate the reaction at the required time. However, no such magic bullet has been discovered. An alternative method of introducing reactive functional groups into the pitch was adopted to circumvent the problems introduced by the chemical functionalization approach. Here, polymers containing labile heteroatoms were used to blend into the pitch and provide another means of accelerating the stabilization process. Organometallic compounds including ferrocene, nickelocene and some molybdenum based compounds were selected for testing. The iron organometallic, ferrocene, was chosen from its known reactivity in catalyzing the pyrolysis of petroleum pitches and simultaneous enhancement of coke yields. This type of material is more “user friendly” than alternative catalytic promoters of polymerization reactions such as those based upon Lewis acids (AlCl_3 , $\text{BF}_3\text{-HF}$) which can be difficult to handle. In contrast the organometallics should be compatible with the pitch matrix. Ideally they should be readily miscible with the pitch, but in addition they need to be stable up to temperatures required for melt spinning and have low volatility, so they will not evaporate before decomposing during pyrolysis. Maleic anhydride was added to this group of polymerization accelerants and dispersed into the pitch in the same way as the organometallics. The chemical structure of maleic anhydride makes it a highly reactive organic species that lends itself to a variety of chemical reactions and was therefore considered to be suitable candidate for accelerating polymerization of the stabilizing pitch fibers.

For the synthesis of the functionalized pitch, it was considered that the attachment of benzene groups to the pitch through an alkyl linkage would enhance polymerization and promote the

stabilization of the parent material. This type of appendage could be achieved through the use of a Friedel-Krafts alkylation type reaction (reaction of an aromatic compound with an alkyl chloride in the presence of a Lewis acid catalyst). Although resorting to the unwelcome use of Lewis acids, it was found from a literature survey that this was the most likely route to achieving functionalization of the pitch. The functionalized pitch could then be melt spun and subsequently thermally processed by heating in air to initiate a radical chain reaction at the appended moiety, causing cross-linking of the pitch compounds.

A search of published information was undertaken to locate alternative, suitable candidates for catalyzing the stabilization reactions. Functionalization of phenanthrene as an adjunct to the pitch was considered in order to explore other stabilization methods beyond air oxidation such as photo-initiated radical and cationic processes, microwave initiated reactions, and thermal, anaerobic processes. The functionalized phenanthrenes could be separated from any by-products and added to the coal-derived pitch. The pitch/phenanthrene mixture is then melt spun and subsequently heated in a manner analogous to the procedure described above with the purpose of initiating polymerization of the phenanthrene with the polyaromatic compounds present in the pitch, and subsequent cross-linking of the pitch matrix. However, this complex approach was not considered to be a particularly attractive proposition or economically viable and was therefore not pursued any further.

Experimental

A batch of pitch was prepared by the dissolution of a Western Kentucky bituminous coal in anthracene oil (a coal tar distillate fraction) at 420°C for one hour in a dedicated autoclave. The product was filtered, vacuum distilled to remove most of the solvent and a pitch produced with a softening point of 250°C. This material was assessed for its suitability as a feedstock for the

series of tests planned for the accelerated stabilization program. However, although the material was then acceptable for the intended purpose, changes in the planned methodology of modified pitch preparation from small scale bench-top experiments to larger mixing tests meant that it could not easily be produced in sufficiently large quantity to satisfy the demand. It was envisioned that a large suite of samples produced in the heated mixing chamber of the Haake high shear mixer would be required. This equipment needs a minimum of ~50ml of feed material in the mixing chamber for optimum performance. Thus, an alternative source of a suitable pitch was needed that could be used as the reference material and for preparing the modified pitch samples.

A Koppers coal tar pitch (Stickney pitch) was identified that was available in sufficiently large quantity and with properties that were generally in the required range, (low ash and QI contents, high aromaticity). However, the softening temperature was too low and it was therefore necessary to treat a large batch of the pitch to increase this value. This was achieved by blowing air through the pitch while holding it in a fluid state at 300°C and at atmospheric pressure in a steel reactor. By air blowing for a period of 5 hours a suitable pitch was produced with a softening point of ~230°C, (increased from 105°C of the original pitch). The pitch yield from this procedure was 85%. Spinning and thermal processing tests were conducted to confirm that this material was a suitable precursor for the synthesis of isotropic carbon fibers. It was used as a bulk supply of pitch in the subsequent test program providing a consistent feed to the mixing and thermal processing experiments. Analysis of the pitch is given in Table 1.

Dispersion of the organometallic catalysts and the heteroatom containing polymers was achieved using a Haake PolyLab high shear mixer. Blends were prepared by mixing at a temperature above the melting point of the components to produce composites with a well dispersed second phase

Table 1 Analysis of Stickney Pitch and an Air Blown Derivative

Sample Type		Stickney Pitch	Air Blown Stickney Pitch
Softening Temp	°C	105	230
H ₂ O	%	0.07	0.16
Ash	%	0.10	0.13
VM	%	52.2	29.6
FC	%	47.6	70.1
C	%daf	93.1	93.6
H	%daf	4.13	3.61
O*	%daf	1.22	1.30
N	%daf	1.02	0.99
S	%daf	0.49	0.49

*Oxygen by difference.

or a homogeneous product from miscible materials. The quality of the pitch/polymer dispersion was assessed by characterization of specimens mounted in resin, sectioned and polished for optical microscopy. Low polymer concentrations (5wt%) were used in the initial series of tests and the proportion increased in some later tests.

The addition of functional groups to the pitch was carried out in bench-top experiments. A solution of the pitch was prepared by dissolving in either tetrahydrofuran (THF) or chloroform and the other reactants then added to the solution, Table 2. In the first test, MCT157, the Stickney pitch was dissolved in THF and ~10wt% anhydrous AlCl₃ (Lewis acid) and ~13wt% of a benzyl chloride then added and the mixture refluxed for 4hours. At completion the sample was quenched in water, filtered and vacuum dried. The purpose in this experiment was to add alkyl

Table 2 Synthesis of the Functionalized Pitch

Run No		MCT157	MCT159	MCT160
Solvent	type	THF	Chloroform	THF
	ml	200	200	200
Stickney air blown pitch	g	10.1	17.1	13.1
AlCl ₃ (anhydrous)	g	1.1	3.4	11.2
Additional Reagent	type	Benzyl chloride	-	Adipoyl chloride
	structure
	g	1.31	-	6.00

benzene groups to the pitch aromatics to increase Van der Waals interactions and thereby promote the stabilization reaction. In the second test, MCT159, the intention was to tether together polyaromatic hydrocarbons (PAH) in the pitch using a Friedel-Crafts type reaction. Chloroform plays an active role in this approach and was used as the solvent for the pitch again with anhydrous AlCl₃ (Lewis acid) as the catalyst. The mixture was refluxed for 6 hours, cooled, quenched in water, filtered and vacuum dried. A third sample, MCT160 was prepared using adipoyl chloride in a Friedel-Crafts reaction. With THF as the solvent the mixture containing Stickney pitch, adipoyl chloride and the anhydrous AlCl₃ (Lewis acid) as the catalyst was refluxed for 5 h and again quenched in water, filtered and vacuum dried. The softening point of

these three pitches were determined using a well-founded practical technique, by heating rapidly on a hot plate while stirring with a fine thermocouple wire and observing the changes in flow characteristics with increasing and decreasing temperature. Although a useful technique, this is a somewhat subjective test and thus additional measurements of softening temperature have been made by Dynamic Mechanical Analysis (DMA). Where possible the samples were then used in the subsequent fiber synthesis tests.

Samples of the parent pitch and the modified pitches were crushed to provide a size fraction (0.2 to 1.2mm) suitable as a feed to the Wayne single screw bench-scale extruder. Where possible samples were melt spun to produce continuous filament by forcing the molten pitch through a die, (either 0.3 or 0.5mm diameter). The thread was drawn down to a small diameter ($\sim 30\mu\text{m}$) by attaching to a wind-up drum rotating at speeds up to 1700rpm. Tows of green fiber cut from the drum were thermally processed into carbon fiber by stabilization in air and carbonization in nitrogen. A control value for the stabilization rate was determined using the green fiber produced from the Stickney pitch to measure the maximum rate achievable that does not result in deformation or “sticking” of the fibers in the tow. The green fiber tows were heated rapidly at $5^{\circ}\text{C}/\text{min}$ in air up to the glass transition temperature T_g , in a tube furnace and then at the selected heating rate up to 310°C . The furnace was then allowed to cool to room temperature for sample inspection and measurement. For the test specimens, the stabilization rate used was increased stepwise from the control value to determine the maximum achievable rate. Stabilization of the pitches and/or green fibers was also characterized by Thermal Gravimetric Analysis (TGA). Stabilized tows of fiber were carbonized in nitrogen by heating from ambient up to 1000°C at $20^{\circ}\text{C}/\text{min}$ in a tube furnace and then allowed to cool to room temperature. The fibers were measured and assessed for changes in weight, dimensions and morphology, and then

characterized by measurement of their physical properties, including: diameter, tensile strength and Young's modulus.

Results and Discussion

The reference material, air blown Stickney pitch, was melt spun and the filament converted into carbon fiber by stabilizing in air and carbonizing in nitrogen. The maximum stabilization rate achieved was 0.5°C/min. At rates above this value there was evidence of adjacent fibers in the tow sticking together. Their physical properties are typical of carbon fibers derived from isotropic pitch, Table 3.

Table 3 Preparation and Properties of Isotropic Carbon Fibers from Stickney Pitch

Fiber Preparation				Fiber Properties			
Fiber No	Spin No	Fiber Shrinkage (%)	Carbon Yield (%)	Diameter (μm)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elastic Strain (%)
CFR 475	Wext 119	16.2	71.5	29.0	395	30	1.3

The melting characteristics of the three chemically modified pitch samples were assessed by direct observation during heating and by DMA. Both tests showed that two of the samples, MCT159 and MCT160 did not flow during heating to 350°C and were therefore unsuitable for melt spinning to convert the pitches into filament. The third sample, MCT157, showed some

flow properties around 310°C, but compared to the flow characteristics of the parent pitch (Stickney) Figures 2, 3, and 4 its conversion into filament by melt spinning was unlikely to be easy. Attempts to spin this material using a range of conditions and temperature profiles in the Wayne extruder proved to be fruitless. Short lengths of ~0.5m were all that could be produced. It is likely that the addition of the functional groups is either too effective in producing a more reactive pitch which polymerizes before reaching a temperature where melting would otherwise take place or that the methods of preparation have made unwanted changes to the character of the pitch – by the removal of a critical component that plays a key role in the mobility of the pitch. Analysis of the pitches by TGA shows that some thermal decomposition does occur below the expected softening temperature, Figure 4 and 5. Unfortunately, a similar behavior was found for the pitch samples modified by the addition and dispersion of the metallocenes (ferrocene and nickelocene), and maleic anhydride. The samples containing low concentrations (1wt%) of the organometallic compounds could not be melt spun. However, when two of the accelerants, nickelocene and maleic anhydride were dispersed in a low softening temperature pitch (softening point ~110°C), conversion to filament by melt spinning was perfectly feasible at the lower temperatures required. It is thus probable that the metallocenes and maleic anhydride are too reactive at the higher temperatures ~275°C required to melt spin the reference pitch, causing rapid polymerization and an inability to extrude the material from the spinneret.

Figure 2 DMA Characterization of Stickney Pitch and an Air Blown Variant

Figure 3 Detemination of Pitch Softening Point by DMA

Figure 4 Comparison of Flow Properties of Air Blown Stickney Pitch and Chemically Modified Pitch

Figure 5 TG Analysis of Functionalized Pitch, MCT 159

Figure 6 TG Analysis of Functionalized Pitch, MCT 157

At this stage the prognosis for successfully identifying and proving the efficacy of suitable stabilizing promoters was not very good. As a last throw of the dice, the introduction of reactive heteroatom rich polymers into the pitch was considered. Two polymers, Nylon 6 and polyethylene terephthalate (PET) both rich in oxygen, were blended into the pitch using the Haake high shear mixer to produce homogeneous composite materials containing 5wt% of the polymer. Both materials were successfully melt spun to produce continuous filament and then thermally processed into carbon fiber. The same stabilization rate used with the parent pitch was effective in generating good quality fibers from the pitch/polymer blend. However, attempts to increase the rate were unsuccessful; doubling the rate to 1°C/min produced fibers that were not completely free from one another. Thus, none of the methods used to increase stabilization rate have proven to be successful.

Although the results from this study were all largely negative, a proposal was made suggesting that the pitch/polymer composite materials could possibly be suitable as precursors for the synthesis of activated carbons with very attractive properties for use in applications such as in the adsorption of CO₂ from combustion sources. New CO₂ capture technologies are needed that offer significant improvements in their environmental impact compared to traditional coal-fired power plant operation. Porous carbons are routinely used to absorb contaminants from gas and liquid process streams but their application to the removal and recovery of CO₂ has not been industrially practical due to low capture efficiency for CO₂. However, activated carbons can in theory be produced that offer the potential for successful implementation as CO₂ adsorbents if a combined chemical capture and physi-sorption process is used in one material. Thus, the pitch/polymer composite materials produced were assessed for their potential as precursors for the synthesis of activated carbons. The samples were activated by heating to 750°C in steam for

residence times of several hours in an Inconel furnace. Suitable gasification rates were achieved by varying the water flow rate for steam generation over the range 100 to 250ml/hr, Table 4.

These conditions are similar to those used in commercial processes for activation of isotropic carbon fibers. Preliminary tests have shown that the capacity for CO₂ adsorption is increased and compares favorably with existing CO₂ adsorbents, Table 5. The activated carbons produced by this method will undoubtedly exhibit a pore size distribution that is characterized by a high proportion of mesopores (pore diameter 2-50nm), that offer selectivity for the capture and subsequent controlled release of CO₂.

Table 4 Steam Activation of Cokes Derived from Pitch/Polymer Blends

Activated Source ⁽¹⁾	Carbon	Polymer content (wt%)	Activation Conditions ⁽³⁾		Wt. loss (%)	BET Surface Area (m ² /g)	Pore Volume (ml/g)	Pore Size Distribution		
			Time (h)	Temp. (°C)				micro (%)	meso (%)	macro (%)
Stickney pitch/Nylon 6		5	-	-	-	<1	-	-	-	-
Stickney pitch/Nylon 6		5	1	750	14.7	13	0.012	38.0	16.3	45.7
Stickney pitch/Nylon 6		5	24	750	68.0	590	0.278	72.2	27.8	0.0
Stickney pitch/Nylon 6		10	-	-	-	<1	-	-	-	-
Stickney pitch/Nylon 6		10	1	750	35.4	21	0.014	53.0	39.3	14.8
Stickney ⁽²⁾ pitch/Nylon 6		10	24	750	75.8	675	0.326	67.8	32.2	0.0
Stickney pitch/Nylon 6		20	-	-	-	<1	-	-	-	-
Stickney pitch/Nylon 6		20	24	750	67.2	590	0.287	73.6	26.4	0.0
Stickney pitch/Nylon 6		30	-	-	-	<1	-	-	-	-
Stickney pitch/Nylon 6		30	24	750	73.6	655	0.326	70.3	29.7	0.0
Stickney pitch/PET		5	-	-	-	<1	-	-	-	-
Stickney pitch/PET		5	1	750	10.0	48	0.021	84.0	13.0	3.0
Stickney pitch/PET		5	24	750	71.0	655	0.335	65.2	34.8	0.0

(1) Precursors were converted into coke by heating in nitrogen to 500°C for 1hour.

(2) Reactivation of material from previous test (time increased from 1 to 24h).

(3) Water flow rates for steam generation in the range 150 to 250ml/h

Table 5 CO₂ Adsorption by Activated Carbons Derived from Pitch/Polymer Blends

Activated Carbon Source	Polymer content (wt%)	CO ₂ Mass Uptake at 1bar (wt %)			CO ₂ Mass Uptake at 9bar (wt %)		
		0°C	50°C	100°C	0°C	50°C	100°C
Stickney pitch	0	8.4	3.7	2.2	21.2	13.3	11.0
Nylon 6	100	5.6	2.3	1.4	10.4	7.7	7.6
Stickney pitch/Nylon6	5	n/a	5.1	n/a	n/a	16.5	n/a
Stickney pitch/Nylon6	10	11.0	4.6	2.3	26.6	12.9	12.5
Stickney pitch/Nylon6	20	10.7	4.9	2.4	24.9	16.3	12.6
Stickney pitch/Nylon6	30	11.0	4.5	2.5	26.6	16.7	12.6
Molecular Sieve*	-	20.0	18.5	16.0			

- (1) Precursors were converted into coke by heating in nitrogen to 500°C for 1hour.
- (2) Samples were activated by heating in steam to 750°C for 24 hours.
- (3) *Data for molecular sieve (“Gas Purification” by Kohl, AL and Riesenfeld, FC, 1985, 670, Gulf Publishing Co, Houston, TX)

Conclusions

The methods explored for significantly accelerating the stabilization process in the synthesis of carbon fibers from an isotropic pitch feedstock have not been totally successful. In the first approach the organometallic compounds ferrocene and nickelocene (and some molybdenum based organometallics), known polymerization promoters for coke formation and for increasing carbon yields, were used. Maleic anhydride was also included in the trial materials as it is a well documented accelerator of polymerization reactions and would offer a distinctly different alternative reagent. Although all of these materials were easily dispersed into the pitch, it was not possible to convert the product modified pitches into filament by melt spinning – the resultant

pitches were too reactive, undergoing polymerization reactions at temperatures below the temperature at which the pitch would otherwise have melted.

The same problem was encountered with modified pitches produced by the second general approach. In this method the pitch reactivity was again apparently increased, this time by chemical modification of the polyaromatics in the pitch. The use of Lewis acids to catalyze the addition of reactive pendant functional groups to the PAH species to promote polymerization was apparently successful. However, although the principles of the method are sound, execution was again flawed as the modified pitches produced were not amenable to melt spinning. In this case, the treatment was either too effective, yielding a pitch which was too reactive, or alternatively, the procedure deleteriously changed the melting characteristics of the pitch during solvent refluxing. In either event the modified pitch could not be melt spun.

The failure of these methods prompted the search for an alternative technique that could potentially accelerate polymerization reactions without radically changing the desirable properties of the pitch. The addition of reactive heteroatom containing functional groups in the form of selected polymers was identified as a possible route to this end. Nylon6 and PET were blended into the pitch to produce homogeneous composite materials containing 5wt% of the polymer. The conversion of the resultant pitch/polymer blends into carbon fiber was achieved and the processing rate compared to the reference pitch. Unfortunately, no significant improvement in stabilization rate was found. However, by chance the materials generated in the process of this investigation were converted into active carbons by carbonization and activation in steam. These new materials have been found to offer a significant potential for CO₂ adsorption from waste gas streams. Further samples were prepared containing higher concentrations of the polymers in order to make comparative studies. Preliminary tests have shown that the capacity

for CO₂ adsorption is increased and compares favorably with existing adsorbents, offering selectivity for the capture and subsequent controlled release of CO₂.

Correlation of Foaming Performance With the Properties of Coal-based Precursor

FINAL REPORT/4th QUARTERLY REPORT

Reporting Period
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ABSTRACT

One of the important issues in carbon foam research is the ability to predict the foaming performance and foam properties based on the properties of precursors. To this end, the properties of precursor and foam properties need to be correlated. A series of foaming precursor with different properties were selected, and their properties were measured. When the foams are made from these precursors, some relationships between the properties of foam and precursor will be found. This will aid in the control of foaming behavior and foam properties.

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INTRODUCTION

Carbon foam is a next generation porous material. It has potential applications in such diverse areas as high temperature thermal insulation, high thermal-conductivity heat sinks, electrodes for battery, energy absorption material, etc. Researchers at West Virginia University have developed a series of coal-based carbon foams which are low cost and high performance as compared with commercial Mitsubishi mesophase pitch-based carbon foam. Up to now, carbon foam has been made by using raw coal, coal/NMP solvent extracts, hydrogenated coal/solvent extract and coal tar pitch. The properties of carbon foam are determined by both the foaming method and the precursor properties. However, the prediction of the properties of carbon foam from the properties of its precursors is very complex. The goal of this project is to correlate the foaming performance and foam properties with the characteristics of its precursor material.

The precursor fluidity and dilatation are two key factors that controls the foaming process. To investigate their relation with foaming performance, the fluidity and dilatation rate of a series of foaming precursors will be assessed by means of a Plastometer and a Dilatometer. It is anticipated that the foam properties such as the foam density, bubble size and distribution and strength can be correlated to these properties of the precursors.

Raw coal can be foamed directly, but hydrogenated coal extract and coal tar pitch have to be heat-treated before they can be used to make carbon foam. The changes of

fluidity during the heat treatment will be monitored, and the fluidity of these heat-treated pitches will be correlated to their foaming performance.

PROJECT STATUS

In the last three quarters, we selected foaming precursors, treated pitch and made foams. In this report, some properties of coal-derived carbon foams were summarized. These properties include optical texture, microstructure, compressive strength and coefficient of thermal expansion (CTE), etc.

Optical texture was observed by microscopic under polarized light. There are two classes carbon foam made from coal and coal derived pitch precursors, i.e., nearly isotropic and anisotropic texture. As shown in Figure 1, raw coal derived carbon foams show a nearly isotropic optical texture, while the coal tar pitch and SynPitch derived foams show an anisotropic texture. The results imply that raw coal derived foam will be a potential electrical and thermal insulator; while the pitch derived foam will be a potential conductor.

Figure 2 show the microstructure of foams observed by SEM. These foams have a relative uniform cell with some membrane, but the foam cell shows an open structure. Raw coal and extract derived foam have complete cell wall without major cracks. However, the mesophase pitch(coal tar pitch based) derived foam shows some cracks on the cell wall, which is probably because the CTE mismatch in these area.

Compressive strength measurement was carried out on an Instron 5869 by using a stainless steel cylinder sample holder and a matched piston (diameter, 25 mm). Sample size is 25 mm diameter by 20~30 mm height. The yield strength alone with the bulk

density and porosity of corresponding foams are listed in Table 1. The compressive strength ranges from 2.5 to 9.9MPa.

The coefficient of thermal expansion(CTE) was measured in N₂ atmosphere by Netzsch Model 402 Dilatometer. The results were listed in Table 2. Raw coal derived foams show a higher CTE then the foam derived from mesophase pitch(coal tar pitch derived).

Figure 1. Optical texture of coal-derived carbon foam. Bakerstoun raw coal, upper left; Powellton coal NMP extract, upper right; coal tar pitch, lower left; coal-based SynPitch, lower right

Figure 2. SEM image of coal-derived carbon foam. Bakerstown raw coal, upper left; Powellton coal NMP extract, right; coal tar pitch, lower center

Table 1. Compressive strength and general properties of selected coal-derived carbon foams

Precursor of carbon foam	Bulk density, g/cm ³	Porosity, %	Open-cell, %	Compressive Strength, MPa
Kingwood raw coal	0.32	84.1	96.8	2.9
Bakerstown raw coal	0.40	79.3	97.7	9.9
Powellton coal NMP extract	0.25	87.0	97.1	2.5
Coal tar pitch	0.56	72.0	98.2	8.0
Coal-based SynPitch	0.42	79.7	95.6	2.8

Table 2. Coefficient of thermal expansion (CTE) of selected foam samples

Samples	CTE, $\times 10^{-6}/^{\circ}\text{C}$, Heating rate: $5^{\circ}\text{C}/\text{min}$ Temperature range: $50\sim 290^{\circ}\text{C}$, N_2 atmosphere
Raw coal-I	5.93
Raw coal-II	6.35
Mesophase pitch	2.41

The on-line monitoring the change of viscosity/fluidity should be reported in the 2nd quarterly reported, but due to the delay of apparatus, it is reported here.

The viscosity, which inverses to fluidity, increases as the heat treatment time. This change was monitored by a “home made” apparatus showing in Figure 3. A stir motor with torque measurement was attached to the stir on the autoclave. The motor rotation speed is fixed at 400 rpm, the increase of the torque (delta torque in Figure 4) indicates the increase of viscosity but decrease of fluidity. The curve in Figure 4 shows that delta torque does not increase significantly for first 500min of heat treatment, in which stage low molecular weigh fraction is driven off by N₂ purge; while the delta torque increases significantly after 500min of treatment, which indicates polymerization and condensation reaction speed up after removal of light fractions. In this run shown in Figure 4, the last point corresponds to delta torque 30Ncm, and softening temperature 350°C. Therefore, the desired softening temperature can be controlled by on-line monitoring the torque change.

Figure 3. Apparatus for on-line monitoring the change of viscosity during heat treatment of pitch

Figure 4. Change of torque of stir motor during heat treatment of coal tar pitch at 400°C in N₂

NANOSTRUCTURED ANTHRACITE-METAL COMPOSITES FOR HYDROGEN STORAGE

Final Report

Start Date: March 1, 2004

End Date: August 31, 2005

Principle Investigator: Dr. Angela Lueking

Report Issue: August 2005

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ABSTRACT

The overall goal of the proposed work is to develop coal-magnesium composites for hydrogen storage materials utilizing the hydrogen spillover mechanism.

We investigated the hydrogen uptake of different samples with varying ratios of carbon to metal content. The presence of a solvent during ball milling, which is the technique used to make these composites, was found to have a profound effect on the extent of carbon-metal interaction and the graphitic nature of the carbon and so all the work was done in the presence of an organic solvent. X ray diffraction was used as the primary method of characterizing the extent of change in the graphitic nature of the carbons. The ball milling time was determined using graphite ball milled in similar conditions as the coal-metal samples.

The samples were subjected to different pretreatment conditions prior to introduction to hydrogen and it is found that by using 50 ml/min hydrogen reduction at 350 °C, sample preparation time was reduced from around 7 - 10 days to 3 – 4 days with no compromise in the quality of pretreatment itself. Air exposure to the samples was determined to be detrimental to the uptake of H₂ since it was an energy intensive process to reduce the oxides and hydroxides of magnesium and hence care was taken to eliminate exposure to air and moisture by all means at every step. It was also determined that temperature played a more significant role in H₂ uptake than pressure, even in carbon-rich samples. The temperature programmed desorption data collected for these samples showed that the desorption temperature of the carbon-metal samples were around 480 °C. The amount of carbon also doesn't affect the desorption temperature significantly.

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INTRODUCTION

The recent uncertainty in the availability of fossil fuels has heightened the need to move to a more reliable fuel. The Hydrogen Fuel Initiative announced by President Bush in his January 2003 State of the Union Address addresses the development of a hydrogen fuel economy for improved energy efficiency and the diversification of the nation's energy sources. The development of materials able to store sufficient hydrogen to enable a 300-mile vehicle range is a key technology requirement for enabling a successful hydrogen fuel economy. This 300-mile range is the basis for hydrogen storage targets for new materials set by the DOE: 4.5% by 2005 and 6.0% by 2010, both at 100 atm with delivery temperatures between - 20 and 85 °C. Materials identified with promise to meet this goal include: (a) carbon nanomaterials; (b) high-surface area materials; (c) synthetic metals; and (d) chemical and metal hydrides. However, at the present time, no existing hydrogen storage technology meets the challenging performance requirements to make hydrogen-powered automobiles competitive with conventional vehicles: carbon nanomaterials generally do not reproducibly meet the mass storage requirements, and hydrides generally do not supply hydrogen at a sufficient rate at relevant operating temperatures.

HYDROGEN UPTAKE OF GRAPHITE

Ball-milling of graphite has been used to obtain a total hydrogen capacity of 7.4%, measured by total gasification [1]. Neutron diffraction showed evidence of two chemisorbed hydrogen storage sites. Unfortunately, the desorption temperatures of 650 and 950 K of the chemisorbed hydrogen fell short of the DOE targets.

HYDROGEN UPTAKE OF METAL-GRAPHITE COMPOSITES

Adding graphite to pure magnesium or magnesium-based alloys is one strategy by which to increase the hydriding/dehydriding characteristics of magnesium; this serves to increase the surface area of the composite and generally lowers the desorption temperature [3-12]. The performance of the magnesium-graphite composite material is generally a function of ball-milling time [10], the presence of a solvent during processing [4, 5, 8], and the breakdown of the graphitic structure [8, 12]. The addition of carbon to form a magnesium-carbon composite typically lowers the overall hydrogen capacity of the material, such that results are often reported as "fraction of hydride" formed. However, the magnesium-composite material still has a high storage capacity and moderate operating temperatures relative to several reports for carbon nanotube materials. Imamura et al. found a synergistic effect when carbon and magnesium were combined by ball milling: a new hydrogen storage site was found upon carbon addition when compared to pure magnesium [6]. This new hydrogen storage site took up hydrogen reversibly at a lower temperature than pure magnesium. Both the total hydrogen uptake and the uptake temperature were dependent upon hydrogen pressure. This observed hydrogen behavior is similar to that observed by Lueking and Yang for a composite material made up of multi-wall carbon nanotubes and a NiMgO catalyst in which a hydrogen spillover hypothesis was invoked [13, 14].

OBJECTIVE

The primary objective of this work is to explore the possibility of substituting anthracite for graphite in carbon-metal hydrogen storage materials. A secondary objective is to explore the

possibility of thermal treatment on the milled composites in the formation of carbon nanostructures. The use of anthracite carbon is based on its similarity to graphite and polycondensed ring compounds (e.g., anthracene, perylene and chrysene). Previous results show that the graphitic structure breaks down both physically and chemically during ball-milling of graphite metal composites, so there is reason to believe that anthracite will be a feasible substitute in these materials. Anthracite materials will serve as the starting point for future work with other coals to investigate the role of graphitic order in formation of hydrogen storage composites. Magnesium will be chosen as the initial probe metal based on its previous use to form magnesium-graphite composites.

EXPERIMENTAL

I. COAL SELECTION

ANTHRACITE SELECTION, PRETREATMENT, AND CHARACTERIZATION

Anthracite coals from the Penn State Coal Sample Bank and chosen based on rank, mass, and particle size. Graphite (Carbon) was used as a control material, and used as received. Acid and heat treatments removed the mineral matter via dissolution and amorphous content via oxidation, as described previously [15]. Powdered graphite (Carbone of America) was used as the control material, and used as received. The eight coals were demineralized by treatment with HCl, HNO₃ and HF acids, as described previously [15]. Proximate analysis (Thermogravimetric Analyzer MAC – 400) characterized the anthracite coals, with a moisture temperature set at 105 °C, volatile matter temperature of 950 °C, and ash temperature of 750 °C. X-ray diffraction (XRD) measurements with a Phillips X'pert MPD with Cu K α radiation operated at 30 kV and 50 mA. determined the graphitic content of the coals, based on previous methods [15]. XRD and proximate analysis characterized the graphitic ordering and metal content, respectively, before and after demineralization.

Neutron activation analysis (NAA) was conducted on a GEM series HPGe with Ortec 672 Spectroscopy amplifier and Ortec 459 Bias supply. Residual metals affect hydrogen storage results, and thus NAA served to identify metals that would potentially affect hydrogen storage results.

As discussed in the previous report, [15a] PSOC 1468 had the highest level of graphitic ordering and lowest metal content, and was thus selected for further study. NAA on PSOC 1468 coal indicated the presence of aluminum, antimony, arsenic, barium, bromine, cerium, chromium, hafnium, iron, lanthanum, magnesium, potassium, scandium and tungsten of which most metal quantities were reduced by acid treatment including the ones with hydrogen storage affecting capabilities (Table 1). NAA was not able to neither detect nor quantify silicon due to interferences with aluminum; any silicon present in the sample is likely to act as a diluent rather than a catalyst for hydrogen storage. As discussed in the previous quarterly report, acid treatment also gave a stronger graphite peak in the demineralized PSOC 1468; however this is likely due to removal of inactive or amorphous regions from the coal.

II. METHOD DEVELOPMENT

BALL MILLING

Milling with a solvent showed to effectively grind coal without completely eliminating the graphitic order of the anthracite coal. Initial ball milling studies with graphite determined that beyond 21 h, the graphitic nature was completely destroyed. Graphitic order (as determined by the height of the 002 graphite XRD peak) decreases rapidly from 0-5 h, then decreases slowly from 5-21 h. Milling with a solvent (e.g. cyclohexene) slows this loss of graphitic order, thus cyclohexene was used as a lubricant in these studies.

Magnesium rapidly forms oxides and hydroxides upon exposure to air, thus the following techniques significantly reduced air and moisture exposure: (1) all ball milling was under an inert atmosphere; (2) the magnesium vial was always handled in an Argon environment; (3) loading and unloading the ball mill were in an Argon environment; (3) samples were stored wet with excess cyclohexene under an Argon blanket; (4) the cyclohexene slurry reduced air exposure upon IGA loading, the cyclohexene was removed *in situ* in the IGA via evaporation (Normal Boiling Point = 83 °C). The hydrogen cylinders used in the experiments are an Ultra High Purity Grade (99.9999%) obtained from Messer and the hydrogen was further purified with a 3A zeolite trap to remove any trace moisture present in the cylinder. This zeolite trap is pretreated every 8 weeks to remove the moisture trapped within

NEUTRON ACTIVATION ANALYSIS (NAA)

NAA determined metal content in samples that was residual despite the acid treatment and introduced during the milling process. For dry ball milled coal, the metal contamination was small, even after 80 h. However, for coal ball milled in solvent, metal contamination, particularly iron, is more significant, particularly at 80 h.

NAA also helped determine the best possible milling material (balls and bowl) which would possibly yield higher hydrogen uptake.

RESULTS AND DISCUSSION

SAMPLE PREPARATION

Magnesium exposed to air verified that $\text{Mg}(\text{OH})_2$ or MgO conversion to Mg or MgH_2 required exposure to higher temperatures and pressures and was often less than a 100% conversion. Hence, all samples were handled in an inert atmosphere all throughout the experiment to avoid this energy-intensive and incomplete process. Demineralized coal milled with magnesium (Coal: $\text{Mg} = 90:10, 80:20, 50:50$).were loaded unto the gravimetric analyzer without exposure to air, as described above.

HYDROGEN STORAGE MEASUREMENTS

Two kinds of pretreatments were tested – one in a vacuum state and another in flowing hydrogen. The hydrogen reduction reduced the pretreatment time and led to formation of MgH_2 . Adsorption isotherms to 20 bar (the limit of the instrument) conducted at several temperatures indicated hydride formation was complete by 1 bar. This is consistent with standard Mg - MgH_2 phase diagrams. Temperature played a large roll in the adsorption isotherm. Based on these initial adsorption isotherms, temperature programmed desorption (TPD) measurements at 1 bar

were used to evaluate the hydrogen uptake of the materials. The TPD experiment tracks hydrogen desorption as a function of temperature; the total area under the TPD curve gives an indication of the total hydrogen adsorption. Thus, TPD experiments have an advantage for metal hydrides in that one may track both the total hydrogen desorbed and the operative adsorption temperature. The temperature of desorption also gives an indication of the strength of the hydrogen bond and whether the hydrogen is bound via chemisorption or physisorption. As a quality check, we have compared the amount desorbed during the TPD to the amount of hydrogen uptake during the preparation and reduction steps in which MgH_2 was formed.

Figure 1 shows the TPD of the various samples, normalized per total mass of sample. The amount of desorbed hydrogen increases with increasing magnesium content of the sample (Figure 1), implying the carbon fraction does not affect the sorption capacity. There is no real shift in the TPD temperature maxima upon varying the carbon content, thus implying the carbon fraction does not affect the desorption temperature nor the sorption energy. When the TPD curves are normalized for magnesium content (Figure 2), Coal:Mg = (90:10) and (50:50) overlap further illustrating the adsorbed hydrogen is determined by the magnesium content of the sample. However, the Coal:Mg (80 : 20) sample exceeds the uptake of the other samples by a factor of approximately two. We are currently investigating this anomaly. Our first step will be to conclusively rule out the possibility of water adsorption. Despite the efforts taken to eliminate water in the sample preparation and loading (see Methods), it is difficult to impossible to completely exclude air and/or moisture from this process.

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FIGURES & TABLES

Figure 1 - Temperature programmed desorption curve of samples containing Coal:Mg ratios - 90:10, 80:20, 50:50 normalized per mass of sample

Figure 2 - Temperature programmed desorption curve of samples containing Coal:Mg ratios - 90:10, 80:20, 50:50 normalized per mass of magnesium in sample

**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:
CORRELATION OF CHAR PROPERTIES AND
MERCURY UPTAKE CAPACITIES**

Reporting Period Start Date: *March 1, 2004*

Reporting Period End Date: *August 31, 2005*

Submission Date: *November 8, 2005*

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Abstract

On March 15, 2005, the U.S. Environmental Protection Agency (EPA) issued the Clean Air Mercury Rule designed to permanently cap and reduce mercury emissions from coal-fired power plants – the single largest contributor to human-generated mercury emissions in the U.S. reported at over 40% of the total annual emissions (EPA, 2005a). When the rule is fully implemented in 2018, nearly a 70% reduction in annual mercury emissions from the utility sector is expected (EPA, 2005b). Today, there is no single technology that can feasibly provide mercury control suitable for all power plant configurations and fuel types. Activated carbon injection (ACI) has shown the most promise as a near-term mercury control technology; however, due to the high price of commercial activated carbon and also the large excess of activated carbon required to meet the high capture goal, DOE's cost estimate for ACI technology is \$25,000-70,000/lb of mercury removed (Feeley III, *et al.*, 2003). Furthermore, there is a lack of understanding of the interaction between mercury and the carbon sorbent; therefore, it is very difficult to predict the amount of carbon sorbent needed for a specific plant configuration.

The objective of this project is to understand how the properties (*e.g.*, elemental composition, porous texture, generation conditions, and surface properties) of the chars collected during the previous CPCPC project (DE-FC26-98FT40360) affect their mercury sorption capacities in order to optimize their mercury capture performance. This project continued conducting mercury capture tests on the samples procured during the previous project. An in-depth study was conducted to correlate char properties with their mercury uptake capacity, including porous texture, surface chemistry and elemental composition.

The result of this study was that a correlation exists between the carbon content and loss-on-ignition (LOI) values of the samples and their ability to capture mercury. The samples that adsorbed a significant amount of mercury had relatively high LOI values and carbon percentages. There may also be a relationship between the amount of nitrogen on the surface of the sample with its ability to uptake mercury vapor. The samples that demonstrated mercury capture had the highest nitrogen concentrations on the surface of all the samples. It may also be important that the nitrogen species on the surface of the samples were observed to resemble protonated amines or ammonia species rather than the more common nitrogen oxides. It also appears that the surface area and porosity of the samples play a role in mercury capture. The fly ashes with the three largest measured surface areas and pore volumes were observed to uptake the most mercury. The remaining samples that captured mercury vapor had only moderate values for these two properties.

Overall, the properties with the greatest affect on mercury capture in this study were the carbon content or LOI of the sample, the amount of nitrogen on the surface of the fly ash, and the surface area and total pore volume of the sample. Modifications to improve the mercury capture of fly ash should focus on enhancing these properties.

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FINAL TECHNICAL PROGRESS REPORT

March 1, 2004 – August 31, 2005

1. Introduction

1.1. Rationale

On March 15, 2005, the U.S. Environmental Protection Agency (EPA) issued the Clean Air Mercury Rule designed to permanently cap and reduce mercury emissions from coal-fired power plants – the single largest contributor to human-generated mercury emissions in the U.S. reported at over 40% of the total annual emissions (EPA, 2005a). When the rule is fully implemented in 2018, a reduction in annual mercury emissions from the utility sector from 48 tons to 15 tons is expected – which is nearly a 70% reduction (EPA, 2005b).

Today, there is no single technology that can cost effectively provide mercury control suitable for all plant configurations and fuel types. Activated carbon injection (ACI) has shown the most promise as a near-term mercury control technology; however, due to the high price of commercial activated carbon and also the large excess of activated carbon required to meet the high capture goal, DOE's cost estimate for ACI technology is \$25,000-70,000/ lb of mercury removed (Feeley III, *et al.*, 2003). This is due to the very low concentration of mercury in the flue gas (1 ppb vol), the complexity of the flue gas composition, and the poor selectivity of the carbon sorbent towards mercury, thereby resulting in required carbon-to-mercury ratios around 1000:1 to 100,000:1 for commercially-available activated carbons (Granite *et al.*, 2000).

Furthermore, there is a lack of understanding of the interaction between mercury and the carbon sorbent; therefore, it is very difficult to predict the amount of carbon sorbent needed for a specific power plant configuration.

High carbon content chars, which are a by-product stream from coal-fired combustors or gasifiers, are currently disposed as a waste; however, due to the increasingly restricted landfill use the coal industry needs to find beneficial applications for these chars. Following this demand, the proposers have previously developed a one-step activation protocol to produce activated carbons from coal chars (Maroto-Valer *et al.*, 2001). 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, since they have already gone through a devolatilization process while in the combustor or gasifier. Therefore, these chars could be used as a precursor to produce value-added mercury sorbents. Furthermore, these char materials also present a fine particle size, which promotes mass transfer, and therefore are desired for mercury capture sorbents.

During the previous CPCPC project (DE-FC26-98FT40360), the proposers procured a suite of gasification and combustion chars (Maroto-Valer, *et al.*, 2004a). The samples were characterized and tested for mercury capture in a simulated flue gas at 140°C. The studies conducted by the proposers showed that coal chars prior to activation can capture mercury in the flue gas stream (Maroto-Valer *et al.*, 1999; Zhang *et al.*, 2003a and 2003b). However, the mercury capacity of non-activated chars appears to be lower than that of commercial activated carbons, 0.2 mgHg/gsorbent vs. 2.8 mgHg/gsorbent, respectively, presumably due to the reaction

being capacity-limited for low surface area materials (Zhang *et al.*, 2003a and 2003b). Consequently, the chars were activated to increase their surface area and tested for mercury capture and the resultant samples were found to have different mercury capacities before and after activation. In addition, the mercury capacity changed significantly across the different samples collected.

1.2. Program Objective

The objective of this project is to understand how the properties (*e.g.*, elemental composition, porous texture, generation conditions, and surface properties) of the chars collected during the previous CPCPC project affect their mercury sorption capacities in order to optimize their mercury capture performance. This project continued conducting mercury capture tests on the samples procured during the previous project. An in-depth study was conducted to correlate char properties with their mercury uptake capacity, including porous texture, surface chemistry, and elemental composition.

This project addresses two needs identified by both the coal industry and DOE. Firstly, due to the increasing restricted use of landfills, the utility industry must find uses for high carbon chars, instead of their current disposal practice. Consequently, DOE has established, as a goal, a 10% increase in the overall national rate of combustion chars in fly ash use by 2005 (Feeley III, *et al.*, 2003). Hence, this program aims to turn chars from a liability into an asset for the coal utility industry. Secondly, coal-fired utilities must comply with mercury emissions standards. DOE consequently identified the need to develop and evaluate advanced concepts for reducing

mercury emissions by 50-70% by 2005 and by 90% by 2010 (Feeley III, *et al.*, 2003). Therefore, in this research program, the utilization of coal chars for mercury capture was investigated. This provides a double environmental and economical impact for both the coal and utility industry, since the utilities can simultaneously increase their char utilization, as well as reduce their mercury emissions.

1.3. Research Design and Tasks

This research program was divided into the following activities:

- Mercury capture tests. The suite of samples collected during the previous project were used for this work. The suite included chars from different combustor and gasification units that were selected in collaboration with Southern Company and Penn State University. This task investigated the mercury sorption capacity of these samples and compared them to those of commercial activated carbons.
- Correlate char properties and their mercury uptake capacity. In this task, a systematic study of the effect of the chars' properties, such as pore structure, surface properties, and elemental makeup, on their mercury capture performance was conducted. This was accomplished using state-of-the-art analytical techniques available at Penn State, such as a Quantachrome Autosorb-1 Porosimeter, X-ray Photoelectron Spectroscopy (XPS), and Cold Vapor Atomic Adsorption (CVAA) Spectroscopy, as well as those at Nottingham University, UK, such as an in-house mercury sorbent evaluation facility.

2. Experimental

2.1. Study Samples

Eleven fly ash samples and two commercial activated carbon samples, which are used typically as the benchmark for mercury capture study and field tests, were evaluated in this work (see Table 1). Two of the samples, FA1 and FA2, were collected from the Pennsylvania State University pulverized coal-fired demonstration boiler (20 MM Btu/h) when high volatile bituminous coal from the Middle Kittanning seam was utilized. Five of the fly ash samples were provided by Southern Company, including three samples collected from a boiler at Plant Miller in GA burning Powder River Basin (PRB) coal (DarkAsh99, DarkAsh00, and F9830) and two samples collected from a gasifier feeding lignite (Gasif1 and Gasif2). CPC-Filter and CPC-Knockout were collected from a gasifier fed with wood and provided by Community Power Corporation. Tra-Woodchar was provided by Tractebel Electricity & Gas International cogeneration facility in Northumberland, PA, which is burning wood. Five samples were generated in gasifiers and six were generated in boilers. The two lignite-based commercial activated carbon samples, Darco FGD and FGL, were provided by Norit Americas Inc.

The final sample, GTI-Woodchar was also a wood-based sample provided by Gas Technologies Institute. During characterization, it was noted that the GTI sample used in the current project did not have properties that matched the previously obtained data (*i.e.*, from the previous CPCPC project) for this sample. The sample was sieved during the previous project to separate aluminum beads from the char and it was deduced that it was these beads that were tested during this project. This conclusion was reached after noting the exceptionally low carbon and high

aluminum content of the sample when compared to the sample tested previously. It was subsequently determined that the separated ash tested previously was entirely consumed and could not be re-tested during this project.

Table 1. Generation conditions of the samples in this study.

Sample	Feed used	System
Gasif-1	Lignite	Gasifier
Gasif-2	Lignite	Gasifier
CPC-Filter	Wood	Gasifier
CPC-Knockout	Wood	Gasifier
GTI-Woodchar	Wood	Gasifier
Tra-WoodFA	Wood	Boiler
FA1	Bituminous	Boiler
FA2	Bituminous	Boiler
F9830	Subbit. (PRB)	Boiler
DarkAsh99	Subbit. (PRB)	Boiler
DarkAsh00	Subbit. (PRB)	Boiler
Darco FGD	Lignite	Activation
Darco FGL	Lignite	Activation

2.2. Characterization Methods

2.2.1. Loss-on-ignition

The loss-on-ignition (LOI) contents of the samples were determined according to the ASTM C311 procedure. Approximately 1 g of sample was oxidized in air for three hours at 800°C to constant weight in a muffle furnace. The LOI content was then calculated from the weight loss

of the sample after oxidation (Maroto-Valer *et al.*, 2004a and 2004b). The corresponding ash content was determined for each sample by subtracting the LOI (%) from 100%.

2.2.2. Inherent mercury content

Prior to any mercury capture tests, the inherent mercury content of all the samples was determined by using a cold vapor atomic absorption (CVAA) spectrophotometer according to EPA method 7470.

2.2.3. Elemental analysis

An elemental analysis was performed on all the samples to determine the concentrations of carbon, hydrogen, nitrogen, and sulfur. A LECO CHN-600 analyzer was used in accordance with ASTM method D 5373-02 to determine the carbon, hydrogen, and nitrogen weight percentages of each sample. A LECO Sulfur Determinator SC-132 was utilized in accordance with ASTM method D 5016-03 to determine the sulfur concentrations of the samples.

2.2.4. Major and minor elemental ash chemistry

The major and minor elemental ash chemistry analyses were determined by using a Leeman Labs PS3000UV inductively coupled plasma spectrometer (ICP). The samples were ashed at 900°C. The ash was then dissolved by a lithium metaborate fusion procedure into a solution that was injected into the ICP. The major and minor elements are reported on a percent oxide basis. This

does not mean that pure oxides are necessarily present in the original sample, but may be present in combination with other elements.

2.2.5. XPS surface chemistry analysis

Investigation into the surface chemistry of the samples was carried out by an XPS analysis. Each fly-ash powder was prepared by lightly pressing the powder onto a 3M double sided tape with a mortar and pestle. Loose powder was blown free with dry N₂ and then transferred to a sample plate for analysis. Uniform coverage of the 3M tape was verified using a stereo microscope. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) for the Kratos instrument to the integrated peak areas using linear background subtraction per ASTM E 995. These RSFs take into consideration the X-ray cross section and average mean free path of the photoelectrons. The instrumental transmission function of the spectrometer has been measured for each of the separate pass energies and applied to the samples to ensure reproducible results per ASTM E 2108-00. The approximate sampling depth under these conditions is 80Å. A survey scan was initially recorded for the samples to identify elements present and overall composition. The relative composition of the surface species were quantified from the high sensitivity scans and finally the chemical state of the carbon species were determined from the charge corrected hi-resolution scan of the C 1s (Hengestebeck, 2005).

2.2.6. Porosity studies

The porous texture of the char and activated char samples was characterized by conducting N₂ 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_T). The total specific surface area, S_T , was calculated using the multi-point BET equation in the relative pressure range 0.05-0.35.

2.3. Mercury Capture Studies

A test unit at the University of Nottingham, UK, was utilized to test the suite of samples for their mercury uptake capacities. The apparatus was designed to enable various novel sorbents to be assessed fairly rapidly for their mercury-adsorption capabilities (Snape, 2005). A schematic of the mercury vapor generation/adsorption system is shown in Figure 1. It operates at a temperature of 30°C and ensures a constant flow of carrier gas (N₂) through each of two mercury vapor generator bottles. The mercury-saturated nitrogen vapor from one bottle passes to the sample tube containing the sorbent being tested, which is maintained at 35°C. From here, the flow is channeled via a 3-way valve to the flow-through cell in the UV beam of an AAS, operated in cold vapor mode (Snape, 2005). The corresponding signal obtained from the analyzer represents the mercury concentration exiting the sorbent tube.

Figure 1. Schematic of the mercury test system at the University of Nottingham.

The outlet vapor stream from the other bottle by-passes the sorbent tube, flows through a second 3-way valve, then is introduced into the flow-through cell of the AAS. This signal obtained from the analyzer represents the sorbent tube inlet mercury concentration. A third nitrogen flow passes via a third 3-way valve into the flow-through cell and is used to check the instrument's baseline concentration (or zero). The operation of the valves is sequenced such that each of the three gas flows is presented to the flow through cell in a strictly timed rotation over a 7-minute cycle. When not being analyzed, the gas flowing through the 3-way valves is passed through an activated carbon trap to vent into a fume hood. The system is designed in this way to ensure a continuous flow of nitrogen through each vapor generator bottles, which minimizes fluctuations in the concentration of mercury vapor generated (Snape, 2005).

For this project, special sorbent tubes were designed with a diameter of 8.5 cm and a sorbent fixed bed length of 2 cm in order to decrease the pressure build-up behind the sample tube. Pressure build-up was being experienced due to the very small particle size of some of the samples in this collection, including the three PRB samples. The very fine particles were migrating through the tube in the standard sample tubes to eventually block the flow of vapor completely. A limiting flow rate of 40 mL/min for the mercury-saturated nitrogen vapor was determined using the newly designed sample tubes and the PRB samples.

3. Results and Discussion

3.1. LOI and Inherent Mercury Content

The LOI values of the char samples, as determined by the ASTM C311 procedure, are reported in Table 2. These values vary greatly among the samples from 0.66% for DarkAsh99 to 89.6% for CPC-Knockout. Some of the samples in this study have much higher LOI values than fly ashes reported in previous studies, which are typically less than 15% by weight. These samples were chosen intentionally in order to study fly ashes with very different properties. Generally, the biomass (wood-based) samples analyzed have higher LOI values than the coal-based samples.

The inherent mercury contents of the char samples were analyzed by CVAA spectrophotometry and the data is also presented in Table 2. The mercury contents are low, mainly below 0.1 ppm. The sample from the GTI gasifier using wood as feedstock, *i.e.*, GTI-Woodchar, has the highest

mercury content (2.84 ppm). The lignite-based commercial activated carbons, namely FGD and FGL, have very low mercury contents of ~ 0.01ppm.

Table 2. LOI and inherent mercury content of the studied samples.

Sample	LOI, wt%	Mercury, ppm
Gasif-1	8.4	0.01
Gasif-2	43.1	0.11
CPC-Filter	70.6	0.03
CPC-Knockout	89.6	0.02
GTI-Woodchar ^a	85.4	2.84
Tra-WoodFA	22.0	0.20
FA1	44.1	0.20
FA2	45.8	0.36
F9830	1.2	0.81
DarkAsh99	0.8	0.27
DarkAsh00	1.4	0.31
FGD	63.8	< 0.01 ^b
FGL	68.3	< 0.01 ^b

^aGTI-Woodchar data from previous project

^bBelow instrument detection level

3.2 Elemental Analysis

The elemental analysis of the char samples was conducted using a CHN-600 and a sulfur determinator SC-132 and the results are reported in Table 3 on a dry basis. Carbon content varies greatly among the samples, ranging from nearly 85% to less than 1% by weight. The sample with the highest carbon content, 84.77%, is CPC-Knockout from a wood-fed gasifier and the lowest at 0.23% is DarkAsh99 from a subbituminous PRB-fed boiler.

The hydrogen content of all the samples is less than 1% by weight with the exception of Gasif-2, which contains 2.28% hydrogen. The low hydrogen contents are expected based on previous fly ash studies; however, any trends that may be present in the hydrogen data are likely to be masked by the error of the analysis stemming from the very low hydrogen concentrations coupled with potential interferences from adsorbed moisture (Maroto-Valer *et al.*, 2001). The amount of nitrogen in all of the samples was measured to be less than 1%. The sulfur content of all the char samples was also less than 1% with the exception of the commercial activated carbons, Darco FGD and FGL, which were determined to have slightly over 1% sulfur by weight. The GTI-Woodchar sample contained the lowest sulfur content at < 0.01%.

Table 3. Elemental analysis data (dry-basis) – arranged by decreasing carbon content.

Sample	Ash (wt%)	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Sulfur (wt%)	Oxygen (diff%)
CPC-Knockout	10.4	84.77	0.06	0.48	0.02	4.37
CPC-Filter	29.4	65.04	0.13	0.26	0.10	5.14
FGD	36.2	62.49	0.11	0.61	1.11	--- ^a
FGL	31.7	61.52	0.50	0.44	1.10	4.82
FA1	37.3	55.77	0.15	0.73	0.47	5.65
FA2	54.2	54.04	0.22	0.55	0.50	--- ^a
Gasif-2	57.1	31.69	2.28	0.41	0.98	9.56
Tra-WoodFA	78.0	17.84	1.11	0.06	1.12	7.91
Gasif-1	91.6	9.47	< 0.01	0.07	0.82	--- ^a
GTI-Woodchar	98.4	0.58	< 0.01	0.03	< 0.01	1.03
F9830	98.8	0.51	< 0.01	< 0.01	0.72	--- ^a
DarkAsh00	98.6	0.25	< 0.01	< 0.01	0.78	0.38
DarkAsh99	99.2	0.23	< 0.01	< 0.01	0.77	--- ^a

^a No oxygen content is recorded because the total analysis is slightly greater than 100% due to rounding errors.

3.3. Major and Minor Elemental Ash Chemistry Analysis

The ash chemistry data, as determined by ICP spectroscopy and displayed in Table 4, shows significant variation among the samples for Al_2O_3 , CaO , and SiO_2 content. The Al_2O_3 values were below 20% for all of the samples with the exception of GTI-Woodchar, which measured 69.6%. It is interesting to note that this sample contained the highest inherent mercury content (2.81 ppm) and an exceptionally high Al_2O_3 concentration. The high value for this sample can be attributed to the aluminum oxide bed material that still remains in the sample. The subbituminous PRB-fed boiler char samples had between 19 – 19.5% Al_2O_3 and the remaining samples were below 13% with CPC-Knockout being the lowest at 1.1%. It may also be important to note that the PRB char samples had relatively high inherent mercury contents compared to other samples in this study.

SiO_2 concentrations also varied greatly among the char samples, with Gasif-1 having the highest value (42.9%) and the lowest values of 3.9% and 3.3% attributed to CPC-Filter and CPC-Knockout, respectively. The values of CaO ranged from less than 1% to a little over 24%. GTI-Woodchar, FA1, and FA2 had the lowest CaO concentrations measuring 0.6%, 0.9%, and 1.0%, respectively. The subbituminous PRB-fed boiler char samples had the highest concentrations ranging from 23.0% to 24.1%. Except for GTI-Woodchar, these samples contained the greatest inherent mercury contents. All of the char samples were determined to have very small concentrations of BaO , K_2O , MnO , Na_2O , P_2O_5 , SrO , and TiO_2 .

Table 4. Spectrochemical analysis (ash chemistry) data – expressed in volume %.

Sample	Al ₂ O ₃	BaO	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	SrO	TiO ₂
Gasif-1	12.5	0.5	13.5	8.4	1.6	3.9	0.1	3.6	0.2	42.9	0.3	0.6
Gasif-2	6.9	0.3	8.6	4.9	0.9	2.4	0.0	1.8	0.1	27.1	0.2	0.3
CPC-Filter	1.3	0.1	11.6	0.7	1.9	2.8	0.4	0.5	1.0	3.9	0.0	0.2
CPC-Knockout	1.1	0.1	5.3	0.4	1.4	1.3	0.2	0.3	0.4	3.3	0.0	0.1
GTI-Woodchar	69.9	0.0	0.6	4.1	0.2	0.1	0.0	0.3	0.1	14.9	0.0	3.2
Tra-WoodFA	6.0	0.1	12.9	3.1	3.8	1.9	0.5	0.7	1.1	36.3	0.0	0.5
FA1	11.5	0.2	0.9	3.2	0.7	0.4	0.0	0.2	0.0	19.3	0.0	0.5
FA2	11.8	0.2	1.0	3.8	0.7	0.4	0.0	0.2	0.0	21.2	0.0	0.5
F9830	19.2	0.7	23.1	6.1	0.5	5.0	0.0	1.8	1.2	37.2	0.3	1.4
DarkAsh99	19.5	0.7	23.0	7.7	0.6	4.5	0.0	1.9	1.1	39.4	0.3	1.5
DarkAsh00	19.1	0.7	24.1	6.9	0.5	4.8	0.0	1.9	1.0	37.2	0.3	1.5
FGD	5.3	0.1	5.5	2.5	0.3	1.4	0.1	0.3	0.0	13.2	0.1	0.4
FGL	4.4	0.1	5.3	2.6	0.2	1.3	0.0	0.2	0.0	10.8	0.1	0.3

3.4. XPS Surface Chemistry

The XPS compositional analysis of the ash powders from the high sensitivity scans are summarized in Table 5. This analysis is performed with the assumption that the surface species are homogeneously distributed in depth and laterally. From the charge-corrected binding energies, the non-carbon species detected on these ash powders included – silicates, aluminates, phosphates and sulfates, and lower levels of iron oxide and cobalt oxide and titania. Interestingly, the nitrogen present on the surface was at an energy consistent with a protonated amine or ammonia species and not as a nitrogen-oxide species that have been common in other ash samples (Hengestebeck, 2005).

Table 5. Concentration of elements detected on powders – expressed as relative atomic %.

Sample	C	N	O	S	F	Cl	Ca	Si	Al	P	Fe	Ti	Na	K	Mg	Ba	Co
DarkAsh99	14.5	0.0	52.2	6.4	0.6	0.0	7.4	6.8	4.1	1.6	1.6	0.1	1.9	0.2	2.0	0.2	0.0
DarkAshO0	15.8	0.0	51.4	6.1	0.6	0.0	8.9	6.8	4.2	1.3	0.9	0.2	2.0	0.1	1.4	0.2	0.0
F9830	16.7	0.1	51.0	6.9	0.7	0.0	7.3	6.4	3.7	1.1	0.9	0.2	1.4	0.1	3.3	0.1	0.0
Tra-WoodFA	48.1	0.0	34.3	1.0	0.0	0.6	4.6	4.2	2.1	0.1	0.3	0.0	0.2	2.7	1.9	0.0	0.0
Gasif-1	44.9	0.3	32.9	1.0	0.2	0.2	4.8	6.9	3.6	0.1	1.2	0.1	2.1	0.1	1.7	0.1	0.0
Gasif-2	55.4	0.4	29.1	1.0	0.1	0.0	2.8	5.7	2.6	0.2	0.7	0.1	0.5	0.0	1.5	0.0	0.0
FA2	63.7	0.6	25.2	0.4	0.2	0.1	0.9	3.9	3.4	0.1	1.0	0.2	0.1	0.0	0.0	0.0	0.2
FA1	66.5	0.7	23.0	0.2	0.2	0.0	0.9	3.4	2.9	0.1	0.7	0.1	0.0	0.0	1.0	0.0	0.2
FGL	81.8	0.4	13.2	0.7	0.0	0.0	1.7	1.1	0.8	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
FGD	82.3	0.4	12.1	0.5	0.0	0.0	1.6	1.5	1.1	0.0	0.2	0.0	0.1	0.0	0.0	0.0	0.0
CPC-Filter	87.0	0.2	10.0	0.1	0.0	0.3	1.6	0.1	0.0	0.0	0.1	0.0	0.1	0.5	0.0	0.0	0.0
CPC-Knockout	93.2	0.1	5.7	0.0	0.0	0.1	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0

Note: Hydrogen cannot be detected by XPS

3.5. BET Surface Areas and Porosity

Based on the N₂-adsorption isotherms, the surface area and pore volume of the char samples were calculated and are listed in Table 6. Corresponding to the high LOI and adsorption capability, CPC-Knockout has the highest surface area and pore volume, 243.2 m²/g and 0.238 ml/g, respectively, of all the samples. It confirms observations made previously by the authors that the remaining carbon in fly ash has generated a certain porosity during the combustion/gasification process (Maroto-Valer *et al.*, 2004b). The sample CPC-Knockout can be expected to have effective sorbent properties prior to any further treatment due to its porosity and surface area values. Another sample collected from the same facility, CPC-Filter, also has a high surface area and pore volume, 119.6 m²/g and 0.196 ml/g, respectively.

The two samples collected from Southern Company's gasifier, Gasif-1 and Gasif-2, have similar surface areas of 45.4 m²/g and 54.5 m²/g, respectively, although they have quite different LOI values, 8.42% and 43.1%, respectively. The three PRB samples collected from the Southern Company boiler, F9830, DarkAsh00, and DarkAsh99, have surface areas as low as 1 – 2 m²/g, which is expected from their low LOI values, which are less than 1.5% by weight. As expected, the Darco commercially activated carbons have the highest surface areas and pore volumes of the studied samples.

Table 6. Surface area and pore volume – listed in descending order.

Sample	S _{BET} , m ² /g	V _t , mL/g
Darco FGD	526	0.473
Darco FGL	476	0.411
CPC Knockout	243.2	0.238
CPC filter	119.6	0.196
Tra-WoodFA	77.4	0.072
Gasif-2	54.5	0.070
FA1	53.1	0.040
Gasif-1	45.4	0.060
FA2	25.5	0.020
F9830	2.1	0.003
DarkAsh00	1.1	0.002
DarkAsh99	0.9	0.002

3.6. Mercury Capture Studies

As previously discussed, each sample was tested for its mercury uptake capacity using a mercury generation/capture system located at the University of Nottingham, UK. The volume of the

sorbent bed was held constant and, because the samples in this study are of various particle sizes and densities, the mass of each sample required to fill the specified volume was noted. The time for mercury breakthrough was recorded and the mercury loading on the sorbent at the time of breakthrough was calculated. These results are displayed in Table 7.

Table 7. Mercury capture analysis.

Sample	Weight of sample, g	Time to breakthrough, s	Time to breakthrough, h	Hg loading, mg Hg	Hg loading, mg Hg per g sample
FGL	0.440	71210	19.78	1.32	3.00
FA2	0.512	60480	16.80	1.34	2.62
FA1	0.513	57185	15.88	1.28	2.50
FGD	0.455	37640	10.46	0.638	1.40
Gasif-1	0.885	978	0.27	0.02	0.023
Gasif-2	0.851	445	0.12	0.01	0.011
CPC-Knockout	0.096	150	0.04	ND ^a	ND
DarkAsh00	1.171	immediate	immediate	none	none
DarkAsh99	1.426	immediate	immediate	none	none
F9830	1.324	immediate	immediate	none	none
Tra-WoodFA	0.449	immediate	immediate	none	none
CPC-Filter	0.135	immediate	immediate	none	none

^aNot determined

The sample with the longest mercury breakthrough time and highest mercury mass loading was Darco FGL, one of the two commercial activated carbon samples in this study. Interestingly, the second and third best samples in terms of length of time to mercury breakthrough and total mercury loading are the Penn State fly ashes, FA1 and FA2. FA1 took an average of 15.9 hours until mercury breakthrough and it captured an average of 2.50 mg of Hg per gram. The FA2 sample did not experience mercury breakthrough until after an average of 16.8 hours and it captured on average a total of 2.62 mg of Hg per gram. The Penn State fly ashes even outperformed the second activated carbon sample, Darco FGD, in this study. The two Southern

Company gasifier samples, Gasif-1 and Gasif-2, were observed to have some mercury capture, although both were noted to experience mercury breakthrough in less than 30 minutes and had very little mercury adsorbed onto the sample at the time of breakthrough, 23 μg and 11 μg , respectively. Five of the samples – Tra-WoodFA, CPC-Filter, and the three PRB samples – demonstrated a mercury breakthrough immediately with negligible mercury loading at the time of breakthrough.

4. Correlations

A study done by Hassett and Eylands found that of their suite of samples, those with the highest LOI contents were the most effective mercury sorbents (1999). Mercury breakthrough was experienced after a very short test time on samples with LOI contents between 0.05 and 2% (by weight), and samples deemed nonsorbers had very low LOI values at around 0.02% (Hassett and Eylands, 1999). According to the results of the present study, the samples with the highest mercury capture and longest time to mercury breakthrough had relatively high LOI values, ranging from 43.1% for Gasif-2 to 89.6% for CPC-Knockout. The activated carbon samples had LOI values of 68.3% for Darco FGL and 63.8% for Darco FGD. The FA1 and FA2 samples had LOI values of 44.1% and 45.8%, respectively. Samples with a low LOI typically displayed immediate mercury breakthrough with little to no mercury retained on the sorbent at the time of breakthrough.

According to a study by Dunham *et al.* (2003), increased amounts of unburned carbon, reported as LOI content, in fly ash samples were positively correlated with increased mercury removal from flue gas for both bituminous and subbituminous coals. They also found that mercury tends to concentrate in the carbon-rich areas contained within the fly ash. Previous studies by Hower, *et al.* (2000a and 2000b) demonstrated that an increase in mercury capture onto fly ash is a function of increasing carbon content (% C, ultimate analysis). Since carbon content tends to increase with increasing LOI in a linear fashion, the trends in mercury uptake capacity are similar to those discussed above for LOI.

According to a study by Dunham *et al.* (2003), alumina and silica proved to be active promoters in the oxidation of elemental mercury. In general, they observed that many of the ash samples in their study oxidized elemental mercury; however, no capture of elemental mercury was observed without accompanying oxidation. The samples that adsorbed a significant amount of mercury vapor did not have outstanding values for alumina or silica compounds. The results of the ash chemistry analysis showed no significant correlations with mercury uptake capacities.

The surface chemistry results for the samples showed that all of the mercury adsorbing samples had the highest percentage of nitrogen atoms on the surface. FA1 had 0.7% atomic N, FA2 had 0.6% atomic N, and the activated carbon samples along with Gasif-2 displayed 0.4% atomic N for nitrogen. All of the other samples had lower or no nitrogen concentration on their surfaces. Referring to the results of the XPS analysis, it is noted that the nitrogen present on the surface of the fly ash samples resembled protonated amines or ammonia species, not the common nitrogen

oxide species seen in other ashes (Hengstebeck, 2005). As for the other elements on the surface, no clear correlations could be established.

The three samples with the largest surface areas and pore volumes, Darco FGD, Darco FGL, and CPC-Knockout, all were determined to uptake mercury vapor in the mercury capacity tests. FA1, FA2, and Gasif-2 had low to moderate surface areas and pore volumes, ranging from 25.5 m²/g and 0.020 mL/g for FA2 to 54.4 m²/g and 0.070 mL/g for Gasif-2.

5. Conclusions

Fly ash is being considered as a candidate for a low-cost, effective mercury vapor sorbent as an alternative to expensive activated carbons and as an alternative to disposal in landfills. The focus of this study was to better understand the properties of fly ashes, such as elemental analysis, porosity, and ash chemistry, that affect their mercury capacity.

A suite of fly ash samples was characterized extensively and tested for their ability to uptake mercury vapor. The result of this study was that a correlation exists between the carbon content and LOI values of the samples and their ability to capture mercury. The samples that adsorbed a significant amount of mercury had relatively high LOI values and carbon percentages. There may also be a relationship between the amount of nitrogen on the surface of the sample with its ability to uptake mercury vapor. The samples that demonstrated mercury capture had the highest nitrogen concentrations on the surface of all the samples. It may also be important that the

nitrogen species on the surface of the samples were observed to resemble protonated amines or ammonia species rather than the more common nitrogen oxides.

It also appears that the surface area and porosity of the samples play a role in mercury capture. The fly ashes with the three highest measured surface areas and pore volumes were observed to uptake mercury vapor. The remaining samples that captured mercury vapor had only moderate values for these two properties.

Overall, the properties with the greatest affect on mercury capture in this study were the carbon content or LOI of the sample, the amount of nitrogen on the surface of the fly ash, and the surface area and total pore volume of the sample. Modifications to improve the mercury capture of fly ash should focus on enhancing these properties.

6. Publications Resulting from this Project

1. A manuscript and presentation were prepared for the World of Coal Ash Conference in Lexington, Kentucky, which was held on April 11 – 14, 2005.
2. A manuscript has been prepared that focuses on correlations with fly ash properties and inherent mercury contents, which will be submitted for publication in *Energy & Fuels*.
3. A manuscript is being prepared that will be submitted to the American Chemical Society, Fuel Division Symposium on Chemistry of Carbon Materials and Nanomaterials, which will be held in Atlanta, GA on March 26 - 30, 2006.

7. Acknowledgements

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“Powdered Activated Carbon Recycling for Mercury Emissions Control”

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ABSTRACT

This research project addressed the removal of mercury present in air emissions (e.g., flue gas generated at coal-fired power plants) by engineering magnetic powdered activated carbon (MPAC) composites that have enhanced capacity for Hg and can be separated from fly ash and subsequently recycled. Currently powdered activated carbon (PAC) injection into the flue gas is the best available technology for mercury removal. It is envisioned that MPAC would be injected exactly the same as PAC. Iron precipitation was used to create the MPAC composites, and an optimum carbon to iron ratio (1:1) was determined based on magnetic strength and surface area measurements. The column tests for mercury removal using the MPACs showed a large difference in performance, with the carbon to iron ratio having the greatest impact on Hg adsorption. Additionally, TiO_2 was loaded onto the surface of some MPAC composites. These tests indicated that TiO_2 can improve performance of MPAC, however additional experiments are necessary to ascertain the full effects.

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EXECUTIVE SUMMARY

The research herein seeks to address the problems associated with PAC injection systems by substantially modifying the PAC's physical properties. First, the challenge of separating the PAC fraction from the fly ash is addressed by engineering magnetic PAC (MPAC) through iron impregnation/precipitation into the carbon's porous matrix and/or onto its surface. The MPAC particles, after cycling through the flue gas, can be collected by a magnetic drum, for example, to separate it from the fly ash. Not only will this enable the use of the fly ash for concrete production, it will also provide a method by which the MPAC composite can be recycled and reused. Because of the short contact times that commonly exist between the flue gas and the carbon particle (e.g., < 1 second), only a fraction of the carbon's surface is actually utilized in removing mercury. Recycling the MPAC to fully exploit its adsorption capacity before disposal offers a plausible means to decrease the mass of PAC that would be required on an annual basis to meet regulations. In summary, the MPAC in itself will promote conservation of resources and a significant reduction in expenditures.

The second goal of this study is to discern if PAC's capacity can be improved from iron enhanced catalysis via titanium dioxide (TiO_2) doping. It is well known that hydroxyl radicals, which are very powerful oxidants, can be generated on the surface of TiO_2 under UV radiation. Pitoniak et al. (2003) presents data that shows doping silica-based gels with TiO_2 enhances mercury uptake by oxidizing the adsorbed mercury, and that adsorption increases with each exhaustion/UV-enhanced regeneration cycle (up to 10 cycles). The advantage in this silica system is the transparent nature of the silica because the UV can penetrate into the substrate and activate the titania. It is reasonable to postulate that for PAC injection systems, Hg capture is likely to take place close to the carbon surface. Therefore, oxidation of the adsorbed mercury could increase the mercury uptake over the cycles.

The first quarter of this project focused on establishing the performance of virgin commercially available coal-based carbons for mercury removal in batch conditions as well as creating MPACs with adequate magnetic properties. In the second quarter, experiments continued in the testing of virgin carbons and additional MPACs were created. Several MPACs were tested for mercury removal using the batch column test stand, and significant Hg adsorption was found for the optimum MPAC. The effects of TiO_2 loading onto the MPACs were investigated in the third quarter. In the presence of UV 365 nm light, the MPAC with 1% loading of TiO_2 did perform better than the MPAC (3:1). The fourth quarter focused on two areas: additional MPAC characterization and bench-scale magnetic separation. Five MPACs were analyzed with a scanning electron microscope (SEM) and electron dispersion spectroscopy (EDS), which helped identify where the iron was located on individual MPAC particles. Bench-scale separation tests illustrated the potential for efficient MPAC recycling. Thorough dispersion of the iron throughout the carbon particles was the most important parameter for effective magnetic separation.

INTRODUCTION

Amongst the numerous hazardous air pollutants (HAPs) currently regulated by the EPA, elemental mercury and mercury containing compounds have recently been highlighted as significant due to their increasing rate of release, and the lack of adequate control technologies. Although the resulting quantity in the environment is usually low, it can transfer to various organisms, and then magnify up the food chain. For example, the concentration of accumulated mercury in some fish can reach levels that are millions of times greater than that in the water. The consumption of such fish by humans, and the resulting buildup of mercury in various tissues, leads to serious neurological and developmental effects such as losses of sensory or cognitive ability, tremors, inability to walk, convulsions, and even death (EPA, 1998). Methylmercury, the most common form of organic mercury, is almost completely incorporated into the blood stream, and can be transferred through the placenta and into all of the tissues of the fetus, including that of the brain (EPA, 2002). Because of the health concerns related to eating mercury contaminated fish, bans on fishing in certain regions such as in the Great Lakes have resulted in considerable losses to the economy (Nriagu, 1988; Nriagu and Pacyna., 1988). The EPA has estimated that nearly 87% of the anthropogenic mercury emissions are from sources such as waste and fossil fuel combustion. Recognizing this, control technologies have been employed in an effort to capture and dispose of the mercury found in combustion exhaust gases. Currently, powdered activated carbon (PAC) injection into the flue gas stream is the best available control technology for mercury removal. However, understanding that an estimated 3 kg of activated carbon, that is currently commercially available, is needed to remove 1 g of mercury (Chang et al., 1993; Brown et al., 1999), to meet regulations, it is anticipated that PAC injection will cost between \$2 and \$5 billion annually. Furthermore, PAC's low mercury adsorption efficiency, low applicable temperature range, slow adsorption rate, and lack of adequate regeneration technologies, all have sparked an interest in modifying the material to either decrease costs or improve its capacity in hopes for optimization.

Another shortcoming in using the current PAC injection system is the accumulation of the waste PAC in the fly ash. Fly ash, the fine particulate fraction of the coal combustion byproducts (CCBs), is collected from flue gas and then commonly sold for the production of concrete and other materials. By using fly ash instead of the lime, cement, or crushed stone materials that are typically used, energy and resources are conserved. However, when the collection devices are coupled with PAC injection systems, the quality of the collected matter deteriorates because of the large fraction of carbon in the ash; consequently, revenue generation by selling the fly ash becomes impossible. Current research geared towards separation technologies has yet to find an adequate method to isolate the PAC from the fly ash.

EXPERIMENTAL

Mercury Testing

The performance of PACs and MPACs for Hg removal was quantified by use of Engineering Performance Solutions' (EPS) column reactor shown in Figure 1. Preliminary studies included developing breakthrough curves for the various virgin PACs to determine their performance under typical flue gas conditions.

Figure 1. Mercury column test stand.

Prior to adsorption testing, the PAC was mixed with a 140 x 200 mesh sieved quartz sand (1/20 carbon to sand ratio) and then heated to the desired temperature (275 °F) for a minimum of 30 minutes. Once heated, high-grade nitrogen gas from a reservoir was passed through an elemental mercury reservoir to create a mercury vapor laden air with the desired concentration of Hg. The mercury vapor was joined with a heated water vapor line to create an environment with the desired relative humidity from a water bubbler and the combination was flowed downward through the packed bed glass column from the top to minimize channeling or selective flow through the column. The effluent stream from the column was passed through a mercury analyzer (Ra-915+ Zeeman Mercury Spectrometer (Ohio Lumex)) and mercury breakthrough curves were generated for comparison of the PAC samples.

MPAC Composites

Activated carbon/iron oxide composites were prepared by first dispersing a known weight ratio of iron species into 100 mL of deionized water. The solution was

continuously stirred using a magnetic stir rod and stir plate. Next, oven dried PAC was added to the slurry by adjusting the weight ratios in order to obtain activated carbon/iron oxide weight ratios of 1:1, 2:1, 3:1, 4:1, and 5:1. For example, a 1:1 composite sample included the addition of 9 g of FeCl_3 , 3 g of FeSO_4 , and 9 g of activated carbon. The solution was magnetically stirred for 30 minutes, and then NaOH (5 mol/L, 50 mL) was added dropwise to precipitate the iron oxide. After the solutions were tested for pH to ensure a value greater than 10, the composites were placed in an oven at 105 °C overnight.

The resultant material (i.e., activated carbon/iron oxide) was then ground using an IKA A11 basic grinder and then passed through a 325-mesh (45 μm) and collected on the 400-mesh sieve (38 μm) by mechanical shaking. The resulting average particle size for all samples was, therefore, equal to 42 μm . All samples were dried in an oven overnight at 105 °C in glass vials and subsequently placed in desiccators with septum caps while not in use.

MPAC Characterization

BET analyses were performed on a Quantachrome NOVA 2200 at -77 °C using nitrogen gas as the adsorbate. All samples were outgassed at 110°C for a minimum of 12 hours.

The magnetic strength of the composite samples was determined by use of a DC Milligauss Magnetometer (AlphaLab, Inc., Salt Lake City, UT). The portable meter's specifications included the measurement of the magnetic field (i.e., flux density) of a sample with a resolution of 0.01 milligauss (1 nanotesla) and a range of +/-2000 milligauss (200 microteslas). The composite samples were tested by holding two magnets on opposite ends of the sample vial for approximately 30 seconds and then subsequently removing the magnets at the same time and angle. The vial was held up to the meter and the maximum residual magnetic field reading was recorded. Almost all samples were saturated with the field used (i.e., a stronger field had no additional effect on residual magnetism).

MPAC samples were analyzed via SEM photographs to learn more about the deposition of the iron species on to the carbon surface. In addition, EDS analyses were used to probe the surface of the MPACs for elemental composition.

MPAC Separation

Once it was determined that MPAC could effectively remove Hg from gaseous streams, its ability to be separated from simulated fly ash was quantified using a bench-scale magnetic drum. Since the MPAC with the 1:1 (carbon/iron) ratio outperformed all others for Hg removal, it was the only one utilized in the separation tests. There were some variations examined however, as four different iron species were used to make MPACs with a ratio of one to one. The MPACs used and their properties are listed in Table 1.

Table 1. MPACs used in bench separation experiments.

Sample ID	GAC Precursor	Iron Precursor # 1	Iron Precursor # 2
A1	Carbochem LQ1240	Ferric Sulfate	Ferric Chloride
B2	Carbochem LQ1240	Ferric Oxide	Ferrous Oxide
C3	Carbochem LQ1240	Ferric Chloride	Ferrous Sulfate
D1	Carbochem LQ1240	Ferric Chloride	Ferrous Sulfate

To evaluate separation efficiency, samples were prepared by mixing one gram MPAC with 4 grams simulated fly ash; a very high ratio, but chosen to demonstrate proof of concept. The sample was mechanically agitated as it was passed under a rotating magnetic drum whereby the MPAC was drawn to the drum and separated from the fly ash. A conveyor belt attached to the drum removed the MPAC from the magnetic field and deposited it into a collection bin. Each portion was weighed and an efficiency percentage was calculated. The recovered MPAC was remixed with fresh fly ash in the same 1:4 (MPAC/ash) ratio, and cycled under the drum an additional three times. This gave an overall recovery percentage accounting for losses in all four cycles. Figure 2 shows a schematic of the separation.

Figure 2. Schematic of magnetic drum separation.

RESULTS AND DISCUSSION

Virgin PAC Performance for Mercury

PAC injection is the established technology in the treatment of mercury in flue gases at coal-fired power plants. Therefore, it was important to establish a baseline performance using PAC in order to properly elucidate MPAC's ability to remove mercury in the same test conditions. Several commercially available virgins PACs were tested in a variety of conditions. An example is in Figure 3, which shows the performance of one virgin coal-based activated carbon (Carbochem LQ 1240) for mercury adsorption; the carbon that was used as the precursor for the MPACs used throughout this project. Although initial breakthrough occurred after just a few minutes, the virgin PAC was able to continue adsorbing mercury from the air stream for over 5 hours. This trend in performance for mercury removal (long run time with a steady increase in effluent mercury concentration) was an excellent baseline for later comparisons to MPACs made from this carbon.

Figure 3. Mercury removal by a virgin coal-based activated carbon* using 1 g carbon, 20 g sand, and 3.6 sec (contact time).

*Carbochem LQ 1240

MPAC Performance for Mercury Adsorption

Carbochem LQ-1240 was used as the base material to create a series of MPAC composites with varying amounts of carbon and iron. Five MPACs with carbon to iron ratios of 1:1 to 5:1 were created and characterized (Table 2).

Table 2. BET surface areas and magnetic strengths of five MPACs and virgin PAC counterparts

Carbon	BET Surface Area (m ² /g)	Magnetic Strength (mgauss)
Virgin	917	0
1:1 Carbon to Iron Ratio	357	121
2:1 Carbon to Iron Ratio	290	53
3:1 Carbon to Iron Ratio	282	46
4:1 Carbon to Iron Ratio	255	28
5:1 Carbon to Iron Ratio	256	11

Breakthrough curves showed that the MPAC with the 1:1 ratio to be the best performer for mercury removal (Figure 4). In fact, for the trial shown below, mercury never broke through over the entire time tested. These results were confirmed in three additional trials.

Figure 4. Mercury breakthrough curves for five MPACs with increasing carbon content as compared to the virgin coal-based activated carbon. (1g carbon or MPAC, 20 g sand, 3.6 sec, 40 ppb Hg influent).

MPAC with TiO₂ for Mercury Performance

Advanced oxidation utilizing catalysts such as titanium dioxide is becoming increasingly popular in treatment of environmental problems, particularly for problems where conventional treatment methods do not meet performance expectations or result in high costs or wastes. The removal of mercury in air emissions from coal-fired power plants is one such example. Therefore, the effects of adding TiO₂ and UV with MPAC were investigated. Thus far in the research project, the capacity of the optimum performing MPAC (1:1) is not known as all tests have shown 100% elemental mercury removal. Therefore, in order to determine the impact of advanced oxidation with UV and TiO₂, other MPACs were used (2:1, 3:1), along with the virgin carbon (Carbochem LQ 1240).

These adsorbents now have several mechanisms in place to remove or react with the mercury present in the gas stream with carbon adsorption and oxidation via iron, TiO₂, and UV. Therefore it was important to investigate the effects of individual aspects of this process as well. First, the effects of using UV 365 nm were studied without TiO₂ present. Figure 5 shows two mercury breakthrough curves generated in the batch reactor both using the virgin activated carbon, but one with a UV 365 nm light on, and one without. The data indicates that UV 365 nm is not affecting mercury in the batch reactor.

Figure 5. Mercury breakthrough curves for the virgin activated carbon with and without a UV 365 nm bulb.

Next, the effects of just TiO₂ loaded onto a MPAC surface were studied. A MPAC (2:1) loaded with 1% TiO₂ reached exhaustion much more rapidly than the same MPAC without TiO₂. This indicates that the TiO₂ is limiting adsorption by the MPAC or oxidation by the iron present.

Figure 6. Effects of TiO_2 loaded onto a MPAC for mercury adsorption.

Lastly, a MPAC (3:1) loaded with TiO_2 was tested in the batch reactor for mercury performance with UV (Figure 7). The TiO_2 loaded MPAC performed better than the MPAC in the presence of a UV 365 nm bulb. This indicates that advanced oxidation is taking place on the surface with UV, which can potentially improve the overall efficiency of the MPAC by increasing the recycling iterations without sacrificing performance. Additional recycling of MPAC particles means improved mercury uptake per mass, which can lower treatment and disposal costs.

Figure 7. Effects of TiO_2 and UV radiation on mercury performance for a MPAC (3:1).

Despite the results shown in Figure 7, it is unclear at this time whether UV and TiO₂ would be necessary along with the MPAC. The UV and TiO₂ did improve mercury capacity, however the optimum MPAC (carbon:iron; 1:1) did not breakthrough in any trials. Therefore, the mercury capacity and thus the amount of potential recycling, is not yet known. Once the number of recycling iterations is better understood, a thorough cost analysis can be performed to determine if UV and TiO₂ would further enhance the MPAC technology.

MPAC Characterization

The EDS data provided some interesting results whereby Fe was detected, but the signal was relatively weak. This could suggest that the majority of the iron is depositing within the pore network of the activated carbon versus onto its surface. The SEM pictures revealed crystal formation on the MPAC surface, which was at first believed to be iron. However, the EDS data does not support this hypothesis. Rather, the EDS data suggests that the crystals on the MPAC surface are likely Na (sodium), which was used to precipitate the iron. The SEM pictures and EDS charts can be found in the Appendix.

MPAC Separation

The separation data for the four MPACs listed above are shown in Table 3. It was found that a fraction of the samples were not substantially affected by the magnetic field, resulting in much lower initial recoveries. The secondary recovery is the combined result of only the last three cycles, and the overall recovery combining all four cycles. Several samples showed excellent first round recoveries, explained by a much more homogenous distribution of magnetic properties. It is believed separation efficiencies can be improved by maximizing distribution through synthesis or adding an additional step in manufacturing to remove the insufficiently magnetic portion of the MPAC.

Table 3. Efficacy of MPAC separation.

MPAC Sample	Residual Magnetism (milligauss)	MPAC & Fly ash		MPAC Only	
A1	23	Initial	35%	Initial	29%
		Secondary	88%	Secondary	89%
		Overall	31%	Overall	26%
B2	777	Initial	98%	Initial	100%
		Secondary	97%	Secondary	101%
		Overall	96%	Overall	102%
C3	320	Initial	96%	Initial	96%
		Secondary	85%	Secondary	98%
		Overall	81%	Overall	94%
D1	48	Initial	64%	Initial	67%
		Secondary	84%	Secondary	87%
		Overall	50%	Overall	59%

Table 3 details the residual magnetism and recovery data for four MPACs tested in the bench-scale separation apparatus. The measured magnetism values show a strong relationship with the overall recovery found in the in batch tests with and without fly ash. The results for the different MPACs show a wide variety in magnetism and in the ability to be separated. The MPAC sample made with only the ferric (Fe^{3+}) ion (A1) had the lowest recovery, indicating the importance that both iron species be present in order to create particles with the greatest magnetic strength. Another important trend found in Table 3 is how similar the recovery data with and without fly ash present. This indicates that the ability of MPAC to be separated in these batch tests lies primarily in the homogeneity of the MPAC particles themselves. Thus when the iron is well distributed throughout the MPAC particles they can be separated very efficiently as evidenced by the most magnetic MPAC (B1). Optimizing the MPAC synthesis process can maximize the recovery while in use on-site. An additional refining step can be taken in the manufacturing of MPAC by magnetically separating the finished product to remove particles without sufficient iron.

PROJECT SUMMARY AND CONCLUSIONS

Overall, the results from the mercury testing and separation experiments indicated that MPAC has potential to improve mercury removal and reduce costs at coal-fired power plants in multiple means:

- Lower doses due to MPACs enhanced uptake
- Higher mass loading on MPAC versus PAC via recycling
- Lower disposal costs
- Magnetic separation maintains integrity of fly ash for future resale.

Specific project conclusions include:

- Bench-scale column reactor tests indicated that Hg adsorption is carbon specific; therefore Hg removal can be optimized with proper selection of the virgin carbon.
- Precipitation of Fe^{3+} and Fe^{2+} into the carbon pores and/or onto the carbon surface creates a composite (MPAC) adsorbent with adsorptive and magnetic properties.
- The 1:1 carbon to iron ratio MPAC composite out performed the virgin carbon in bench-scale tests, and therefore may be able to improve mercury removal, carbon efficiency, and retain the properties of the fly ash needed for concrete production.
- Loading TiO_2 onto the surface on MPACs can improve the performance for mercury in the presence on UV. However, it is unknown whether this improves performance on the optimum MPAC (1:1). Therefore, once breakthrough is established for the optimum MPAC, additional tests with TiO_2 loaded MPACs should follow.
- Bench-scale batch tests with a magnetic drum indicated that MPAC can be separated from a simulated fly ash at nearly 100% efficiency. The homogeneous distribution of the magnetic properties of the MPAC had the greatest impact on separation.

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APPENDIX*Carbochem 1:1 LQ 1240* 20,000x Magnification 6,000x Magnification 3000x Magnification EDS for 3000x Magnification

Carbochem 2:1 LQ 1240

20,000x Magnification

6,000x Magnification

3000x Magnification

EDS for 3000x Magnification

Carbochem 3:1 LQ 1240

20,000x Magnification

6,000x Magnification

3000x Magnification

EDS for 3000x Magnification

Carbochem 4:1 LQ 1240

20,000x Magnification

6,000x Magnification

3000x Magnification

EDS for 3000x Magnification

Carbochem 5:1 LQ 1240

20,000x Magnification

6,000x Magnification

3000x Magnification

EDS for 3000x Magnification