Utilization of unburned carbon from fly ash as precursor for high-value materials

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Rationale

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 5-8 million tons of unburned carbon were disposed, due to the present lack of efficient routes for its utilization. However, 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 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 studies were also presented at the previous 1998 and 1999 Conferences on Unburned Carbon on Utility Fly Ash [3, 4]. Accordingly, this research program focuses on the development of routes for the generation of premium carbon products from the unburned carbon present in fly ash.

The utilization of unburned carbon can bring enormous economical and environmental benefits to both the coal and utility industry. Although several technologies have been successfully developed to separate the unburned carbon from the fly ash, only a few power plants have installed a beneficiation process on their sites. This is due to the low value of the resultant separated materials, since a ton of fly ash is generally sold for as little as $10-20, and the unburned carbon is simply disposed. However, the economics of this process can be greatly enhanced if both separated materials can be used as precursors for high-value products. In fact, this is the case for the unburned carbon, which can be used as an excellent precursor for the generation of premium carbon products, like activated carbons and carbon artifacts. Therefore, the added value generated from the unburned carbon utilization would clearly offset the cost of the separation process. For instance, the average price for a ton of activated carbon

ranges from $500 up to $4000, which implies a potential 25-200 fold increase compared to the price of the ash (<$ 20/tonne). For the case of carbon artifacts, the calcined petroleum coke used for their manufacture usually costs ~ $ 220-250 / ton.

Summary of Work

In this program, fly ashes were collected from two coal-fired power plants, that have units retrofitted with low-NOx burners. The detailed study of these samples revealed that samples from hoppers on the first row (hot-side) of the electrostatic precipitators present the lowest LOI values (~10%), while bins in the last row (cool-side) present the highest LOI values (40-50%). Therefore, these cool-side bins are suitable hoppers for the collection of high carbon content ashes as feedstocks for carbon materials precursors [5].

The work conducted here also demonstrated the ability of unburned carbon from coal combustion by-products to generate activated carbons by steam activation. The inherent porosity of the parent unburned carbon samples with surface areas between 30-40 m^2/g, is mainly due to the presence of meso- and macropores. After 60 minutes activation time, the unburned carbon samples generated activated carbons with microporous structure and surface areas up to 443 m^2/g. Despite the low particle size of the unburned carbon samples, the solid yields are relatively high, since the unburned carbon has already gone through a devolatilization process in the combustor. Furthermore, the activation process can tailor the inherent mesoporosity of these materials into the desired porosity for specific applications [6].

For the second route regarding the use of unburned carbon as a precursor for carbon bodies, the unburned carbon samples were mixed and pelletized with calcined petroleum coke and coal tar binder pitch. The unburned carbon presents similar heat treatment (temperatures 1200-1400°C) and slightly higher H/C ratios than conventional petroleum coke, but it exhibits lower density than petroleum coke, probably due to its larger surface area. However, the density of the carbon pellets prepared with unburned carbon is comparable to that using only petroleum coke, due to a strong interaction between the unburned carbon and the coal tar binder pitch [5]. Therefore, the unburned carbon acts as a good filler for the carbon pellets produced and further tests will be performed to assess whether unburned carbon can be used as a replacement for the fine fraction of petroleum coke in the manufacture of carbon artifacts.

Future directions

We are presently working on Phase II of this project, where the protocols developed during Phase I will be used as baseline to establish optimum routes for the generation of activated carbon materials and carbon artifacts.

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