Title: Development of activated carbons from coal combustion by-products

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ABSTRACT

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. In particular, the implementation of regulations concerning NOx emissions by installing low-NOx burners has resulted in an increase in carbonaceous waste product. In 2000, around 82 million tons of coal combustion by-products (CCBPs) were generated in US, mainly fly ash containing unburned carbon. Due to the present lack of commercial demand for such materials, the fate of these products is mainly disposal. 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. Therefore, 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: 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".

Accomplishments Achieved To Date

Since the last 2001 UCR Contractors Review Meeting, the following accomplishments have been achieved:

- Task 1 "Procurement and characterization of CCBPs" was concluded. Class F fly ash samples from pulverized coal (PC) utility boilers, fixed-bed firing and fluidized beds as well as a class C fly ash were included in this study. The characterization studies showed that the samples collected have significantly different carbon contents, as determined by the ASTM C114 procedure, with the sample from the cyclone unit containing the highest carbon content (LOI of ~ 80%), since this unit has been retrofitted with a technology to separate the unburned carbon form the fly ash. The samples from the PC utility boilers with low-NOx burners were collected from the hot-side hoppers and present carbon contents ~ 50%, while the sample from the research boiler has carbon content around ~59%, while the class C fly ash sample has a low carbon content ~1-2%. The porosity of the samples assembled was characterized by N_2 adsorption isotherms at 77K. The surface areas of the class F fly ash samples from the utility PC units are between 30-40 m^2/g, while the samples from the PC research boiler had surface area around 115 m^2/g, and the sample from the cyclone unit had a very low surface area around10m^2/g. As expected, the surface area of the class C ash is much higher than that of the class F ashes, with values up to 390 m^2/g.
- Task 2 "Development of activated carbons" continued the activation of the samples in a vertical furnace using a one-step process by physical (steam or CO_2) or chemical (KOH pretreatment) methods. Various modifications have been made in the

activation system, including: installation of a HPLC pump to optimize the flow control of water during the steam activation experiments and scale-up of the reactor.

- Task 3 "Characterization of activated carbons" characterized the properties of the activated carbons that have been synthesized under controlled conditions to include a detailed description of the porous structure using conventional adsorption techniques, like N_2 adsorption isotherms at 77K. The samples activated with steam present generally higher surface areas than those using CO_2 or KOH pretreatment, probably due to the faster reaction rate of steam. The samples activated with steam present surface areas significantly higher than the parent samples ($47m^2/g$ vs. $717m^2/g$). It was found that for the steam activation samples, the surface areas increase with increasing activation time and temperature, at the expense of the decrease of the solid yields. However, as the activation time increases, the developing rate of micropore volume also decreases. Chemical pretreatment with KOH resulted in higher surface areas than those obtained by using steam for the same period of time. With increasing KOH load, there seems to be a small decrease of the surface area, as well as a reduction of the solid yield. Finally, it was possible to generate activated carbons with a surface area of $854m^2/g$ and a pore volume of 0.56ml/g, which are comparable to the values reported for commercial activated carbons.

Plans for the Coming Year

The work planned for the remaining months of the project will finish the activation of the unburned carbon samples to include the activation of the parent coal used to generate the unburned carbon samples investigated as well as demineralized samples. In addition, iodine number tests will be conducted to assess the commercial utilization of the resultant activated carbons produced, and compare their properties to commercial activated carbons. Finally, the graduate student involved in this project will be completing her graduate thesis and the final technical progress report will be prepared and submitted to DOE. It is also anticipated that peer-review papers will be produced form this research work.

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

Conference Presentations

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

One step activation of coal combustion waste, M. M.Maroto-Valer, Y. Zhang, Z. Lu, J. M. Andrésen and H. H. Schobert, 26th Biennial Conference on Carbon, 2001.

Environmental benefits of producing adsorbent materials from unburned carbon, M. M. Maroto-Valer, Z. Lu, Y. Zhang, A. Jones, J. M. Andrésen, and H. H. Schobert, 2001 International Ash Utilization Symposium, CD file: 82Maroto.pdf.

Utilization of coal combustion waste for the production of activated carbons, Z. Lu, Y. Zhang, M. M. Maroto-Valer, J. M. Andrésen, and H. H. Schobert, International Conference on Coal Science, 2001.

Tailoring fly ash carbons into commercial activated carbons, Y. Zhang, Z. Lu, M. M. Maroto-Valer, J. M. Andrésen and H. H. Schobert, 18th Annual International Pittsburgh Coal Conference, Australia, 2001,CD file: 52-021.pdf

Students Supported Under this Grant

Zhe Lu, graduate student in the Department of Energy and Geo-Environmental Engineering. The Pennsylvania State University.

Brandon N. Shaffer, undergraduate student of 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.