

ADVANCED GASIFICATION BY-PRODUCT UTILIZATION

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prepared by

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ABSTRACT

The results of laboratory investigations and supporting technical assessments conducted under DOE Subcontract No. DE-FG26-03NT41795 are reported for the period September 1, 2003 to August 31, 2004. This contract is with the University of Kentucky Research Foundation, which supports work with the University of Kentucky Center for Applied Energy Research and The Pennsylvania State University Energy Institute. The work described was part of a project entitled “Advanced Gasification By-Product Utilization”. This work involves the development of technologies for the separation and characterization of coal gasification slags from operating gasification units, activation of these materials to increase mercury and nitrogen oxide capture efficiency, assessment of these materials as sorbents for mercury and nitrogen oxides, and characterization of these materials for use as polymer fillers.

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PROJECT INTEGRATION

This University Coal Research project is a collaborative effort between the University of Kentucky Center for Applied Energy Research (CAER), The Pennsylvania State University Energy Institute, and industry collaborators supplying gasifier char samples. The project has progressed in such a way that UK has processed raw gasifier chars, retained some samples for direct testing, and supplied similar samples to PSU for characterization and further processing steps such as activation.

Principally, the objectives of the work at the CAER were to investigate the potential use of gasifier slag carbons as a source of low cost sorbent for Hg and NO_x capture from combustion flue gas and as a source of activated carbons. Primary objectives are to determine the relationship of surface area, pore size, pore size distribution, and mineral content on Hg storage of gasifier carbons and to define the site of Hg storage. The ability of gasifier slag carbon to capture NO_x and the effect of NO_x on Hg adsorption are secondary goals.

Since gasifier chars have already gone through a devolatilization process in a reducing atmosphere in the gasifier, they only require to be activated to be used as activated carbons. Therefore, the principal objective of the work at PSU is to characterize and utilize gasification slag carbons for the production of activated carbons and other carbon fillers. Increasing the surface area of gasifier carbons should improve their NO_x adsorption potential. Testing the Hg and NO_x adsorption potential of these activated gasifier carbons is a secondary objective of this work.

As the project progress, the activated carbons produced at PSU will be supplied to UK for further testing, and UK will provide additional char samples and sub-samples to PSU for activation and characterization. The division of tasks reduces overall overlap while still assuring redundant characterization and assessment to give an accurate view of the variability inherent to these types of materials. In order to have such a firm comparative basis between samples, the material A1 was chosen for use at both UK and PSU. In the next period, sample A3, which also exhibits good Hg uptake levels, will be used by both groups.

WORK PERFORMED AT THE UNIVERSITY OF KENTUCKY

Executive Summary

A number of different processes for control of Hg emissions from electric power generation are being investigated which involve the use of a sorbent, usually activated carbon, as the primary Hg capture step. One problem associated with the use of activated carbon for Hg flue gas control is its high cost. Two approaches to reducing these costs are reducing the required carbon to Hg ratio or the use of a low cost alternative sorbent. A potential source of less expensive sorbent material is the unburned carbon in gasifier char, which is the focus of this study. The CAER has studied the relationship between Hg capture and fly-ash characteristics and have demonstrated several fundamental relationships which should apply to gasifier chars. Highly significant correlations were found between the magnitude of Hg capture and C content for fly ashes, type of fly ash carbon, and the BET surface area. All these factors point to the possible utilization of high carbon gasifier char for Hg capture.

During the year, the Hg adsorption capacities of four gasifier slag carbon were compared with respect to their Hg capture potential. Two of the gasifier slag carbons, A1 and A3, had exceptional Hg capture capacities. The data indicated that mechanisms determining good Hg adsorption capacity for these carbons are complex. Some of the chemical characteristics of these gasifier slag carbons which our work and others have suggested as important in Hg adsorption on carbons are the carbon and sulfur content, the high oxygen content, the presence of either Cl^- or SO_4^{2-} or both. The carbon contents of A1 and A3 were 46 and 77% respectively and yet had nearly the same Hg adsorption capacity. This suggests that carbon content is not the sole determinant of Hg capture potential. High Cl^- , F, and oxygen in these sample may be important in Hg capture since they have been implicated in the oxidation of Hg^0 to Hg^{+2} which is easier to remove from gas streams.

The surface areas of both good Hg capturing carbons were over $100 \text{ m}^2/\text{g}$. However, the Hg capture capacities of A1 and A3 were higher than a specialty carbon developed specifically for Hg adsorption. The surface area of this specialty carbon was $570 \text{ m}^2/\text{g}$ which suggests that high surface areas may not be important. Similarly carbon B had higher surface area than A1 and A3 and did not adsorb Hg. However, some surface area must be required since sample A2 with a surface area of less than $25 \text{ m}^2/\text{g}$ did not absorb Hg. The total pore volumes of A1 and A3 were substantially greater than A2 and B. The greater pore volume was attributed to meso and macropores. Our previous work suggested that these pores were important in Hg adsorption.

Introduction

A number of different processes for control of Hg emissions from electric power generation are being investigated which involve the use of a sorbent usually activated carbon as the primary Hg capture step¹⁻³. One problem associated with the use of activated carbon for Hg flue gas control is its high cost. Two approaches to reducing the cost of the utilization of a sorbent for Hg capture are the tailoring of activated carbons for Hg sorption to reduce the carbon to Hg ratio^{4,5} and the use of a low cost alternative sorbent⁶⁻⁸. A potential source of less expensive Hg sorption material is the unburned carbon in gasifier char which is the focus of this study.

The CAER has studied the relationship between Hg capture and fly-ash characteristics and have demonstrated several fundamental relationships which should apply to gasifier chars. Highly significant correlations were found between the magnitude of Hg capture and C content for fly ashes, type of fly ash carbon, and the BET surface area⁹⁻¹². All these factors point to the possible utilization of high carbon gasifier char for Hg capture. Four gasifier slags were studied this year for their potential as Hg sorbents.

Mercury x-ray adsorption fine structure spectrometry (XAFS) has been used at the University of Kentucky as a direct, non-destructive probe of the local bonding and structure of Hg complexes involved in the adsorption of mercury species from combustion flue gases on sorbent materials¹³⁻¹⁶. Results indicated that the carbonaceous material in the fly ash is mostly responsible for the sorption of the mercury and provided evidence for different fractions in the carbon having different Hg sorption capabilities. The data also suggested sorption by aluminosilicates in the ash. Hg laden gasifier slag carbons produced during this work were submitted for XAFS to determine the binding sites of Hg on carbons.

The use of a carbon based sorbent for Hg capture from flue gas may have further benefits. Previous research at the CAER has shown that NO_x is captured from simulated flue gas by activated carbons at conditions which appear compatible with Hg adsorption¹⁷⁻¹⁹. Therefore, injection of active carbon may have added benefit of decreased NO_x emissions. This work will be started during the next project year.

During the year, the Hg adsorption capacities of four gasifier slag carbon were compared with respect to their Hg capture potential utilizing a Hg adsorption reactor at the CAER. These slag carbons will also be studied for NO_x adsorption alone and in conjunction with Hg capture during the next year. The data obtained will provide some basic information as to the feasibility of utilizing gasifier chars for Hg/NO_x capture. Another important aspect of Hg adsorption on gasifier char which will be addressed during this study is the thermal stability and leachability of the captured Hg. These issues will be the focus of future work through the characterization of the Hg bonding sites on the char by XAFS spectroscopy and the determination of the mobility of Hg from the char through thermal and leaching studies.

Experimental Methods

Optimization of Separation Process

At the time the original proposal was submitted, Charah, Inc. had installed and was operating a process to separate the gasification by-product produced at TECO's Polk Station. The processing plant produced three distinct products; coarse frit or slag ($> 850 \mu\text{m}$), an intermediate size high carbon fuel ($> 75 \mu\text{m}$, $< 850 \mu\text{m}$) and fines ($< 75 \mu\text{m}$). The coarse frit and high carbon fuel were utilized or marketed while the fines were landfilled. The proposed research focused on evaluating the fines in order to identify potential upgrading alternatives that would enable beneficial reuse (Task 1 and 2).

Charah, Inc. successfully operated the processing plant to remediate the 140K ton stockpile of slag stored at the Polk site along with daily production and completed the remediation project in late summer, 2004. At that time, a decision was made by TECO management to purchase the processing plant and assume operating responsibilities. Leading up to this change in ownership, several modifications were made to the processing plant in response to changes in gasifier operation. The construction of additional oxygen generating capacity at Polk now enables the carbon fuel as well as the fines to be recirculated back to the gasifier as supplemental fuel. Thus the need to segregate the high carbon fuel from the fines was eliminated (requiring modification of Task 2 as proposed). Since the processing plant no longer produces a separate fines product, it was necessary to secure a similar material from an alternative source.

The Eastman Chemical gasifiers operated at the Kingspost, TN site are similar in design to the Chevron-Texaco gasifier operated at Polk, although there are significant differences in the operation of the gasifiers at both sites since the primary objective at Polk Station is to produce electricity while the Eastman gasifiers produce syngas as a feedstock for chemical production.

At the Eastman site, molten slag is removed from the gasifier to a quench tank which is emptied at half-hour intervals through a lock hopper. The quenched slag drops into a settling tank and coarse material settles to the bottom where it is removed by a drag conveyor. Fine suspended solids ($< 150 \mu\text{m}$) are removed as a slurry, are flocculated, filtered on vacuum drum filters and disposed. Since the fines once produced at Polk Station are no longer available and there is no current or historical use for the filter cake produced as a by-product of gasification at Eastman, the Eastman substrate will be characterized and evaluated to identify any potential beneficial reuse options in accordance with the original objectives of the proposal.

Hg adsorption testing of experimental materials A Hg adsorption reactor (Figure 1.1) was used to test as-received gasifier carbons. The device is constructed completely of Teflon tubing and fittings. The major components comprise a Hg permeation tube (VICI Metronics) maintained at a constant temperature in a hot oil bath, a 3/8-inch Teflon fixed bed reactor with quick connect fittings, a VM3000 continuous Hg vapor monitor, and a computer driven data acquisition system. The entire device is heat traced and insulated to maintain a constant temperature throughout the system. Adsorption temperatures up to 200°C are possible. The concentration of Hg^0 vapor can be regulated by the temperature of the permeation tube and dilution of the Hg^0 vapor with a purge gas. The system can be operated continuously 24 hours a day for multiple days. The entire system was tested for Hg retention and was found inert to Hg adsorption.

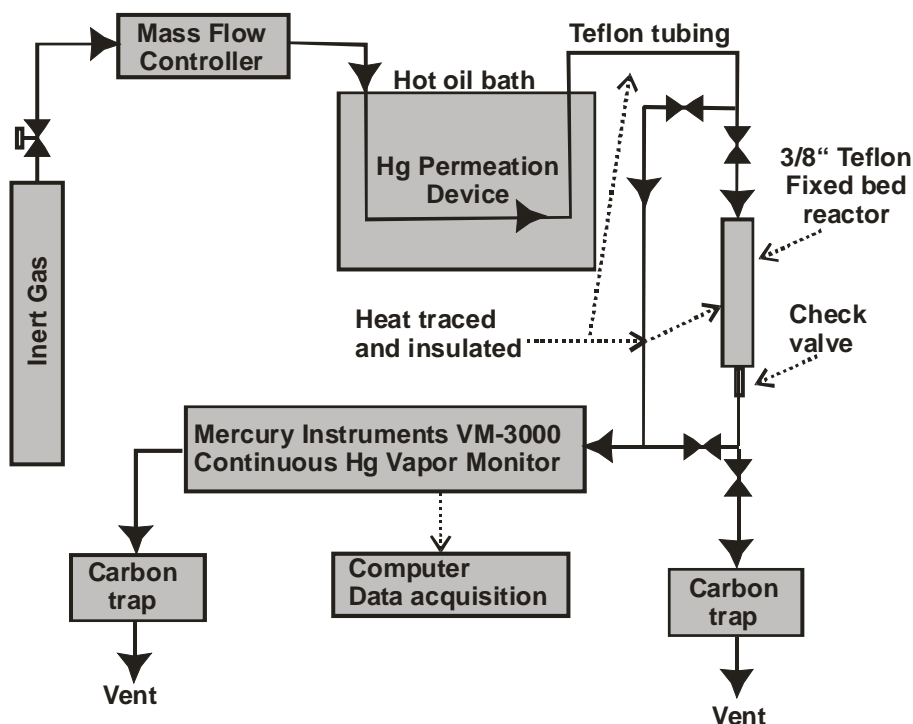


Figure 1.1. Mercury adsorption testing apparatus with continuous Hg vapor monitoring

The device was operated under the following conditions to compare the adsorption capacities of the gasifier carbons: a Hg concentration of 200 ug/m^3 at 50°C ; UPH air as the carrier gas at 75 ml/min metered at room temperature and pressure; and 100 mg of gasifier slag carbon. The Hg concentration in the gas exiting the fixed bed reactor was continuously monitored with data acquired by computer every second. Adsorption capacities were compared as the amount of Hg captured on the char at 10% breakthrough from the reactor of the Hg concentration in the adsorption gas. The data was normalized for the weight of the bed. Hg laden sorbent were analyzed for Hg concentration by x-ray fluorescence (XRF) analysis and standard procedures.

Samples for XAFS were generated under slightly different conditions necessitated by the requirement of larger sample for XAFS analysis. The reactor was loaded with 500 mg carbon and Hg vapor concentration was increased to 300 ug/m^3 in order to decrease the adsorption time for breakthrough with the larger sample size when gasifier slag carbons with high Hg adsorption capacities were used. Otherwise conditions were the same.

Chemical and physical characterization of the experimental materials All as received gasifier carbons were submitted to chemical analysis for ultimate, proximate, forms of sulfur, and anions analyses. Surface areas were done according to the Brunauer, Emmett, and Teller (BET) method²⁰ and pore size distribution by density functional theory (DFT) using Micromeritics DFT Plus software program²¹.

In order to define the relationship between Hg and adsorption sites on the gasifier carbons, two gasifier carbons, A1 and A2 loaded with Hg, were submitted for x-ray adsorption fine structure spectrometry (XAFS) along with a control sample not exposed to Hg.

Results and Discussion

Four different gasifier carbons, labeled A1, A2, A3 and B, were studied. Two of the gasifier slag carbons were separated into different particle size fractions. The particle size fractions were as follows: A1 (-20+80), A2 (-20+80), A2 (-60), A2 (-80), A3 (-20+80), B (-20+80), B (soot), B (-80). The elemental analyses of the four gasifier carbons are shown in Figure 1.2. Carbon content which is thought to be important in Hg capture varied from 46 to 77%. The %O by difference was high in samples A1 and A3. A1 was high in Cl^- and F^- (Figure 1.3). Chlorine has been implicated in good Hg capture whereas A3 was high in SO_4^{2-} , another anion which has been associated with good Hg adsorption. Most of the S in the samples was associated with SO_4^{2-} .

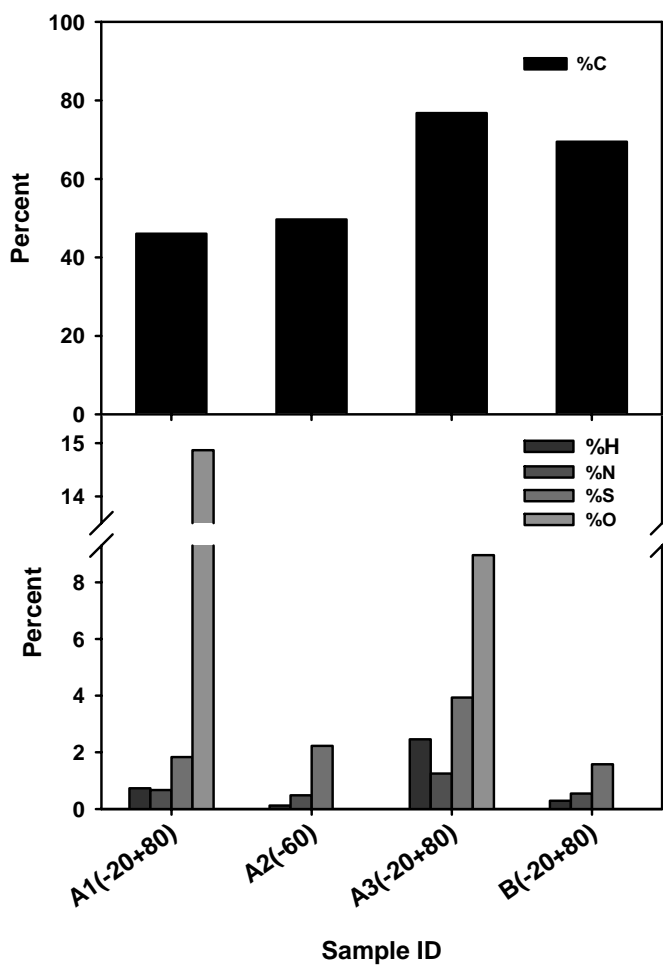


Figure 1.2. Elemental analysis of gasifier carbons.

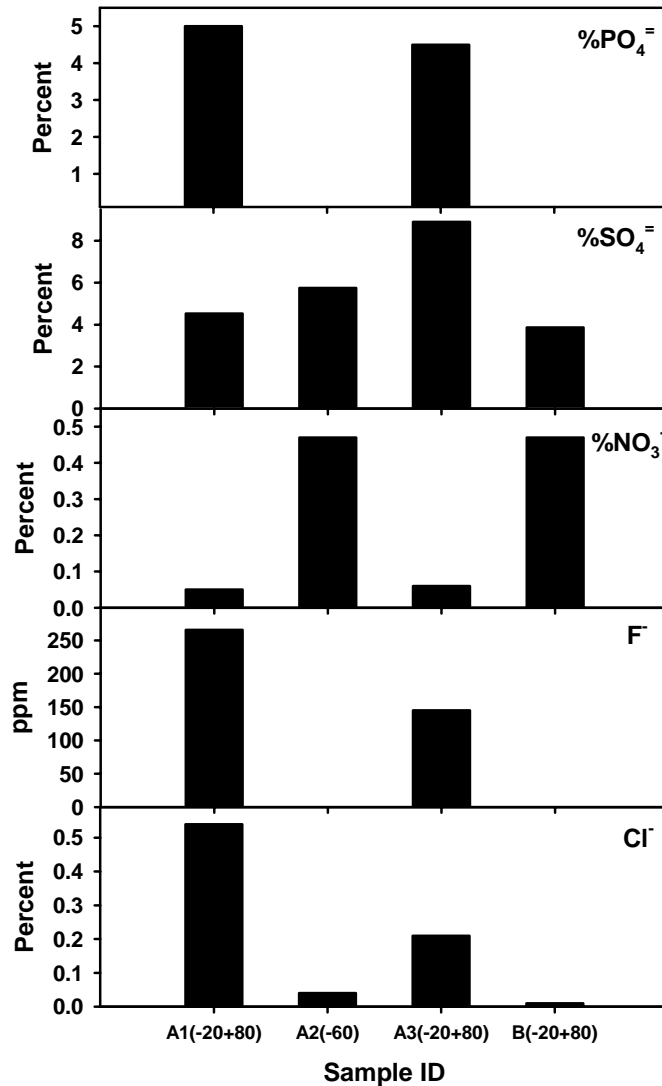


Figure 1.3. Anion analysis of gasifier carbons.

All samples were subjected to BET surface area shown in Figure 1.4. Gasifier slag carbon, A2, had lower surface area than carbons A1, A3, and B. A2 and B, had lower total pore volume than A1 and A3 which had much larger meso and macropore volumes than A2 and B (Figure 1.5). These data will be discussed in relation to the Hg adsorption capacities of the carbons.

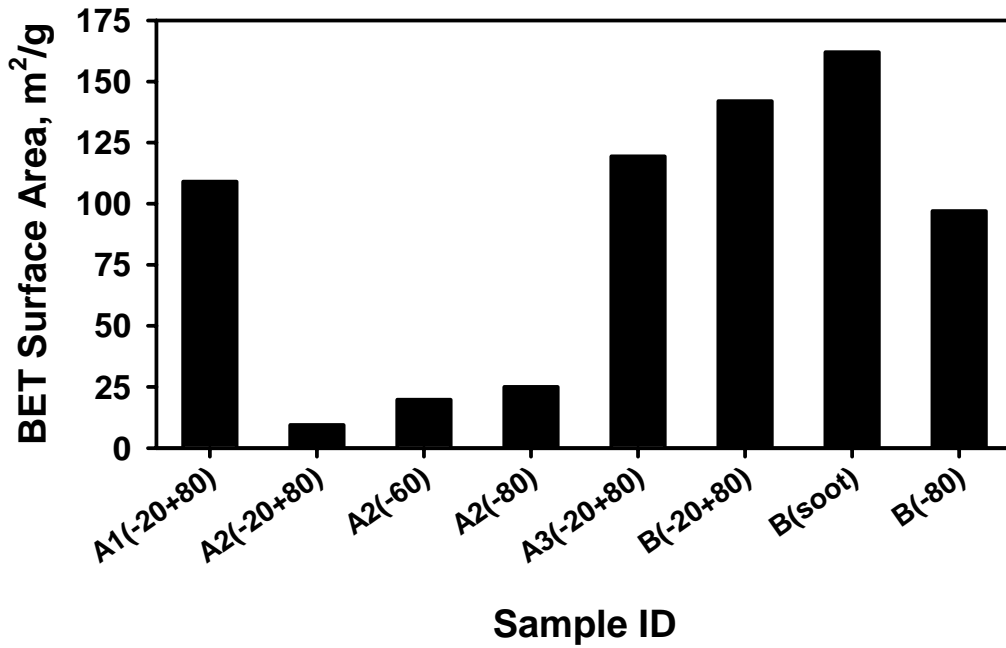


Figure 1.4. BET surface areas of all carbons studied.

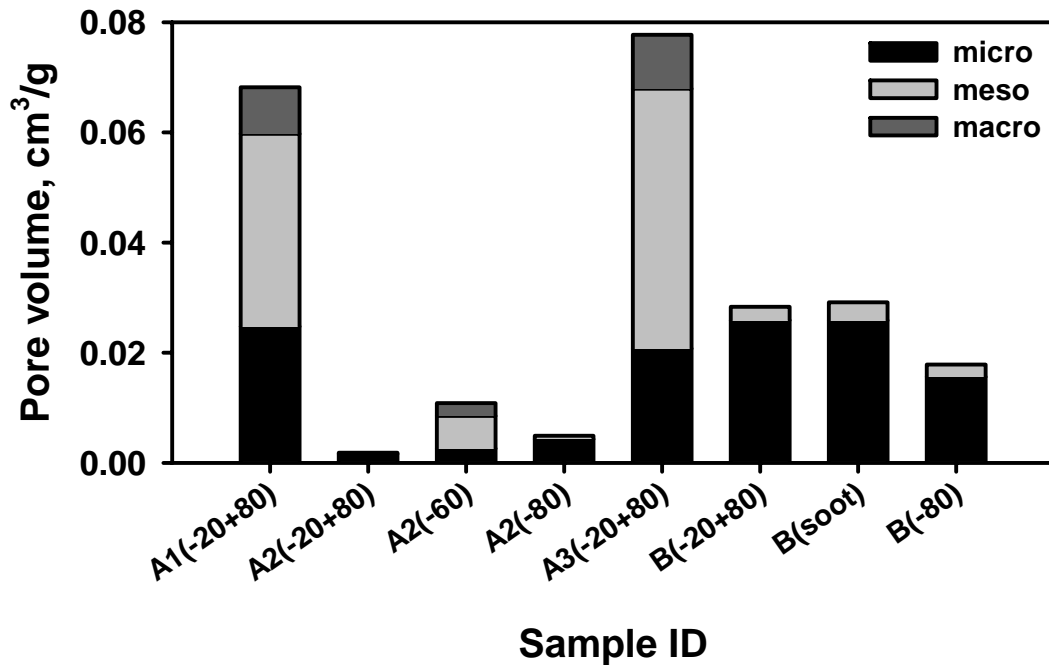


Figure 1.5. Pore size distribution of gasifier slag carbons.

Hg adsorption capacities were compared at 10% breakthrough (20 ug/m^3) of the concentration of the Hg in the gas leaving the Hg permeation cell (200 ug/m^3). Figure 1.6 shows the concentration of Hg in the gas leaving the adsorption reactor containing a carbon (A3) with good adsorption capacity. Breakthrough of 20 ug/m^3 of Hg occurred 19.8 days from the start of the test and the concentration of Hg in the gas leaving the reactor was zero for 3 days before some Hg was detected by the Hg vapor analyzer. However, with a poor Hg adsorbing carbon (A2) 10% breakthrough occurred very quickly (2 hours) and the concentration of Hg in the gas leaving the reactor never went below 7 ug/m^3 (Figure 1.7).

The concentration of Hg in all gasifier carbons tested for Hg adsorption capacities was determined by XRF. The data agreed with the results from the adsorption testing with poor absorbers with rapid breakthrough capturing little Hg and good absorbers being loaded with Hg (Figure 1.8). Carbon A1 and A3 contained $1500+$ ppm Hg whereas the concentration of Hg in the rest of the carbons was 200 ppm or less at the 10% breakthrough point.

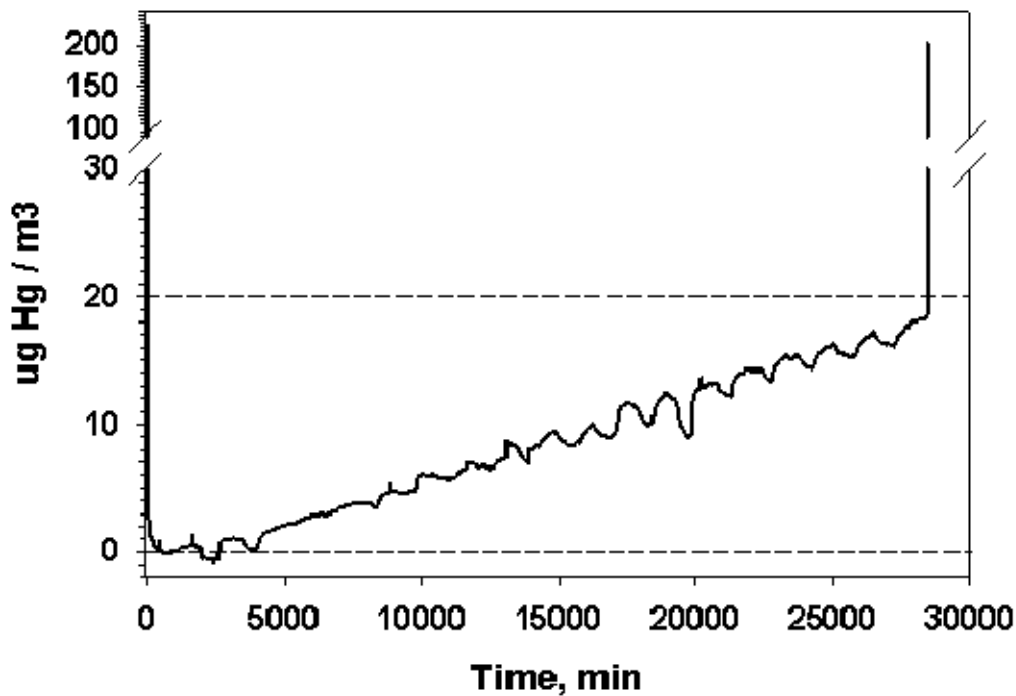


Figure 1.6. Adsorption curve for A3 (-20+80) gasifier carbon.

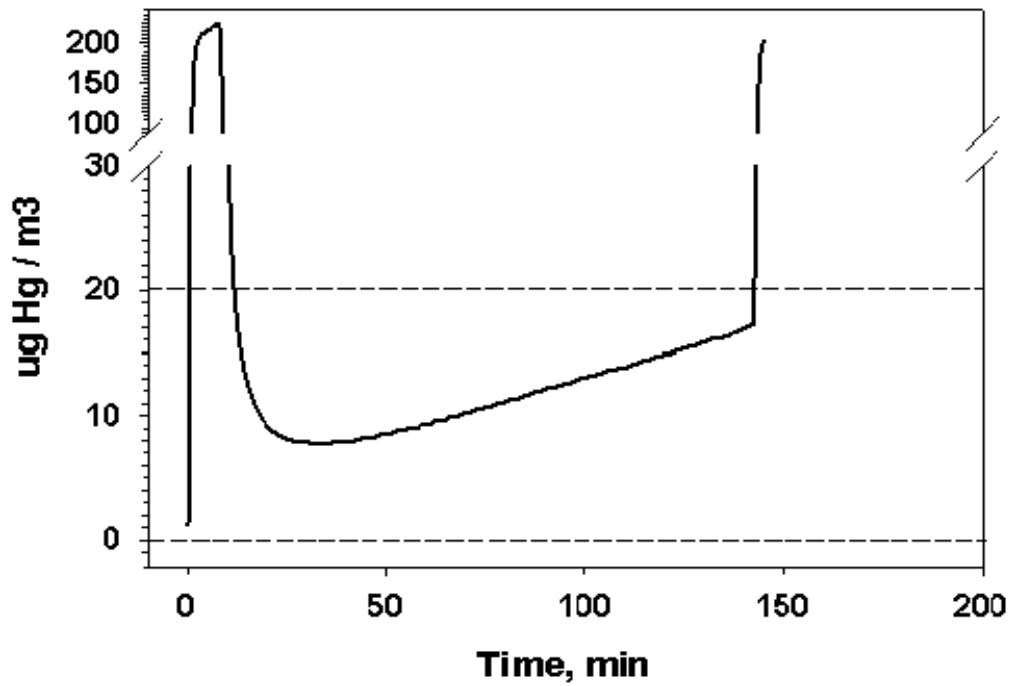


Figure 1.7. Adsorption curve for A2 (-60) gasifier carbon

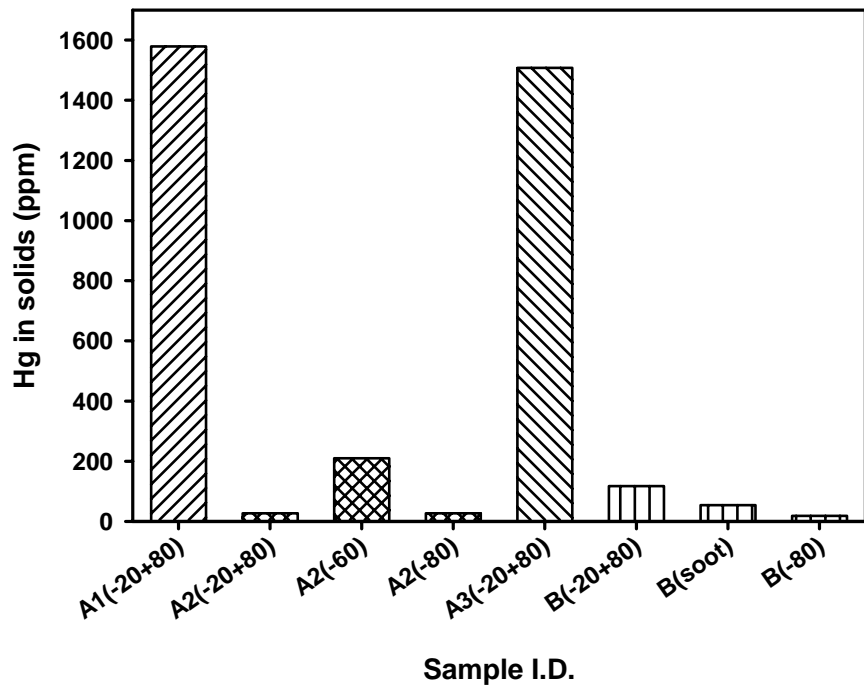


Figure 1.8. Comparison of Hg capture potential of different gasifier carbons.

Conclusions

Two of the gasifier slag carbons, A1 and A3, had exceptional Hg capture capacities. The data indicated that good Hg adsorption capacity for these carbons is complex. Some of the chemical characteristics of these gasifier slag carbons which our work and others have suggested as important in Hg adsorption on carbons are the carbon and sulfur content, the high oxygen content, the presence of either Cl^- or SO_4^{2-} or both. The carbon contents of A1 and A3 were 46 and 77% respectively and yet had nearly the same Hg adsorption capacity. This suggests that carbon content is not the sole determinant of Hg capture potential. High Cl, F, and oxygen in these sample may be important in Hg capture since they have been implicated in the oxidation of Hg^0 to Hg^{+2} which is easier to remove from gas streams.

The surface areas of both good Hg capturing carbons were over $100 \text{ m}^2/\text{g}$. However, the Hg capture capacities of A1 and A3 were higher than a specialty carbon developed specifically for Hg adsorption which was used as part of a previous study²². The surface area of this specialty carbon was $570 \text{ m}^2/\text{g}$ which suggests that high surface areas may not be important. Similarly carbon B had higher surface area than A1 and A3 and did not adsorb Hg. However, some surface area must be required since sample A2 with a surface area of less than $25 \text{ m}^2/\text{g}$ did not adsorb Hg. As Figure 1.5 shows the pore volumes of A1 and A3 were substantially greater than A2 and B. The greater pore volume was attributed to meso and macropores. Our previous work suggested that these pores were important in Hg adsorption.

The relationship of surface area, pore size, and pore size distribution will be explored during the coming year in an effort to define the site of Hg storage. The results from XAFS should shed light on the Hg adsorption sites in these gasifier slag carbons. The current results are encouraging for the use of these carbons in the control of Hg emissions from electric power plants.

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WORK PERFORMED AT THE PENNSYLVANIA STATE UNIVERSITY

Executive Summary

The increasing role of coal as a source of energy in the 21st century will demand environmental and cost-effective strategies for the use of combustion and gasification chars. Unfortunately, these chars are nowadays regarded as a waste product and their fate is mainly disposal, due to the present lack of efficient routes for their utilization. However, gasification chars are a potential precursor for the production of adsorbent carbons, since they have gone through a devolatilization process while in the gasifier, and therefore only require to be activated. Accordingly, the principal objective of this work was to characterize and utilize gasification chars for the production of activated carbons.

The gasification char sample, A1, was analyzed using LOI (loss-on-ignition), proximate, ultimate, and petrographic analyses. The porous properties of the sample, such as surface area and total pore volume, were characterized by N₂ adsorption isotherms at 77 K. The LOI value of the sample was 58.71%. The proximate analysis showed that the sample had very low moisture content, 1.90%. The ultimate analysis showed that the gasification char consisted mainly of carbon with very little hydrogen, nitrogen, sulfur and oxygen. The results of petrographic analysis indicated that the sample was mainly anisotropic (60.2 vol.%) and was derived from different ranks of coal, including high-volatile and medium-volatile bituminous coals. A considerable amount of petroleum coke (6.3%) was also observed in the ash specimen.

In addition, the potential use of gasification chars as precursor for activated carbon was investigated. After steam activation, the surface area was increased to 427 m²/g as compared to 153 m²/g for the parent sample. The porosity of the resultant activated carbons was related to the activation conditions used. It was observed that the surface area of activated cash sample increased with activation time, and reached a maximum value at 120 minutes. Increasing the activation time over 120 minutes resulted in a decrease of the surface area.

Introduction

Coal is the most abundant fossil fuel resource in the US, and therefore it will play an even increasing role as a source of energy in the 21st century. Coal gasification offers one of the most versatile and cleanest ways to convert the energy content of coal into electricity, hydrogen, and other energy forms. Coal gasification electric power plants are now operating commercially in the United States and in other nations, and many experts predict that coal gasification will be at the heart of the future generations of clean coal technology plants for several decades into the future. The U.S. Department of Energy's Office of Fossil Energy has turned its attention to future gasification concepts that offer significant improvements in efficiency, fuel flexibility and economics (www.fe.doe.gov). The potential use of the chars produced from gasification has to be addressed.

Gasification chars are a potential precursor for the production of adsorbent carbons, as described here. The global consumption of activated carbons is over 350,000 tons and is estimated to rise 7% annually (Derbyshire, 1995). The main reason for this expanding market is the ubiquitous use of activated carbons as adsorbent materials in a broad range of increasing household, medical, industrial, military and scientific applications. These range from gas-phase adsorption in household air-conditioning equipment and industrial emissions control, to liquid-phase adsorption for water treatment and even gold recovery. Therefore, due to the expanding market for activated carbons, especially in applications related to environmental protection, such as air and water purification, new precursors are being sought. The conventional production of activated carbons consists of a two-step process that includes a devolatilization of the raw materials, followed by an activation step. In contrast, gasification chars only require a one-step activation process, since they have already gone through a devolatilization process while in the gasifier, and therefore only require to be activated. Furthermore, the average price for a ton of activated carbon ranges from \$500 up to \$4000 (Derbyshire, 1995), which implies a potential 50-400 fold increase compared to the price of the ash (currently \$10-20/ton). Accordingly, this work addresses the characterization of gasifier chars and their potential use as precursor for the production of adsorbent carbons.

Experimental

Sample characterization

The characterization conducted in this study involved LOI analysis, proximate, ultimate and porosity characterization, as described below.

LOI Analysis

The LOI content was determined according to the ASTM C 311 (ASTM C 311) procedure. The analysis was conducted in duplicate. For samples commonly derived from Eastern U.S. coals, the LOI value essentially equates to carbon content.

According to ASTM C 311, a weighed sample was dried to constant weight in an oven at 105 to 110°C to remove the moisture in the sample. Then, the moisture-free sample was ignited to constant mass in an uncovered porcelain crucible in a muffle furnace at a controlled temperature (750±50°C). After a minimum of 15 minutes heating, the percentage of LOI was calculated to the nearest 0.1, according to

$$\text{Loss on ignition, \%} = (A/B) * 100 \quad (2.1)$$

A = loss in mass between 105 and 750°C;

B = mass of moisture-free sample used.

Proximate Analysis

The proximate analysis was performed using a LECO MAC-400 proximate analyzer, including moisture, volatiles, ash and fixed carbon. The values were determined by weighing the sample in a temperature- and atmosphere-controlled environment.

Before an analysis was begun, an empty crucible was placed on the turntable. The furnace was purged with nitrogen and the furnace temperature was raised to 106°C. The sample was continuously and automatically rotated and weighed inside the furnace. Weight loss during this period could be attributed to loss of moisture in the sample. The empty reference crucible was also being weighed, and change in the weight of this crucible was used to correct the result obtained from the sample. When the corrected sample weight stopped changing, the moisture analysis was ended and moisture result was computed for the sample. A cover was placed on the crucible and the temperature was then increased to 950°C in a nitrogen atmosphere to drive off the volatile matter in the sample. The weighing procedure was identical to that during the moisture analysis.

When the temperature was reduced to 600°C, the crucible cover was removed. After the temperature was increased to 750°C, and the atmosphere was changed to oxygen, the carbon in the sample began to combust. The sample was continuously weighed as it was in the moisture analysis. When the corrected weight stabilized, the weight loss was attributed to fixed carbon, and the remaining weight was considered ash. Based on these weights, the sample's ash and fixed carbon contents were then computed.

Ultimate Analyses

The carbon, hydrogen, and nitrogen contents in the sample were measured using a LECO CHN-600 elemental analyzer. The determination of carbon, hydrogen, and nitrogen was

made by burning a known weight of sample in pure oxygen at ~950°C after grinding to 60 mesh (~250 μ m) in accordance with ASTM Method D 2013 (ASTM D 3180-89). Carbon dioxide, water vapor, oxides of nitrogen, elemental nitrogen, and oxides of sulfur were possible products of combustion. Oxides of sulfur were removed with calcium oxide in the secondary combustion zone so that water vapor cannot combine to form sulfuric acid. The remaining gases of combustion were collected in a ballast volume. For the nitrogen determination, a 10cc aliquot was taken. The aliquot was carried by helium into a reagent train for the removal of O₂, CO₂, H₂O and the reduction of NO_x to N₂. The thermal conductivity cell was used for measuring the remaining elemental nitrogen. At the same time as the nitrogen measurement, the carbon and hydrogen infrared cells measured CO₂ and H₂O levels. The results for the three elements were displayed in weight percent. This method gives the total percentages of carbon, hydrogen, and nitrogen in the organic sample as analyzed, and includes the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates. If the moisture content is known, results can be calculated on a dry basis.

The sulfur content was determined using a LECO SC-32 and SC-132, which are microprocessor-based instruments. The sample was combusted in an oxygen atmosphere where the sulfur oxidized to SO₂. After moisture and dust were removed, SO₂ gas was then measured by a solid-state infrared detector. It detected total sulfur, as sulfur dioxide, continuously.

Petrographic Analysis

The petrographic composition analysis was conducted using a Zeiss Universal research microscope at 800X magnification in reflected, white-light illumination and oil immersion. The carbon particles were grouped as isotropic and anisotropic carbon.

Before conducting the analyses, the samples were prepared by mixing them with a cold-setting epoxy resin. The specimens were then impregnated in vacuum and centrifuged to produce a density/particle-size graded sample upon hardening of the epoxy. Petrographic mounts were prepared by cutting the impregnated samples in half to expose the density-graded particles, mixed with epoxy, and polished for microscopic examination. Samples were ground and polished using a succession of grit papers (400 and 600 silicon carbide) and alumina polishing compounds (0.3 μ m on a medium nap and 0.05 μ m on silk).

Porosity Characterization

The porosity was characterized by obtaining N₂ adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The BET surface area was calculated from the BET equation, using the adsorption points at the relative pressures (P/P₀) 0.05-0.35. The values reported were corrected to a mineral-free basis. The total pore volume, V_{TOT}, was calculated using the bulk density of nitrogen at 77K from the amount of vapor adsorbed at the relative pressure of 0.95. The average pore diameter was calculated from the pore volume assuming the pore was cylindrical, and then, the average pore diameter was expressed as equation 2.2.

$$\overline{D}_n = \frac{4V_p}{S} \quad (2.2)$$

where

\overline{D}_n = average pore diameter;

V_p = total pore volume;

S = BET surface area.

The mesopore (pores 2–50 nm in width) and micropore (pores <2 nm in width) volumes were calculated using the BJH (Barrett-Joyner-Halenda) and H-K (Horvath-Kawazoe) equations, respectively (Maroto-Valer et al, 1999b), and the pore volumes were derived from the α_s method using a nongraphitized carbon black sample as standard (Kruk et al, 1997).

Preparation of Activated Carbon

There are two principal processes for the preparation of activated carbon: physical and chemical activation. The agents used commonly in physical activation processes are steam and CO₂, while KOH and ZnCl₂ are used in chemical activation processes (Ahmadpour, et al., 1996). In this work, steam was selected to prepare activated carbon from gasification chars.

The activation system used for the steam was a stainless steel reactor, which was heated by a horizontal furnace that has a 9 cm inside diameter. The versatility of the design allowed the use of different particle size, activating agent, heat treatment, residence time, flow rate of activation agent and amount of sample. Typically 2 to 3 g of sample was placed in the reactor that was then placed in the middle of the furnace to assure a uniform temperature zone. The furnace was then heated to the desired activation temperature under a flow of an inert gas. A thermocouple was used to monitor the temperature of the reaction zone inside the reactor. When the sample reached the desired activation temperature, a flow of steam was then introduced into the reactor. For this purpose, a HPLC pump was used to provide water at a constant flow rate of 2.5–3.0 ml/min, and a steam generator to provide the activation agent. The steam was swept through the furnace using a flow of N₂ and introduced from the bottom of the reactor to react with unburned carbon sample. During the activation process, liquid products were condensed, while gases were vented off. After a certain activation period (60-180 minutes), the flow of steam was stopped, the furnace was shut off and the reactor was quenched by N₂ inside the reactor (Lu, 2003; Zhang, et al., 2003).

Characterization of Activated Carbons

The porous properties of the activated carbons produced under controlled conditions were characterized following the same procedures described above. for the parent sample. The characterization includes the BET surface area S_{BET} , the total pore volume V_{total} , and the micropore and mesopore volumes. The average pore width of activated carbon was calculated using Equation 2.3 under an assumption of slit-shaped pores, where is the average pore width, $V_{\overline{D}_n}$ is the total pore volume, and S is the BET surface area.

$$\overline{D}_n = \frac{2V_p}{S} \quad (2.3)$$

Results and Discussions

Sample characterization

This section presents the characterization of the char sample, A1, including the LOI, proximate, and ultimate analyses, as well as surface area, and pore volume. The sample was provided by the Center for Applied Energy Research at the University of Kentucky.

Proximate and LOI analysis

Table 2.1. lists the proximate and LOI analysis of the sample on a dry basis. The proximate analysis showed that the sample had very low moisture and low volatile matter contents of 1.90% and 13.07%, respectively. This was due to the devolatilization undergone during the gasification process. The ash content of the unburned carbon was 36.08%, and the fixed carbon content was 50.85% as obtained by difference.

Table 2.1. Proximate and LOI analysis of the parent char sample, A1.

Proximate Analysis				LOI, %
Moisture, % (as recd.)	Ash, % (Dry)	V.M., % (Dry)	Fixed Carbon, % (Dry)	
1.90±0.16	36.08±0.05	13.07±0.34	50.85	58.71±0.12

The LOI value of the sample was 58.71%, which was higher than the value of fixed carbon of 50.85%. This could be explained by the difference between the analytical methods used to determine LOI and proximate analyses. Fixed carbon content was calculated by subtracting moisture, volatile matter and ash from the total, i.e., 100% (ASTM D 5142-90). In contrast, when determining the LOI, the components that could decompose at the LOI test temperature (750±50 °C according to ASTM C 311), such as volatile matter, and some inorganic compounds, for example, alkali salts (Sloss, et al., 1996) were also accounted as the LOI.

Ultimate Analysis

The results of ultimate analyses (dry and ash-free basis) are listed in Table 2.2. As previously reported for combustion chars, the sample consists mainly of carbon with very little hydrogen, nitrogen, sulfur and oxygen (Maroto-Valer, et al., 2001; 1999c; 2000).

Table 2.2. Ultimate analysis of the parent char sample, A1.

Carbon, % (Dry)	Hydrogen, % (Dry)	Nitrogen, % (Dry)	Sulfur, % (Dry)	Oxygen, % (Dry)
89.47±0.14	0.25±0.02	0.81±0.01	2.80±0.02	6.66

Petrographic Analysis

As shown in *Table 2.3*, about 40% of the carbonaceous fraction of the sample was isotropic carbon, largely derived from the vitrinite portion of a coal as opposed to inertinite. However, the majority of the carbon showed signs of anisotropy and was coal derived, as shown in *Figure 2.1*. Isochromatic areas varied from those less than 0.5 μm and those less than 2.0 μm to a few that were in the 4.0-5.0 μm range, shown in *Figure 2.2*. Those regions less than 2.0 μm are usually regarded as being high volatile A bituminous, whereas those greater than 2.0 μm are usually considered to be derived from medium volatile rank coals. The majority of the char particles exhibited isochromatic areas of less than 1.0 μm and were most certainly derived from a relatively low rank high-volatile A bituminous coal similar to the 0.7 % (by volume) of coal found contaminating this sample.

Table 2.3. Point count analysis of anisotropic versus isotropic carbon for the parent char sample, A1.

Anisotropic carbon, vol%			Isotropic carbon, vol%
Coal-derived	Petroleum-derived	Pyrolytic	
51.8	6.3	2.1	39.8

A considerable amount of petroleum coke (6.3%) was observed in the specimen that showed a concentric alignment of isochromatic regions and porosity similar to shot coke. Other particles exhibited significant porosity and could be considered a sponge coke, as shown in *Figure 2.3* and *Figure 2.4*. The isochromatic regions were distinctively larger (5-10 μm) and the carbon was much higher in reflectance than those particles derived from coal.

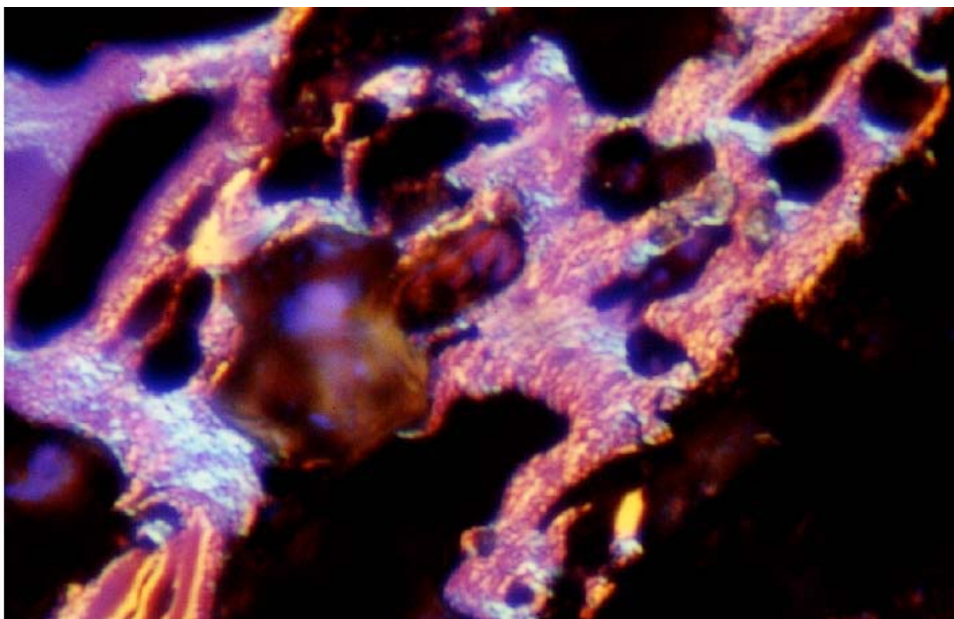


Figure 2.1 Part of a more porous char particle that displays anisotropic textures.

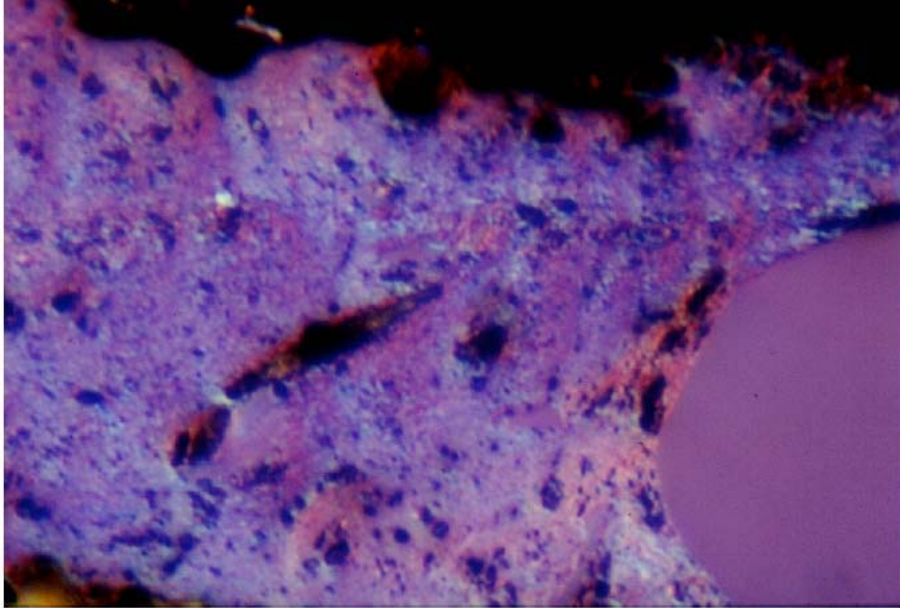


Figure 2.2 Low porosity char particle containing some isotropic inertinite and displaying isochromatic textures.

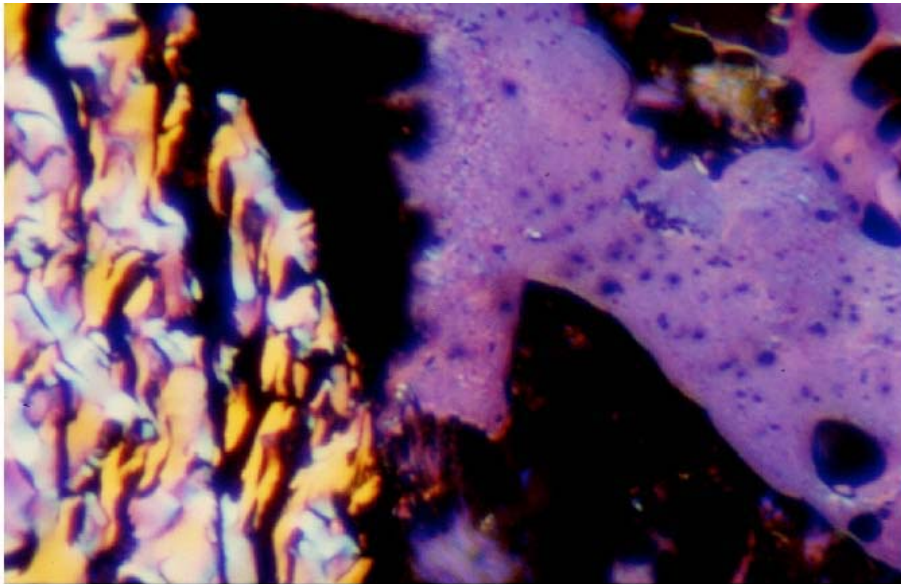


Figure 2.3 Comparison between coal-derived char particle (isotropic, blue/purple and porous) with a petroleum coke particle (highly birefringent).

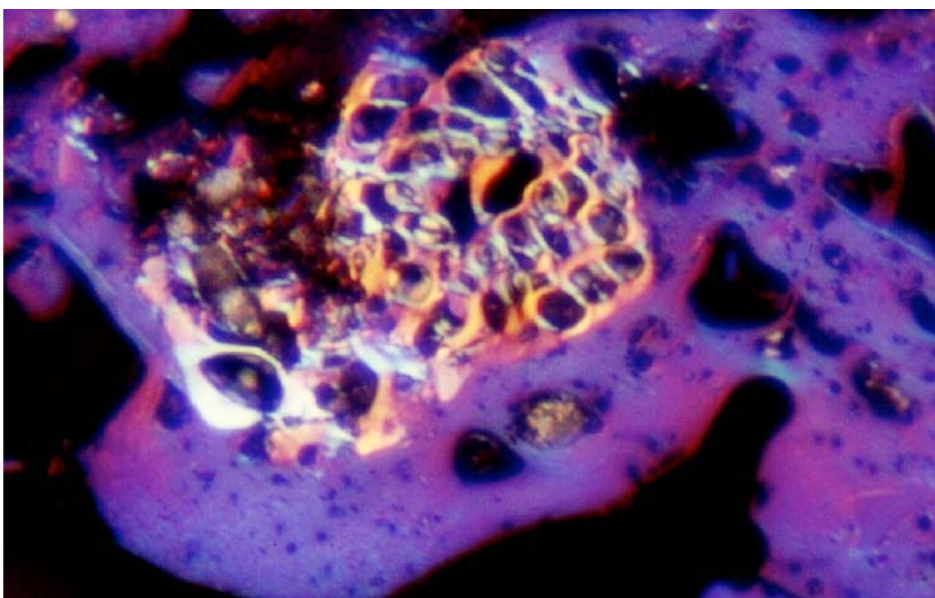


Figure 2.4 Small particle of sponge coke included within the thermoplastic remains of a coal particle.

Pyrolytic carbon was also distinctively higher in reflectance than coal-derived and possessed isochromatic regions suggesting alignment of the carbon parallel to the depositional surface upon which it rested. This carbon is generally deposited from the cracking of gas phase hydrocarbon and carbon oxide molecules under a reducing atmosphere. It is also known to impede carbon gasification reactions by reducing the reactive surface area of the carbon upon which it is deposited. Consequently, even the low concentration of pyrolytic carbon observed in this sample (2.1%) could have had an important influence char reactivity/burnout (Mitchell, 2004).

Characterization of activated carbons

The nitrogen adsorption isotherms at 77K were obtained on the parent sample and its activated counterparts using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT, as described above. The isotherms throughout this report are presented on a carbon basis by subtracting the volume of “pure ash” from the total volume obtained from the BET measurement at $P/P_0=0.95$, and then being divided by the carbon content. In this study, the “pure ash” was obtained by completely burning the sample in the presence of air at 850°C (the moisture, carbon, and volatile matter were removed with only the ash being left).

Figure 2.5. shows the N_2 -77K adsorption isotherms for the parent sample and its steam-activated carbons produced at 850°C for different times ranging from 60 to 180 minutes from the ash sample with different activation times at 850°C. The activated samples are named with the activation times in minutes. For example, A1A-60 indicates that the sample was generated after 60 minutes activation.

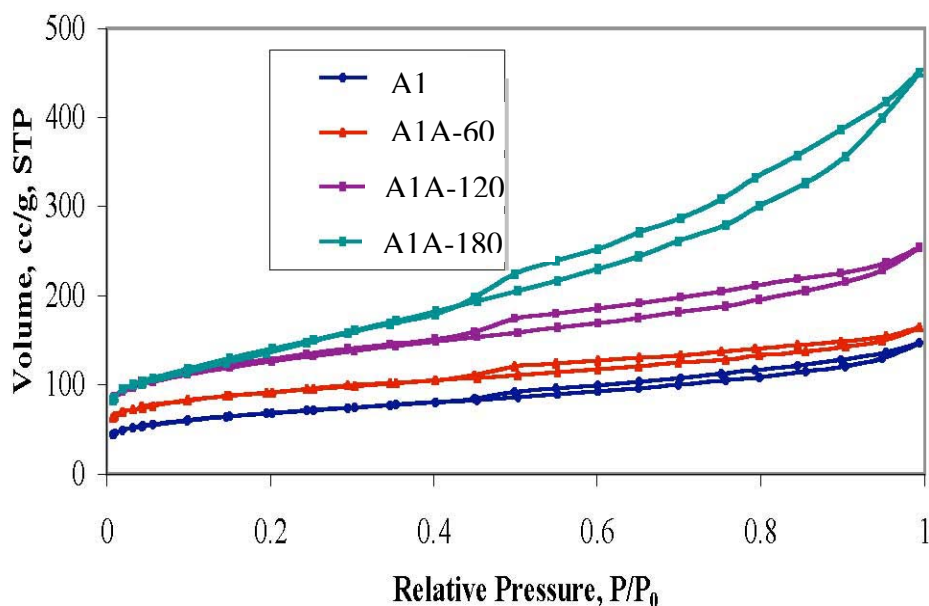


Figure 2.5 N₂ adsorption isotherms at 77K for the parent char sample (A1) and its steam activated counterparts at 850°C.

It can be observed that the parent sample (A1) presented a typical Type IV according to the Brunauer, Deming, Deming, and Teller (BDDT) classification (Brunauer, et al., 1940). The Type IV isotherm is concave to the P/P_0 axis at low relative pressure, where this initial region dominates the whole isotherm and is associated with micropore filling. The isotherm then tends to level off at high relative pressure, but exhibits a hysteresis loop, which is usually associated with the filling and emptying of mesopores by capillary condensation (Gregg, et al., 1982). In addition, the isotherm of the parent sample presented a tail as saturation pressure was approached, indicating the presence of some macropores.

The isotherms of the activated carbons were typical Type IV, and the adsorbed volume of the isotherms increased with the activation time. There was a small increase of the adsorbed volume at low relative pressure ($P/P_0=0.01-0.30$), and a significant increase at high relative pressure. Furthermore, there was a distinct hysteresis loop in the isotherm, which was associated with the filling and emptying of mesopores. This indicated that both micropores and mesopores were developed by extending the activation time from 60 to 180 minutes.

Table 2.4. presents the BET surface areas, total pore volumes, pore distribution, average pore diameters, and carbon yields for the parent char sample (A1) and its steam-activated counterparts after different activation times at 850°C. The carbon yields here are calculated using the carbon weight after activation divided by the carbon weight before activation. The surface areas of the activated samples are significantly larger than the parent sample. The surface area kept initially increases with activation time, and reaches a maximum value for sample A1A-120.

Table 2.4. Surface areas, pore volumes and average pore width of the parent char sample (A1) and its steam activated counterparts at 850°C.

Sample	Carbon yield, %	Surface area, m ² /g	V _{tot} , cc/g	V _{mic} , cc/g	V _{mes}	V _{mic} , %	\overline{D}_n , nm
A1		153	0.1410	0.0415	0.0996	29.4	3.6927
A1A-60	80	294	0.2319	0.0928	0.1391	40.0	3.1536
A1A-120	63	427	0.3540	0.1161	0.2379	32.8	3.3178
A1A-180	47	323	0.3968	0.0377	0.3591	9.51	4.9344

As expected, the carbon yields for the activated carbons decreased with increasing activation time, and the weight loss probably included the loss of the remaining volatile matter, which took place at the early activation stage, and the burn-off of the carbon (Rodríguez-Mirasol, et al., 1993; Bansal, et al., 1988). The change of surface area with activation time could be related to the carbon yields. In the early stages of activation, 60-120 minutes, the activation process led to increasing surface areas and decreasing carbon yields. When increasing the activation time to 180 minutes, the carbon yield continued to decrease while the surface area decreased also. This was probably due to pore wall consumption, and consequently formation of larger pores.

The total pore volume of the activated carbons V_{total} increased with the activation process (0.1410cc/g for A1, 0.2319cc/g for A1A-60, 0.3540cc/g for A1A-120, and 0.3968cc/g for A1A-180). The results of average pore width are also shown in *Table 2.4*. The average pore size \overline{D}_n for activated carbons here is estimated using *Equation 2.3*. The pore width of the activated carbons decreased significantly for samples A1A-60 and A1A-120, compared to their precursor, due to the pore structure development during activation. The pore width increased for A1A-180, probably due to the development of large pores by extensive activation.

Table 2.4 also lists the micro-and mesopore volume of the parent sample and its activated counterparts. The steam activation seemed to promote the development of both micropores and mesopores with the decrease of carbon yields. This corresponded to the increase of surface areas and total pore volumes, as shown in *Table 2.4*. After 60 and 120 minutes activation, the micropore volume increased to about 40% and 33% of the total, respectively, compared to about 29% for the parent sample. This indicated that the development of porosity for samples A1A-60 and A1A-120 was mainly due to micropores, probably resulting from the opening of blocked pores of the parent sample. When the activation time was extended to 180 minutes, the micropore volume only accounted for around 10% of the total. This indicates that increasing the activation time to 180 minutes led to a widening of the porosity, mainly in the mesopore range.

Conclusion

In this study, one gasification char sample, A1, was characterized using LOI, proximate, ultimate, petrographic analyses, and N₂ adsorption isotherms. The sample was then activated using steam at 850°C for different periods of time (60, 120 and 180 minutes). The parent sample presented very low moisture, volatile matter and hydrogen, nitrogen contents, due to the devolatilization undergone during the gasification process. The LOI value of the sample was 58.71%, which was higher than the value of fixed carbon. This could be explained by the difference between the analytical methods used to determine LOI and proximate analyses.

The results of petrographic analysis showed that the majority of the carbon was anisotropic and was coal derived. The chars were derived from different ranks of coal, including high volatile A bituminous, and a medium volatile bituminous. The ash sample contained a considerable amount of petroleum coke (6.3%), which was identified as shot coke and sponge coke. Pyrolytic carbon was also distinctively higher in reflectance than coal-derived and possessed isochromatic regions suggesting alignment of the carbon parallel to the depositional surface upon which it rested.

The one-step steam activation process used here increased the porosity of the sample, with the surface area increasing to 427m²/g for activated carbon A1A-180 compared to 153m²/g for the parent sample. A parametric study was conducted to understand the effect of activation time on the properties of the resultant activated carbons. The results show that the surface area and the percentage of micropores increased with the activation time at the expense of carbon yields and reach a maximum value at 120 minutes. The total pore volume increases continuously with activation time.

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Future Work

The relationship of surface area, pore size, pore size distribution, and mineral content especially Cl⁻, F⁻ and O of gasifier carbons on Hg adsorption will be explored during the coming year in an effort to define the site of Hg storage. The results for Hg loaded gasifier carbons submitted for x-ray adsorption fine structure spectrometry, XAFS, will be available in 2005 and should shed light on the Hg adsorption sites in these gasifier chars.

The activated carbon generated from the gasifier char carbon at PSU will be tested for Hg and NO_x adsorption potential. Samples will be tested at both UK and at PSU. All parent gasifier slag carbons will be tested for NO_x adsorption potential and the best Hg adsorbing carbons will be tested for both Hg and NO_x in a simulated flue gas at UK.

PSU will continue work on activation of the other gasifier char carbons, and supply activated materials to UK for Hg adsorption testing. Similarly, Gasifier carbons and activated carbons will be tested at PSU for other uses such as coke additives and sorbents.

Work is progressing as per the task schedule previously established.