***DEVELOPMENT OF ACTIVATED CARBONS
FROM COAL COMBUSTION BY-PRODUCTS***

ANNUAL TECHNICAL PROGRESS REPORT

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Principal Authors: *Prof. Harold H. Schobert
Dr. M. Mercedes Maroto-Valer
Ms. Zhe Lu*

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

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Abstract

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 coal combustion by-products (CCBPs), mainly unburned carbon in fly ash. Unburned carbon is nowadays regarded as a waste product and its fate is mainly disposal, due to the present lack of efficient routes for its utilization. However, unburned carbon is a potential precursor for the production of adsorbent carbons, since it has gone through a devolatilization process while in the combustor, and therefore, only requires to be activated. Accordingly, this report evaluates and compares several routes for the production of activated carbons from unburned carbon in fly ash, including physical and chemical activation methods.

During the present reporting period (June 30, 2001-June 29, 2002), additional characterization work was conducted under Task 1 "Procurement and characterization of CCBPs". The suite collected includes samples from pulverized utility boilers, a utility cyclone unit equipped with a beneficiation technology, a stoker, and a fluidized bed combustor. Proximate, ultimate, and petrographic analyses of the fly ash samples previously collected were measured. Furthermore, the surface areas of the samples assembled were characterized by N₂ adsorption isotherms at 77K. The proximate analyses showed that all the samples had very low moisture contents (0.17 to 3.39wt%), while volatile matter contents of the samples varied between 0.45 to 24.8wt%. The ultimate analyses of all the fly ash samples showed that they contained primarily carbon, while the hydrogen contents of all the samples were very low.

In addition, during the current reporting period, also Task 2 "Development of activated carbons" and Task 3 "Characterization of activated carbons" were continued. The samples were activated in a vertical furnace using a one-step process by using physical (steam or CO₂) or chemical (KOH pretreatment) methods. The surface areas of the steam activated samples increase with the increase of activation times, at the expense of the carbon yields. The samples activated with steam present generally higher surface areas than those using CO₂ or KOH pretreatment, probably due to the faster reaction rate of steam. However, CO₂ activation can produce a more uniform porosity and most of the surface area is due to the contribution of micropores.

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1. INTRODUCTION

1.1. Rationale

In 1999, around 90% of the total US coal production was used in coal-fired units to generate over 56% of the total electricity. Furthermore, coal is the most abundant fossil fuel resource in the US, and therefore it will even play an increasing role as a source of energy in the 21st century (Song and Schobert, 1996). However, the use of coal for power generation faces environmental challenges due to the emissions of pollutants such as NO_x and SO_x from coal combustion furnaces and such pressures will only intensify in the coming years. Therefore, to guarantee a key role of coal as energy source, the conventional processes for coal utilization have to be redesigned to comply with Clean Air Act Amendments.

The implementation of regulations concerning NO_x emissions is being addressed in coal combustion furnaces mainly by a combination of low-NO_x burners and catalytic reduction systems. Although low-NO_x burner technologies efficiently decrease the emissions level by lowering the temperature of combustion, they also reduce the combustion efficiency, resulting in an increase in carbonaceous waste product (Maroto-Valer et al, 1998). This has restricted the principal use of the inorganic ash in the cement industry, since the unburned carbon tends to adsorb the air-entrainment agents, which are added to the cement to prevent crack formation and propagation. Consequently, the carbon-rich ash is either placed in holding ponds or landfilled. The landfill option results in rising costs for the utility companies in addition to the loss of revenue from ash sales. In 1999, the combustion of over 1,045 million tons of coal generated around 82 million tons of coal combustion by-products (CCBPs), mainly fly ash containing unburned carbon (Stewart, 2000). Due to the present lack of commercial demand for such materials, the fate of these products is mainly disposal. Moreover, the increasingly severe regulations on landfill and the limited access to new disposal sites with the subsequent rise in the cost of disposal, may demand the utility industry to begin offsetting coal combustion with natural gas, or require additional coal cleaning to remove the ash prior to combustion, or

simply start utilizing the unburned carbon. The first two alternatives could compromise the coal industry, since the utilities could potentially reduce the NO_x emissions and the ash disposal problem by using gas instead of coal as fuel, or require additional coal cleaning, which would increase the cost of the coal as fuel and reduce its competitive advantage. Consequently, the third alternative, concerning the use of unburned carbon, will benefit both the coal and utility industries, and accordingly, environmental and cost-effective strategies need to be established for the use of these carbonaceous products from coal combustion.

The carbonaceous residue in fly ash, unburned carbon, is a potential precursor for the production of adsorbent carbons, as described here. The present global consumption of activated carbons is over 350,000 tons and it 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 (Song and Schobert, 1996). 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, unburned carbon only requires a one-step activation process, since it has already gone through a devolatilization process while in the combustor, and therefore, only requires 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). Therefore, the use of unburned carbon as precursor for the production of activated carbons would help the utilities to offset the cost of installing and running a beneficiation process. Accordingly, this work addresses the potential use of unburned carbon from coal combustion as precursor for the production of adsorbent carbons.

1.2. Program objectives and research design

The overall objective of this program is to develop adsorbent materials from coal combustion by-products (CCBPs) that are mainly unburned carbons in fly ash. In this research program, the following three tasks have been defined:

Task 1: Procurement and characterization of unburned carbon in fly ash. In this task, samples from different combustion processes are collected, including pulverized, cyclone, stoker, and fluidized-bed combustion. The properties of the suite of CCBPs collected are characterized by different techniques, including LOI, proximate, ultimate, and petrographic analyses and surface area characterization by N₂ adsorption isotherms at 77K.

Task 2: Production of activated carbons from unburned carbon. Several routes for the preparation of activated carbons are investigated, including physical activation with different gases, such as steam and CO₂, and chemical activation with KOH.

Task 3: Characterization of the properties of the activated carbon materials. In this task, the properties of the generated activated carbons are systematically characterized, especially their porosity. This will help to establish the optimum route for the production of activated materials.

Upon completion of this research program, a novel process for the production of adsorbent materials from CCBPs will have been investigated. This will have a double environmental and economical impact, since CCBPs that are currently being disposed, can be used as precursors for the production of premium carbon products like activated carbons.

2. EXECUTIVE SUMMARY

The implementation of increasingly stringent Clean Air Act Regulations by the coal utility industry has resulted in an increase in the concentration of unburned carbon in coal combustion fly ash. In 1998, around 6 million tons of unburned carbon were disposed, due to the present lack of efficient routes for its utilization. However, the increasingly severe regulations on disposal and the limited access to new disposal sites coupled with the subsequent increase in the cost of disposal, will force the coal and energy industry to recycle a larger amount of CCBPs. Consequently, there is a clear need to establish environmental and cost-effective strategies for the use of these carbonaceous waste products from coal combustion. The carbonaceous residue in fly ash, unburned carbon, is a potential precursor for the production of adsorbent carbons. 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, unburned carbon only requires a one-step activation process, since it has already gone through a devolatilization process while in the combustor. Accordingly, the overall objective of this program is to develop adsorbent materials from coal combustion by-products (CCBPs) that are mainly the unburned carbon in fly ash. In this research program, the following three tasks have been defined: Task 1 "Procurement and characterization of coal combustion by-products"; Task 2 "Production of activated carbons from unburned carbon" and Task 3 "Characterization of the properties of the activated carbon materials".

During the current reporting period (June 30, 2001-June 29, 2002) under Task 1 samples were collected from pulverized utility boilers, a utility cyclone unit equipped with a beneficiation technology, a stoker, and a fluidized bed combustor. The characterization studies showed that the samples collected have significantly different carbon contents, as determined by the ASTM C311 procedure, with the sample from the cyclone unit containing the highest LOI of ~ 85%, since this unit had been retrofitted with a technology to separate the unburned carbon from the fly ash. The samples from pulverized combustors (PC) presented LOI of 61.3-71%, while the sample from the stoker had the lowest LOI of 21.8%. In contrast, the LOI of the fly ash obtained from the fluidized bed combustor was around 45%. The proximate analyses showed that all the samples had very low moisture contents, varying between 0.17 to 3.39wt%, while volatile matter contents of the samples varied greatly between 0.45 to 24.8wt%. Both the ash contents and consequently fixed carbon contents of the samples changed in a wide range, where the ash contents ranged from 13.7 to 79.5wt%, and the fixed carbon contents varied from 7.55 to 84.3wt%. The ultimate analyses of all the fly ash samples showed that they contained primarily carbon, where the carbon contents were between 94.9-97.7%, with the exception of samples F and G that have lower carbon contents amount of 77.5 and 88.8wt%, respectively. The hydrogen contents of all the samples varied from 0.01 to 1.03wt%. The sulfur contents of all the samples changed between 0.01-8.50%, while the nitrogen contents varied from 1.25wt% to 1.77wt%. The oxygen contents changed in the range of 0.01 to 12.5wt%. Furthermore, the results from petrographic analyses showed that both the isotropic and anisotropic contents of the samples varied greatly in the range of 15.6-99.8vol%, and 0.2-84.4vol%, respectively. Moreover, the surface areas of the fly ash samples were characterized by N₂ adsorption isotherms at 77K. The surface areas of the fly ash samples from pulverized coal combustors

were between 44-120 m²/g, and the sample from cyclone unit presented the lowest surface area of 8.6 m²/g, while the surface area of sample from the stoker was around 16 m²/g. The sample from the fluidized bed combustor had the highest surface area of 361 m²/g.

The activation system used to conduct Task 2 is a fluidized-bed reactor, whose design versatility allows the use of different particle size, activating agent, heat treatment, residence time, flow rate of activation agent and amount of sample, and typically 2~3 g of sample are used. The samples physically activated with steam or CO₂, and chemically activated using KOH. The steam and CO₂ activations were conducted at 850°C. For the chemical activation, a fly ash sample was physically mixed with KOH using a KOH/unburned carbon ratio of 1:2 wt/wt. The mixture was put inside the reactor and then heated up to the activation temperature of 775°C in N₂ atmosphere.

All the produced activated carbons were characterized under Task 3. For all the samples, the surface areas of the steam activated samples had a significant increase compared to their parent samples, where the activated carbon obtained from fly ash D presented the highest surface area of 1075 m²/g after 120 minutes activation. The change of surface area with activation times could be related to the carbon yields, where increasing the activation time led to increasing surface areas and decreasing carbon yields. The steam activation generated microporous samples. However, extending the activation time resulted in widening of the porosity due to destruction of walls between micropores as a result of the higher carbon weight loss. The activated carbon obtained from activation using CO₂ presented a lower adsorption volume compared to the activated carbon obtained from steam activation. However, the isotherm for the activated carbon obtained CO₂ activation was typical for microporous materials. In this study, KOH had little effect on the activation of unburned carbon in fly ash compared to the activation with steam and CO₂, and the adsorption isotherm of the carbon obtained from KOH activation was similar to that of the parent sample. The reason for the different reactivity of these three activation agents on unburned carbon in fly ash should be explained by further studies.

3. EXPERIMENTAL

3.1. Task 1: Procurement and characterization of fly ash samples

3.1.1. Procurement of fly ash samples

The objective of this task is to assemble a suite of fly ash samples generated by different combustion technologies and to carry out a systematic characterization of the fly ash samples. In this study, seven fly ash samples that have been generated in a variety of combustion processes are investigated, as listed below:

The fly ash sample marked as A came from a PC unit located in Eastern Kentucky with a net capacity of 70MW. The unit uses a high-volatile bituminous coal and the sample was collected from the mechanical precipitators.

The fly ash sample marked as B was collected from a PC unit in Wisconsin with a net capacity of 136 MW. The unit uses high-volatile bituminous coal and the sample was collected from the electrostatic precipitators.

The fly ash sample marked as C came from a PC unit located in Northampton County, PA with a net capacity of 243 MW. This unit has been retrofitted with a low-NO_x burner and uses primarily Pittsburgh seam high volatile bituminous coals.

The fly ash sample marked as D was collected at Penn State University, University Park, from a 2 MW pulverized coal-fired suspension firing research boiler equipped with a low-NO_x burner, using Middle Kittanning seam bituminous coal with high volatile matter content.

The fly ash sample marked as E in this work came from a cyclone unit located in Willoughby, OH with a net capacity of 216 MW retrofitted with a fly ash beneficiation technology and using a low-volatile bituminous coal.

The fly ash sample marked as F was collected from a vibra-grate stoker of the west steam power plant at Penn State University, University Park, using a high-volatile Pennsylvania bituminous coal. The fly ash was collected from the baghouse.

The fly ash sample marked as G was from a continuous fluidized-bed reactor that is operated at 1500°F (850°C) and 170psi (1.172*10⁶Pa). This combustion system is

installed in the Energy and Environmental Research Center (EERC) in the University of North Dakota, and the coal used in this system is a North Dakota lignite coal. The fly ash was collected from the Hot-Gas Filter Vessel (HGFV).

3.1.2. Characterization of fly ash samples

The characterization of fly ashes conducted in this study involves LOI analysis, proximate, ultimate and petrographic analyses and porosity characterization, as described below.

3.1.2.1 LOI analyses

The LOI content of the fly ashes was determined according to the ASTM C 311 procedure. These analyses were conducted in duplicate. For fly ashes commonly derived from Eastern U.S. coals, the LOI value essentially equates to carbon content. According to ASTM C 311, a weighed fly ash 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 fly ash 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 the following equation (3.1):

$$\text{Loss on ignition, \%} = (A/B) * 100 \quad (3.1)$$

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

B = mass of moisture-free sample used.

3.1.2.2 Proximate analyses

The proximate analyses of fly ash samples were determined by the LECO MAC-400 proximate analyzer, which included the contents of moisture, volatiles, ash and fixed carbon. These contents were determined by weighing the samples in a temperature and atmosphere controlled environment.

Before an analysis was begun, empty crucibles are placed on the turntable. The furnace was purged with nitrogen and the furnace temperature was raised to 106°C. The fly ash samples were continuously being 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 changes in the weight of this crucible were used to correct the results obtained from the samples. When the corrected sample weights stopped changing, the moisture analysis was ended and moisture results were computed for each sample. Covers were placed on the crucibles 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 covers were 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 samples were continuously weighed as they were in the moisture analysis. When the corrected weight kept stable, 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.

3.1.2.3 Ultimate analyses

The carbon, hydrogen, and nitrogen contents in fly ash samples were measured using the LECO CHN-600 elemental analyzer. The determination of carbon, hydrogen, and nitrogen was made by burning a weighed quantity of fly ash samples in pure oxygen at ~950°C after grinding to 60 mesh (~250 μm) 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 O_2 , CO_2 , H_2O and the reduction of NO_x to N_2 . 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 CO_2 and H_2O 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 in fly ashes was determined using a LECO SC-32 and SC-132, which are microprocessor-based instruments. Samples were combusted in an oxygen atmosphere where the sulfur oxidized to SO₂. Moisture and dust were removed and SO₂ gas was then measured by a solid-state infrared detector. The IR cell was used as both a reference and measure chamber. It detected total sulfur, as sulfur dioxide, continuously. It consisted of an IR source, a chopper motor, a precise wavelength filter, a condensing cone, an IR energy detector, and the cell body.

3.1.2.4 Petrographic analyses

The petrographic analyses of the fly ash samples were inspected using a Zeiss Universal research microscope at 800X magnification in reflected, white-light illumination and oil immersion. Before conducting the analyses, 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 µm on a medium nap and 0.05 µm on silk).

3.1.2.5 Characterization of surface area

The surface area of the fly ashes was characterized by conducting N₂ adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The BET surface areas were 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 using the surface area measured for ash samples obtained from different fly ashes and the TGA-derived inorganic contents for the respective density fractions (Maroto-Valer, et al, 1999d).

3.2. Task 2: Production of activated carbons from unburned carbon in fly ash

The activation system used is presented in *Figure 3.1*. The stainless steel reactor was the most important part of the system, which was heated by a vertical furnace that has a 3.5" inside diameter. The reactor was designed to withstand temperatures up to 1200°C and worked like a fluidized-bed reactor. 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.

Figure 3.1. Schematic of the activation system (not to scale).

Typically 2~3 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 $\sim 0.5\text{--}1.0$ ml/min, and a horizontal furnace was used to generate steam at 500°C as the activation agent. The steam was swept using a flow of N_2 with a flow rate of ~ 300 ml/min and introduced from the bottom of the reactor to react with fly ash samples. During the activation process, liquid products were condensed, while gases were vented off. After a certain activation period, the flow of steam was stopped, the furnace was shut off and the reactor was quenched by flowing air in the outside of the reactor and N_2 through inside of the reactor.

Figure 3.2 shows the diagram of the activation reactor. The stainless steel reactor with a 1" external diameter and a 0.8" internal diameter consisted of an upper filter installed to prevent the fly ash flowing outside the reaction system, and a distribution plate installed in the bottom part of the reactor.

Figure 3.2: Diagram of activation reactor (not to scale).

The CO₂ activation was conducted in the same reactor system and using similar procedures as described for the steam activation. Around 3g of fly ash sample was located in the fluidized-bed reactor and was heated to 850°C in the furnace in a flow of nitrogen. When the activation temperature was reached, nitrogen was replaced with CO₂ and the sample was hold for 90 minutes. After the activation process, the sample was cooled under N₂ flow.

The KOH activation of the unburned carbon in fly ash was also conducted in the same reactor system as described for steam and CO₂ activation, and the activation procedures are similar to those used for the conventional precursors, such as wood and coal. A fly ash sample was physically mixed with KOH using a KOH/unburned carbon ratio of 1:2 wt/wt. The mixture was put inside the reactor and then heated up to the activation temperature 775°C in N₂ atmosphere. The mixture was hold at the activation temperature for 90 minutes activation before cooling down under N₂. Then, the sample was washed with HCl and finally with distilled water to remove residual Cl⁻, and dried at 110°C for 24 hours.

3.3. Task 3: Surface area characterization of activated carbons

The surface areas of the activated carbons produced from unburned carbons in fly ashes was characterized conducting N₂ adsorption at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The BET surface areas were calculated using the adsorption points at the relative pressures (P/P₀) 0.05~0.35, as previously described (Schobert et al, 2000 and 2001).

4. RESULTS AND DISCUSSION

4.1. Procurement and characterization of the suite of CCBPs

As previously described in Section 3.1, seven fly ash samples marked as A, B, C, D, E, F, and G are investigated in this study. The samples have been produced in a variety of combustion processes, including samples from pulverized utility boilers that used high-volatile bituminous coals, a sample collected from a utility cyclone unit using a low-volatile bituminous coal, a sample from a stoker using a high-volatile bituminous coal, and a sample from a fluidized bed using lignite. A series of analysis were conducted on the above samples to characterize their properties, including loss-on-ignition (LOI), proximate, ultimate, petrographic analyses and surface area measurements, as described below.

4.1.1. Loss-on-ignition (LOI)

The determination of the loss-on-ignition (LOI) content was conducted according to the ASTM C 311 procedure. The LOI results of different fly ash samples A, B, C, D, E, F, and G are compared in *Figure 4.1*. Sample A had a high LOI of 71% and was collected from a mechanical precipitator. The LOI of B was around 61%, and this sample was collected from a triboelectrostatic precipitator. Samples C and D were from the combustion units retrofitted with Low-NO_x burners, and the LOI of these two samples were around 67.6% and 63.7%, respectively. Fly ash E presented the highest LOI of ~85%, where the sample was collected from a cyclone unit retrofitted with a beneficiation technology. In contrast, while the LOI of sample F was as low as ~21%, where this sample came from a stoker using baghouses to collect the fly ash. Finally, the sample G which was collected from the Hot-Gas Filter Vessel (HGFV) had a LOI of ~45%.

Figure 4.1: LOI analyses of the fly ash samples.

4.1.2. Proximate and ultimate analyses

Table 4.1 lists the proximate analyses of all the fly ash samples investigated in this study, and the analytical data are reported on a dry basis. The proximate analyses showed that all the samples had very low moisture contents, varying between 0.17 to 3.39wt%, while volatile matter contents of the samples varied between 0.45 to 24.8wt%. Both the ash contents and consequently fixed carbon contents of the samples changed in a wide range, where the ash contents ranged from 13.7 to 79.5wt%, and the fixed carbon contents varied from 7.55 to 84.3wt%. The differences between the volatile matter of the fly ash samples could probably be related to the combustion conditions that the parent coals underwent, such as the combustion temperature, rate, and residence time. It is well documented that volatile matter content of less than 1% could be considered as an indication of complete combustion (Koba et al., 1981). Among the fly ash samples, sample B had volatile matter content lower than 1%, indicating that this sample underwent a complete combustion. The volatile matter contents were slightly

higher than 1% for samples D and E, and much higher than 1% for samples A, F, and G. This uncompleted combustion was probably due to the low combustion temperature and less excess air during the combustion processes (Borman, et al., 1998).

Table 4.1: Proximate analyses of the fly ash samples.

	Moisture (%) (As Rec'd)	Ash (%) (Dry)	Volatile Matter (%)(Dry)	Fixed Carbon* (%)(Dry)
A	0.95	28.7	9.79	61.5
B	1.27	35.9	0.45	62.4
C	0.68	29.9	8.05	61.8
D	1.57	32.9	1.84	63.7
E	0.17	13.7	1.97	84.3
F	3.39	79.5	12.9	7.55
G	1.24	54.4	24.8	20.8

* Determined by difference.

The fixed carbon values of the fly ash samples obtained from the proximate analysis were lower than the LOI for samples A, C, E, F and G, and the LOI for all the parent fly ash samples were almost equal to the sum of volatile matter and fixed carbon. This is probably due to the different analytical methods used to determine LOI and proximate analysis. For the case of fixed carbon content, it was calculated by subtracting of moisture, volatile matter and ash from the total, i.e. 100% (ASTM D 5142-90). In contrast, when determining the LOI, some components that could decompose at the LOI test temperature (750°C according to ASTM C 311), such as mineral carbonates, are also accounted as the LOI. However, samples B and D

slightly higher fixed carbon contents than their LOI results, presumably due to the experimental error in the LOI determination.

Table 4.2 shows the ultimate analyses (dry and ash free basis) of the fly ash samples obtained from different types of coals and combustion systems, marked as A, B, C, D, E, F, G. All the fly ash samples contained primarily carbon, where the carbon contents were between 94.9-97.7%, with the exception of samples F and G that have lower carbon contents amount of 77.5 and 88.8wt%, respectively. The hydrogen contents of all the samples varied from 0.01 to 1.03wt%.

Table 4.2: Ultimate analyses of the samples investigated.

	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen* (%)
A	97.2	0.17	1.77	<0.01	0.86
B	97.3	0.23	1.25	1.23	<0.01
C	96.5	0.18	1.30	1.16	0.89
D	94.9	0.70	1.27	0.63	2.49
E	97.7	0.02	1.40	0.94	<0.01
F	77.5	<0.01	1.512	8.50	12.5
G	88.8	1.03	1.07	3.90	5.17

* Determined by difference

The sulfur contents of all the samples changed in a broad range of 0.01-8.50%, while the nitrogen contents varied from 1.25wt% to 1.77wt%. The oxygen contents, which were determined by difference, changed in the range of 0.01 to 12.5wt%. The carbon and oxygen content in the fly ash samples was expected to be dependent on the temperature that the coal had undergone during the combustion, and it was also expected that the lower the combustion

temperature, the lower the carbon and oxygen loss (Sun, et al., 1997). Therefore we suspected that difference between carbon and oxygen contents of the fly ash samples was attributed to the different temperature that coals underwent during their combustion processes, though the exact combustion temperature for each fly ash sample was unknown.

4.1.3. Petrographic analyses

The petrographic analyses reported on a volume% basis for the fly ash samples A, B, C, D, E, F and G are given in *Table 4.3*. Both the isotropic and anisotropic contents of the samples varied greatly in the range of 15.6-99.8vol%, and 0.2-84.4vol%, respectively. Among the fly ashes, samples A, B, C, D, E, and F that were obtained from combustion of bituminous coals presented higher anisotropic content than that of fly ash G that was from the combustion of lignite. This was probably due to the different ranks of coals from which the fly ash samples derived, where it was believed that bituminous coals tend to convert into an optically anisotropic char during combustion. This was probably because the bituminous coals were thermoplastic to a considerable extent, melted and became fluid upon heat treatment to form anisotropic coke. Fly ash sample G, which was obtained from combustion of a lignite, presented very high isotropic content (99.8%), this result was consistent with previous research that has shown that low-rank coals (generally less than 85% carbon content) produced isotropic chars or chars with low percentages of small anisotropic components (<1µm diameter) (Mochida, et al., 1979).

Table 4.3. Petrographic analyses of the fly ash samples.

	Isotropic (vol.%)	Anisotropic (vol.%)
A	41.1	58.9
B	78.9	21.1
C	15.6	84.4
D	22.3	77.7
E	12.7	87.3
F	17.8	82.2
G	99.8	0.20

However, the extent of development of anisotropic in different fly ash samples obtained from bituminous coals was quite different. For example, sample B had 21.1% of anisotropic, while sample E had 87.3%, which could be explained by the process of the development of anisotropic carbon. It had been reported that two factors are desirable for the development of anisotropic carbon: 1) the moderate growth of constituent molecules with ordered stacking of lamellae in the liquid crystals; and 2) the creation of high fluidity of matrix during pyrolysis to maintain the sufficient mobility of the constituent molecules (Mochida, et al., 1979; Koba, et al., 1981). Fly ash samples A, B, C, D, E, and F presented higher contents of anisotropic compared with fly ash G, because they were obtained from the combustion of bituminous coals that became fluid and passed through a liquid-crystal phase during the combustion process.

4.1.4. Surface area

The BET surface areas, total pore volume and the average pore diameter of the fly ash samples A, B, C, D, E, F, and G are listed in *Table 4.4*. All the reported data here and throughout this report are on carbon basis, where for each sample, the surface area of the “pure ash” content in the fly ash is subtracted from the total surface area obtained from the BET measurement, and the result is divided by carbon content of this sample. In this study, the “pure ash” sample was obtained by burning the fly ash completely, and its total volume was also obtained from BET measurement at $P/P_0=0.95$.

Table 4.4: Surface area of the fly ash samples.

Samples	A	B	C	D	E	F	G
BET Surface Area							
(m ² /g)	44	47	82	120	8.6	16	361

The fly ash samples had surface areas in the range of 8.6-361 m²/g. It was clear that sample G that was produced from the combustion of lignite coal presented the highest surface area of 361 m²/g, which was 3~40 times as large as those reported for the other samples. Furthermore, fly ash D presented higher surface area than the other fly ash samples derived from combustion of bituminous coals. This suggested that sample D had created some porosity during the combustion processes. This was probably determined by both the nature of the coal from which fly ash D obtained and the combustion process that this coal had undergone.

4.2. Development and characterization of activated carbons from unburned carbon.

The fly ash samples A, B, C, and D are selected as precursors for the activation in this study, and the effect of activation time, and activation agents (steam, CO₂ and KOH) were investigated here.

4.2.1. Effect of activation time

Table 4.5. presents the BET surface areas and carbon yields for the parent fly ash samples A, B, C, and D, and their steam activated counterparts after different activation times at 850°C. The carbon yields here and throughout this thesis are calculated using the carbon weight after activation divided by carbon weight before activation. For all these fly ash samples, the surface areas of the activated samples had a significant increase compared to their parent samples (553m²/g vs. 44m²/g for sample A; 717m²/g vs. 47m²/g for sample B; 307m²/g vs. 82m²/g for sample C, and 1075 m²/g vs. 120m²/g for sample D). The activated carbon obtained from fly ash D presented the highest surface area of 1075 m²/g after 120 minutes activation, while activated carbon from fly ash C had the lowest surface area of 307 m²/g after 120 minutes activation. This was probably attributed to the intrinsic structure of the unburned carbon in the fly ash, and further studies are necessary to understand the mechanisms of activation of unburned carbon.

Table 4.5: Surface areas and carbon yields of the precursors and their activated counterparts for different activation times at 850°C.

Samples	Time (minutes)	Carbon Yield (%)	BET Surface Area. (m ² /g)
A	--	--	44
A-60	60	73	378
A-120	120	35	553
B	--	--	47
B-60	60	47	477
B-120	120	32	717
C	--	--	82
C-60	60	87	163
C-120	120	70	307
D	--	--	120
D-30	30	89	372
D-60	60	86	538
D-90	90	52	825
D-120	120	33	1075

Furthermore, the carbon yields for the activated carbons decreased with increasing activation time, and the weight loss probably included the remaining volatile matter that was probably lost at the early activation stage as well as the burnoff of the carbon (Rodríguez-Mirasol, et al., 1993; Bansal, et al., 1988). The change of surface area with activation times could be related to the carbon yields, where increasing the activation time led to increasing surface areas and decreasing carbon yields of the activated carbon. This indicated that for these samples, the activation processes developed the porosity of activated carbons, where the surface areas and pore volumes became larger with increasing carbon burn-off within the activation times selected in this study. It has been reported that the surface area of activated

carbons develop gradually with increasing carbon weight loss and activation times reaching a maximum, and then the extensive activation would result in a decrease in surface area due to destruction of the walls between micropores after a certain burn-off level (Sun et al., 1997). This behavior was not observed in this study, probably because the burn-off achieved for the activated carbons obtained from fly ashes A, B, C, and D was not high enough to reach their maximum surface areas. Furthermore, samples A, B, and D presented much lower carbon yields at 120 minutes activation of around 30% compared with those of sample C of around 70%, indicating that fly ash samples A, B, and D were more reactive with steam than sample C. This was presumably attributed to the intrinsic composition and structure of the unburned carbon in fly ash (Hippo, et al., 1979). It is suggested that the variation of surface area with activation time is probably due to different composition and structure of the unburned carbon in fly ash.

It is well documented that activation is a gasification reaction, where reactivity is associated with the carbon active sites of the precursors (Rodríguez-Reinoso, 1991). It has been found experimentally that reactivity is affected by factors such as rank of parent coal, particle size, heat treatment conditions, reaction temperature, nature and pressure of reactant gas, and inorganic catalytic impurities (Taylor, 1982). The carbon active sites included sites all the way from those bonded to heteroatoms (H, N, O, S), to edge carbon atoms, and to disordered carbon atoms (Radovic, 1982; Rodríguez-Reinoso, 1991). Furthermore, isotropic char was believed to exhibit higher reactivity during the gasification process (Koba, et al., 1980). Therefore, fly ash D, which had the highest oxygen content, as shown in *Table 4.2*, and fly ash B, which had the highest concentration of isotropic char, as shown in *Table 4.3*, could be expected to have higher reactivity during the activation processes. This was confirmed by the results of carbon yields of each sample as shown in *Table 4.5*, where after 120 minutes activation, samples D and B present carbon yields ~ 32%, while sample C has a carbon yield as high as 70%.

Figure 4.2 shows the N₂-77K adsorption isotherms for fly ash D and its steam activated carbons produced with different activation times at 850°C. The nomenclature used indicates the activation times in minutes following the letter D. For example, D-30 indicates that the sample was generated after 30 minutes activation. For fly ash sample D, the isotherms changed from

Type II for the parent sample into Type I for the activated carbons after 30 and 60-minute-activation, and Type IV for the activated carbons with 90 and 120 minutes activation. The adsorbed volume of the isotherms for activated carbons D-30 and D-60 increased rapidly at low relative pressure ($P/P_0 \approx 0.01-0.3$), while rised very slowly at high relative pressure, indicating a highly microporous nature of the activated carbons. For the isotherms of activated carbons D-90 and D-120, the adsorbed volumes kept increasing progressively with relative pressure. Furthermore, there was a distinct hysteresis loop in the isotherm, which was associated to the filling and emptying of mesopores, indicating that both micropores and mesopores were developed by extending the activation from 60 to 90 and 120 minutes.

Figure 4.2. N_2 isotherms for fly ash D and its steam activation counterparts.

Figure 4.3 compares the micro- and mesopore volume of fly ash D and its activated counterparts with different activation times at 850°C , where the total volume was obtained from BET measurement using N_2 adsorption isotherm at $P/P_0=0.95$. For the parent fly ash D, the total pore volume was mainly due to micropores, with the micropore volume accounting for around

60% of the total, and these micropores were probably obtained from the combustion processes that coal had undergone. After 30 minutes activation, the micropore volume increased and accounted for around 67% of the total. When the activation time increased to 60 and 90 minutes, the micropore volume increased to around 78% and 75%, respectively, while the mesopore volume accounted for around 25%. This indicated that the development of porosity of activated carbons D-60 and D-90 was mainly due to the contribution of micropores. When activating sample D for 120 minutes, the percentage of micropores decreased compared to the activated carbons obtained after 30, 60 and 90 minutes activation, and now accounted for around 60% of the total. This indicated that for fly ash D, increasing the activation time to 120 minutes led to a large widening of the porosity resulting from burning away of the walls between micropores with higher carbon weight loss.

Figure 4.3: Distribution of micro- and mesopores of fly ash D and its activated counterparts at 850°C.

4.2.2. Effect of activation agent

The activation of fly ash using steam had been proven to be a possible way for the production of activated carbon. In this study, other two classical activation methods for preparing activated carbon – activation using CO_2 and KOH – were also investigated for fly ash D, following the experimental procedures described in Section 3.2. *Figure 4.4* shows the isotherms of fly ash D and its activated counterparts with steam, CO_2 , and KOH at 850°C for 90 minutes, where the suffix indicates the activation agent used. For example, D- CO_2 indicates the activated carbon obtained from fly ash D using CO_2 . The isotherm of the activated carbon using steam activation presented a higher adsorption than those of the activated carbons using CO_2 and KOH activation, indicating that the activated carbon from steam activation had a highly developed porosity. This was probably due to the fast reaction rate of steam-carbon resulting from the higher diffusivity of steam compared to CO_2 -carbon and KOH-carbon (Koba, et al., 1980). Furthermore, the isotherm indicated that the activation with steam resulted in the development of both micropores and mesopores.

Figure 4.4: N_2 adsorption isotherms at 77K on unburned carbon D and its steam, CO_2 and KOH activation counterparts.

The activated carbon obtained from activation using CO₂ presented a lower adsorption volume compared to the activated carbon obtained from steam activation. However, the isotherm for the activated carbon obtained CO₂ activation was Type I according to BDDT classification, which was typically for micropores. This indicated that micropores were predominant in this activated carbon, probably because that activation with CO₂ developed mainly microporosity over the entire range of burnoff (Bansal, et al., 1988). In this study, KOH had little effect on the activation of unburned carbon in fly ash compared to the activation with steam and CO₂, and the adsorption isotherm of the carbon obtained from KOH activation was similar to that of the parent sample. This could be because the inherent structure and composition of the unburned carbon in fly ash D was not suitable for KOH activation, and/or the amount of KOH used in this study was too low. Further investigations are needed in order to understand this phenomenon. It has been documented that prolonged activation time with higher KOH/carbon ratio was recommended to produce activated carbon with well-developed porosity, where high ratio of KOH created more micropores, while the mesopore contribution was kept almost constant (Ahmadpour, et al., 1996).

Table 4.6 presents the BET surface areas and carbon yields for the activated carbons obtained from fly ash D using steam, CO₂ and KOH at 850°C for 90 minutes.

Table 4.6: Surface area and carbon yields of the activated carbons obtained from fly ash D using steam, CO₂ and KOH activation.

	BET Surface Area (m ² /g)	Carbon Yields (%)
D-steam	764	60
D-CO ₂	385	85
D-KOH	161	82

The activated carbon from steam activation presented the highest BET surface area ($764\text{m}^2/\text{g}$ vs. 385 and $161\text{m}^2/\text{g}$) than those of the activated carbons from CO_2 and KOH activation, and also had the highest carbon burnoff. This was consistent with the results obtained from the adsorption isotherms shown in *Figure 4.4*, and was probably attributed to the fast reaction rate of steam-carbon resulting from the higher diffusivity of steam (Koba, et al., 1980). The reason for the different reactivity of these three activation agents on unburned carbon in fly ash should be explained by further studies. However, it was anticipated that although the activation with steam produces activated carbons with highly development of porosity under the same activation conditions compared with the activation with CO_2 and KOH , the CO_2 activation can produce a more uniform porosity and most of the surface area is due to the contribution of micropores. Furthermore, the KOH activation is potentially attractive because it is performed in a single-step in the presence of chemical reagents, and the activation takes place at lower temperatures compared to that used in the physical processes with a usually high carbon yield, and is more flexible for the preparation of activated carbons with desired pore size distribution (Ahmadpour, et al., 1996).

5. CONCLUSIONS

During the present reporting period (June 30, 2001-June 29, 2002), additional characterization work was conducted under Task 1 "Procurement and characterization of CCBPs". Proximate, ultimate, and petrographic analyses of the fly ash samples previously collected were measured. Furthermore, the surface areas of the samples assembled were characterized by N_2 adsorption isotherms at 77K. The suite collected includes samples from pulverized utility boilers, a utility cyclone unit equipped with a beneficiation technology, a stoker, and a fluidized bed combustor. The proximate analyses showed that all the samples had very low moisture contents, varying between 0.17 to 3.39wt%, while volatile matter contents of the samples varied greatly between 0.45 to 24.8wt%. The ultimate analyses of all the fly ash samples showed that they contained primarily carbon, while the hydrogen contents of all the samples were very low. Furthermore, the results from petrographic analyses showed that both the isotropic and anisotropic contents of the samples varied in the range of 15.6-99.8vol%, and 0.2-84.4vol%, respectively. The investigated samples had surface areas in the range of 8.6-361m²/g.

In addition, during the current reporting period, also Task 2 "Development of activated carbons" and Task 3 "Characterization of activated carbons" were continued. The samples were activated in a vertical furnace using a one-step process by using physical (steam or CO₂) or chemical (KOH pretreatment) methods. For all the samples activated with steam, the surface areas presented a significant increase compared to their parent samples, where the activated carbon obtained from fly ash D presented the highest surface area of 1075 m²/g after 120 minutes activation. The change of surface area with activation times could be related to the carbon yields, i.e., where increasing the activation time led to increasing surface areas and decreasing carbon yields. The steam activation generated microporous samples. However, extending the activation time resulted in widening of the porosity due to destruction of walls between micropores as a result of the higher carbon weight loss. The activated carbon obtained from activation using CO₂ presented a lower adsorption volume compared to the activated carbon obtained from steam activation. However, the isotherm for the activated carbon obtained CO₂ activation was typical for microporous materials. In this study, KOH had little

effect on the activation of unburned carbon in fly ash compared to the activation with steam and CO_2 , and the adsorption isotherm of the carbon obtained from KOH activation was similar to that of the parent sample. The reason for the different reactivity of these three activation agents on unburned carbon in fly ash should be explained by further studies.

6. PLANS FOR THE COMING YEAR

The work planned for the coming year will continue the activation of the unburned carbon in fly ash samples under a wider range of controlled operating variables in order to establish the optimum route for the generation of activated carbon materials. It is also anticipated that this study will include the activation of the parent coals used to generate the unburned carbon samples investigated. Furthermore, the unburned carbon separated from the fly ash samples using acid washing will be activated and the resultant activated carbons will be compared to those obtained without acid washing. In addition, a comparison of the activated carbons produced from unburned carbon in fly ashes with commercial activated carbons will also be conducted.

7. PUBLICATIONS RESULTING OF THIS PROJECT

Harold H. Schobert, M. Mercedes Maroto-Valer and Zhe Lu, Development of Activated Carbons from Coal Combustion By-Products, 2000 University Coal Research Contractors Review Meeting, 128-130.

Zhe Lu, M. Mercedes Maroto-Valer and Harold H. Schobert, Development of Activated Carbons from Coal Combustion By-Products, 17th Annual International Pittsburgh Coal Conference, 2000, Paper 29-7.pdf (CD-ROM publication).

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Zhe Lu, Yinzhi Zhang, Akhnuwkh Jones, M. Mercedes Maroto-Valer, John M. Andrésen, Joel L. Morrison and Harold H. Schobert, Assessment of the commercial utilization of activated carbons produced from high carbon fly ashes, 2001 Conference on Unburned Carbon on Utility Fly Ash, 9-11.

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