TITLE:	DEVELOPMENT OF ACTIVATED CARBONS FROM COAL COMBUSTION BY-PRODUCTS
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GRANT NO.:	DE-FG26-99FT40593
PERIOD OF PERFORMANCE:	July 1, 1999 – June 30, 2002
DATE:	March 14, 2001

1. ABSTRACT

Program Objective

The overall objective of this research program is to develop adsorbent materials from coal combustion by-products (CCBPs), mainly unburned carbon in fly ash. Compared to the conventional two-step process that includes a devolatilization of the raw materials, followed by an activation step, unburned carbon only requires a one-step activation process, since it has already gone through a devolatilization process while in the combustor. In this research program, the following three tasks have been defined:

- Collection of samples from different combustion processes to ensure that the findings can be applied to the different combustion technologies used by the power industry. The properties of this unique suite of CCBPs are extensively characterized by a wide range of analytical techniques.
- Several routes for the preparation of activated carbons are investigated, including physical activation with different gases, such as steam and CO_2, at various flowrates and temperatures, as well as chemical activation.
- The properties of the resultant activated carbons have been systematically characterized, especially their porous structure and possible commercial applications. This will provide information for the understanding of the mechanisms involved in the generation of activated carbon from unburned carbon and also to establish the optimum route for the production of activated materials.

Accomplishments Achieved To Date

Procurement and characterization of the suite of CCBPs. The samples collected have been produced in a variety of combustion processes, including: (i) pulverized utility boilers, where samples were collected from systems retrofitted with low- NOx burners and from units that have been retrofitted with a Selective Non Catalytic Reduction system; (ii) samples collected from an utility cyclone unit equipped with a beneficiation technology; (iii) class C fly ashes; and (iv) samples from a suspension-fired research boiler (2 MM Btu/hour).

A battery of tests was used to characterize the samples assembled. The determination of the loss-on-ignition (LOI) or carbon contents according to the ASTM C113 procedure showed that the samples collected have significantly different carbon contents. As expected, the sample from the cyclone unit contained the highest carbon content (LOI of ~ 80%), since this unit has been retrofitted with a technology to separate the unburned carbon from the fly ash. The samples from the utility boilers with low-NOx burners were collected from the hot-side hoppers and present carbon contents ~ 50%, while the samples from the suspension-fired research boiler have carbon contents around 59%. In contrast, the samples from the unit retrofitted with a Selective Non Catalytic Reduction system showed the lowest carbon content with values below 4%. The porosity of the unburned carbon samples assembled was characterized by N_2 adsorption isotherms at 77K. The results showed that the surface areas of the class F fly ash samples from the pulverized utility boilers were between 30-40 m^2/g, while the samples from the suspension-fired research boiler had surface areas around 115 m^2/g. As expected, the surface areas of the class C ashes have much higher surface areas than the class F, with values up to 390 m^2/g.

Development and characterization of activated carbons from unburned carbon. The activation of the unburned carbons was successfully carried out in a vertical furnace using a one-step process, that includes simultaneous carbonization and activation. This is due to the nature of the fly ash carbon, that has already gone through a devolatilization step while in the combustor, and therefore, only requires to be activated. The activation process used involves physical activation with steam of the unburned carbons at temperatures around 850°C for periods of 1-2 hours. The properties of the activated carbons that have been synthesized under controlled conditions, were systematically characterized to include a detailed description of the porous structure using conventional adsorption techniques, like N_2 adsorption isotherms at 77K. The samples activated for the longest time (2 hours) present higher BET surface areas than their counterparts activated for 1 hour. Steam activation of the unburned carbon can tailor its inherent mesoporosity into the desired porosity for a specific application and surface areas as high as 750 m^2/g were achieved after only 2 hours steam activation.

Significance to Fossil Energy Programs

The rise in unburned carbon concentration in coal combustion fly ashes may lead to the demand for the coal utility industry to begin offsetting coal with natural gas, or require additional coal cleaning to remove the ash prior to combustion. Both alternatives would clearly compromise the future of the US electric power industry that uses coal as the main energy source. Hence, the implication of this research program is to turn unburned carbon from a liability into an asset for the coal industry. Upon completion of this research program, a novel process for the production of adsorbent materials from unburned carbon will have been extensively investigated.

Plans for the Coming Year

The work planned for the coming year will continue the activation of the unburned carbon samples under a wider range of controlled operating variables in order to establish the optimum route for the generation of activated carbon materials. In addition, various modifications are being conducted in the activation system, including: installation of a HPLC pump to optimize the flow control of water during the steam activation experiments; development of a data acquisition control unit using commercial software; and scale-up of the reactor. In addition, an assessment of the commercial utilization of the resultant activated carbons produced will be conducted.

2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS AND STUDENTS RECEIVING SUPPORT FROM THE GRANT

Conference presentations

- Development of Activated Carbons from Coal Combustion By-Products, Zhe Lu, M. Mercedes Maroto-Valer, and Harold H. Schobert, 17th Annual International Pittsburgh Coal Conference, 2000, Paper 29-7.pdf (CD-ROM publication).
- Utilization of coal combustion waste for the production of activated carbons, Zhe Lu, M. Mercedes Maroto-Valer, and Harold H. Schobert, Penn State University Graduate Research Exhibition, 2001, Submitted.
- Assessment of the commercial utilization of activated carbons produced from high carbon fly ashes, Zhe Lu, Yinzhi Zhang, Akhnuwkh Jones, M. Mercedes Maroto-Valer, John M. Andrésen, Joel L. Morrison and Harold H. Schobert, 2001 Conference on Unburned Carbon on Utility Fly Ash, Submitted.
- One step activation of coal combustion waste, M. Mercedes Maroto-Valer, Yinzhi Zhang, Zhe Lu, John M. Andrésen and Harold H. Schobert, 26th Biennial Conference on Carbon, 2001, Submitted.
- Environmental benefits of producing adsorbent materials from unburned carbon, M. Mercedes Maroto-Valer, Zhe Lu, Yinzhi Zhang, Akhnuwkh Jones, John M. Andrésen, and Harold H. Schobert, 2001 International Ash Utilization Symposium, Submitted.
- Utilization of coal combustion waste for the production of activated carbons, Zhe Lu, Yinzhi Zhang, Akhnuwkh Jones, M. Mercedes Maroto-Valer, John M. Andrésen, Joel L. Morrison, and Harold H. Schobert, International Conference on Coal Science, 2001, Submitted.

Students Supported under this Grant

- Zhe Lu, graduate student in the Department of Energy and Geo-Environmental Engineering. The Pennsylvania State University.
- Akhnuwkh Jones, undergraduate student of The Pennsylvania State University.
- Christian Andrésen, visiting undergraduate student, now at University of Sydney, Australia.
- Kristin Jensen, visiting undergraduate student, now at Auburn University.