

Assessment of the commercial utilization of activated carbons produced from high carbon fly ashes

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Rationale

The U.S. electric power industry relies heavily on the use of coal as the main primary energy source. In 1998, more than 950 million tons or 90% of the total U.S. coal production was used in coal-fired units to generate over 55% of the total electricity produced. Furthermore, coal is the most abundant fossil fuel resource in the U.S., and therefore it will even play an increasing role as a source of energy in the 21st century. However, the implementation of more stringent environmental regulations, especially concerning NO_x emissions, has resulted in an alarming rise of carbonaceous wastes from coal combustion, also referred to as unburned carbon¹. Due to the present lack of routes for its effective use, around 6 million tons of unburned carbons are disposed every year in the U.S. 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, could force the coal and energy industry to recycle a larger amount of unburned carbon. Consequently, there is a clear need to establish environmental and cost-effective strategies for the use of these carbonaceous waste products from coal combustion.

Unburned carbon is a potential precursor for the production of adsorbent carbons due to its unique properties, as described here. The present global consumption of activated carbons is over 350,000 tons and it is estimated to rise 7% annually due to the ubiquitous use of activated carbons as adsorbent materials in a broad range of increasing household, medical, industrial, military and scientific applications. 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. 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. The authors have previously conducted extensive studies on the characterization of unburned carbon and showed that its properties are similar to those of conventional precursors for the production of premium carbon materials^{1,2}. These characterization studies were also presented at the previous 1998 and 1999 Conferences on Unburned Carbon on Utility Fly Ash^{3,4}. Furthermore, at last year 2000 Conference on Unburned

Carbon on Utility Fly Ash the authors demonstrated the potential of unburned carbon to be converted into activated carbons by steam activation ⁵. Accordingly, this last year the authors have focused on the optimization of the activation process and the characterization of the activated carbons produced.

Summary of Work

The activation of the fly ash carbons was carried out in an activation furnace that was designed and used by the proposers to activate carbons from coal-fired power plant ashes. The proposers have demonstrated that a one-step process, that includes simultaneous carbonization and activation, can be employed successfully for these materials ⁵. This is due to the nature of the unburned carbon, that has already gone through a devolatilization step while in the combustor, and therefore, only requires to be activated. The identified process is now being optimized to design a superior route for the generation of activated carbon materials from carbon in fly ash. This process 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 unburned 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 N₂ adsorption isotherms at 77K as well as an assessment of their commercial utilization.

Several routes for the preparation of activated carbons were investigated, including physical activation with different gases, such as steam and CO₂, at various flowrates and temperatures, as well as chemical activation. The samples activated with steam present generally higher surface area than those using CO₂ catalytic pretreatment, probably due to the faster reaction rate of steam. The activation studies have shown that despite the low particle size of the unburned carbon samples, the solid yields were relatively high, since the unburned carbon has undergone devolatilization in the combustor. This makes unburned carbon an attractive precursor for the production of activated carbons, since they present much higher solid yields than conventional precursors, such as wood. In addition, the particle size of the precursor strongly affects the solid yields of the resultant activated samples, with higher yields for the unburned carbon samples presenting bigger particle size distributions.

The raw unburned carbon materials have low surface area (40 m²/g) and pore volume. In contrast, the surface area of the activated samples are greatly increased compared to the parent samples, reaching surface areas over 750 m²/g, where high surface areas are characteristic for commercial activated carbons. 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 m²/g were achieved after only 2 hours steam activation.

The pore volume of the parent samples was mainly due to mesopores, with the mesopore volume accounting for over 60% of the total pore volume. In contrast, the steam activation process promotes the development of micropores with the micropore volume accounting for over 65% of the total pore volume. This microporosity feature is very desirable for commercial activated carbons for applications like water treatment.

Conclusion Remarks

This work shows that unburned carbon, which is regarded as a waste to be disposed, can be converted into a valuable activated carbon product with possible environmental applications. Furthermore, the activation process could successfully tailor the inherent mesoporosity of the raw materials into the desired microporosity, which makes these materials suitable activated carbons for potential environmental applications like water treatment. Finally, it is envisaged that increasing the activation time will result in higher surface area at the expense of some expense of the solid yield, and these experiments are now underway in our laboratory.

Literature cited

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