MICROPOROUS ACTIVATED CARBONS PRODUCED FROM UNBURNED CARBON IN FLY ASH AND THEIR APPLICATION FOR CO_2 CAPTURE

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Introduction

Fossil fuel electricity generation units rank as the first target to reduce anthropogenic emissions due to their stationary nature. Coal is the most abundant fossil fuel in the U.S., and therefore the reduction of CO_2 emissions from coal-fired units is an imperative to mitigate global climate change, and consequently, to guarantee the key role of coal in the 21st century. The costs of current CO_2 separation and capture technologies are estimated to be about three-fourths of the total cost of ocean or geological sequestration, where the processes involved are very energy intensive and the amine solutions used in the process have very limited lifetimes[1]. Therefore, novel solid sorbents with high CO_2 capacity at flue gas temperatures are being sought.

High carbon content fly ash, which is a byproduct stream from coal-fired combustors or gasifiers, is currently disposed as a waste, and there is a demand to develop technologies to utilize high carbon content fly ash. Following this demand, a one-step activation protocol has been developed by the authors to produce activated carbons from the residual carbon in fly ash, also referred to as unburned carbon[2, 3]. 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 or gasifier. The produced activated carbons with a fine particle size are not only rich in micropores, but they also present a high content of mesopores, which leads to good mass transfer properties during the adsorption process. Furthermore, a pretreatment process has been previously developed by the authors to modify the properties of unburned carbon in order to produce activated carbons with high surface area and high microporosity[4]. The present paper focuses on the CO_2 adsorption properties of this microporous activated unburned carbon. In addition, a chemical impregnation method to improve the CO_2 capacity of activated unburned carbon is also described.

Experimental

Fly ash samples. Two fly ash samples, FA1 and CC1, were collected and characterized. FA1 was collected from the Penn State University pulverized coal-fired suspension firing research boiler (2 MM Btu/hour) that uses a high volatile bituminous coal from the Middle Kittanning seam. CC1 was collected from a gasifier that uses a sub-bituminous coal as feedstock.

Deashing and oxidation. A conventional acid ($HCl/HNO_3/HF$) digestion step was conducted to remove the ash from the samples and concentrate the unburned carbon. Typically, 50 g of sample was treated with the above acids at 65°C for 4 hours. The deashed samples were labeled as FA1-DEM and CC1-DEM. The FA1-DEM was further treated with 5N HNO_3 at boiling temperature for 1 hour, then washed with distillated water until pH reached 7, and the resultant samples was labeled as FA1-N1.

Characterization of the samples. The loss–on-ignition (LOI) contents of the samples were determined according to the ASTM C311 procedure. The porosity of the samples was characterized by conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The pore volume was calculated from the volume measured in the nitrogen adsorption isotherm at a relative pressure of 0.95 (V_t). The total specific surface area, S_t, was calculated using the multi-point BET equation in the relative pressure range 0.05-0.35, as described previously[2,5]. From the adsorption isotherm, the micropore (<2nm) volume, V_{mi}, and external surface area, S_{mi}, were calculated using the α_S-method, where non-graphitized non-porous carbon black Cabot BP 280 (S_{BET}=40.2m^2/g) was used as a reference adsorbent[6]. The mesopore (2-50nm) volume (V_{me}) was calculated by subtracting the volume of V_{mi} from the V_t. The pore size distribution was calculated using the BJH method.

One-step activation and chemical impregnation. Both the parent (FA1) and pretreated samples (FA1-DEM and FA1-N1) were activated by steam using a horizontal furnace. The samples were heated under nitrogen flow to 850°C, and then steam was introduced in the reactor, while the reactor was kept under isothermal conditions for 1 hour. The activated carbon samples (AC-FA1, AC-FA1-DEM and AC-FA1-N1) were then impregnated with a PEI (polyetherimine) methanol solution and dried in a vacuum oven at 75°C overnight.

CO_2 adsorption studies. CO_2 adsorption and desorption studies were conducted using a PE-TGA 7 thermogravimetric analyzer at 30°C and 75°C. The weight change of the adsorbent was recorded and used to determine the adsorption capacities of the samples. More experimental information can be found elsewhere[7]. The adsorption capacity was reported in mg-adsorbate/g-adsorbent and was used to evaluate the performance of the samples prepared.

Results and Discussion

Deashing and oxidation. The LOI and pore structure parameters of the studied samples CC1 and FA1 are listed in Table 1. The LOI of the original samples CC1 and FA1 are 38.4% and 58.9%, respectively, which are higher than those reported in previous studies that are typically <15wt%[8]. However, this work focuses on the study of high carbon fly ashes as feedstock for activated carbons, and therefore, fly ash samples with high LOI contents were intentionally selected. The total surface area (S_{mi}+S_{me}) and total pore volume (V_{mi}+V_{me}) of sample CC1 are as high as 284m^2/g and 0.277ml/g, respectively, even prior to any treatment. This is consistent with our previous studies that indicated that some porosity is developed during the combustion or gasification process[2].

Table 1. LOI and pore structure parameters of the studied samples.

Sample	LOI %	Surface area, m^2/g		Pore Volume, ml/g	
		S_{mi}	S_{me}	V_{mi}	V_{me}
CC1	38	48	236	0.021	0.256
CC1-DEM	97	99	632	0.038	0.702
FA1	59	57	18	0.027	0.020
FA1-DEM	97	32	21	0.014	0.026
FA1-N1	99	189	20	0.094	0.024
AC-FA1	43	329	58	0.151	0.062
AC-FA1-DEM	89	704	159	0.318	0.172
AC-FA1-N1	97	1053	86	0.518	0.097

The deashing step used in the present paper can successfully concentrate the unburned carbon, where the resultant unburned carbons, CC1-DEM and FA1-DEM, have LOI values as high as 96.7% and 97.0%, respectively. In the case of CC1, the deashed sample (CCA-DEM) has a total surface area as high as 731m^2/g, compared to only 284m^2/g for the parent sample (CCA). This increase in surface area may partly come from the removal of the inorganic fly ash, which is virtually non-porous. However, the

same deashing step resulted in a decrease of the surface area for sample FA1, from $75m^2/g$ to $53m^2/g$ for FA1 and FA1-DEM, respectively. This surface area decrease was accompanied with a pore size enlargement, where FA1-DEM has more mesopores and less micropores than FA1. Further studies are needed to understand the effect of removing the ash in the porous texture of the samples.

XPS data has shown that the HNO_3 oxidation introduces oxygen functional groups on the surface of unburned carbon[4]. Furthermore, the HNO_3 treatment also resulted in an increase of the surface area of the samples, mainly due to the formation of new micropores, as shown in Table 1. The micropore surface area and pore volume of FA1-N1 are $189m^2/g$ and 0.094ml/g, respectively, compared to $32m^2/g$ and 0.014ml/g before treatment. In contrast, its mesopore surface area and pore volume are very similar before and after HNO_3 treatment ($21m^2/g$ and 0.026 ml/g vs. $20m^2/g$ and 0.024ml/g). Additionally, the HNO_3 oxidation also increased the carbon content of sample to 99 % for FA1-N1 compared to 97% for FA1-DEM.

The pororus texture properties of the samples after activation are also listed in Table 1. Without any pretreatment, the FA1 activated sample (AC-FA1) has a total surface area of 387 m^2/g, compared to 863 m^2/g for the activated sample produced following deashing (AC-FA1-DEM) and 1,139 m^2/g for the HNO_3 treated sample (AC-FA1-N1). In addition to the significant increase in surface area, the HNO_3 treatment can also modify the pore size distribution of the activated sample, resulting in a more microporous sample ($1,053m^2/g$ and 0.518ml/g).

CO_2 adsorption studies. The CO_2 adsorption studies of the CC1 and CC1-DEM samples were conducted at both 30°C and 75°C, and the capacity results are shown in Figure 1. At 30°C, the parent sample CC1 can adsorb around 17.5 mg CO_2/g, while CC1-DEM can adsorb as much as 43.5 mg CO_2/g. This is consistent with the much higher total surface area of the latter, $284m^2/g$ vs. $731m^2/g$ for CC1 and CC1-DEM, respectively (Table 1). As expected from a physical adsorption process, the CO_2 adsorption capacities of both sample decreased to 10.2 mg CO_2/g and 22.0 mg CO_2/g for raw CC1 and CC1-DEM, respectively, when the temperature was rised from 30 to 75°C.

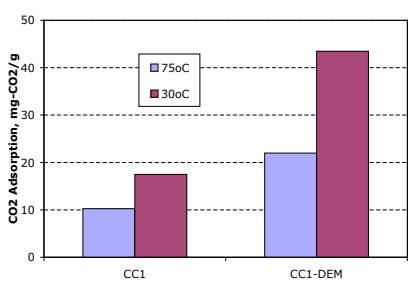

Figure 1. CO_2 adsorption capacities of samples CC1 and CC1-DEM at 30°C and 75°C.

The CO_2 adsorption capacities of samples FA1, FA1-DEM and their activated counterparts at 75°C are shown in Figure 2. Corresponding to its highest surface area and microporosity, AC-FA1-N1 has the largest CO_2 adsorption capacity, 23.2 mg CO_2/g.

The parent samples FA1 and CC1, their deashed and activated counterparts were impregnated with PEI and their CO_2 adsorption capacities at 75°C are shown in Figure 3. After PEI impregnation, all samples have higher CO_2 adsorption capacities, especially the PEI modified CC1-DEM can adsorb as much as 93.6 mgCO_2/g, compared to only 9.7 mgCO_2/g for its non-impregnated counterpart. However, the PEI impregnation was not as effective for all the samples. For example, the CO_2 adsorption capacity of AC-FA1-N1 only doubled after PEI impregnation, 43.8 mgCO_2/g vs. 23.2 mgCO_2/g.

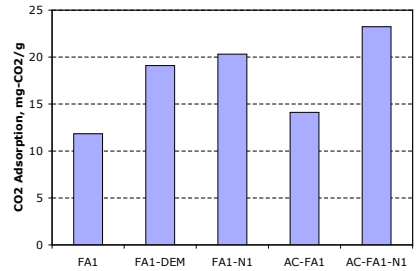

Figure 2. CO_2 adsorption capacities at 75°C for FA1 and its demineralized and activated counterparts.

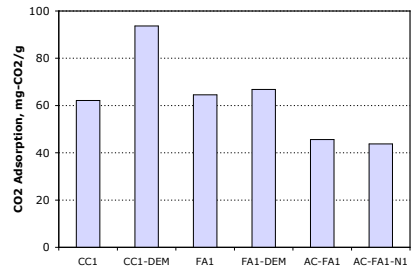

Figure 3. CO_2 adsorption capacities at 75°C for the PEI chemically impregnated samples.

Conclusions

Unburned carbon with carbon content ~97% can be concentrated from fly ash by using conventional acid digestion The deashing process not only can remove the fly ash from unburned carbon, but also changes the porous structure and surface properties of unburned carbon. Activated carbons with high surface area and microporosity, and CO_2 adsorption capacities can be produced from the unburned carbon treated with boiling HNO_3. The impregnation of PEI can improve significantly the CO_2 adsorption of unburned carbon and its activated counterparts, where the PEI impregnated deashed CC1 sample can adsorb as much as 93.6 mg CO_2/g at 75°C.

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References

(1) International Energy Agency, CO_2 reduction – Prospects for coal, 1999
(2) Zhang, Y.; Lu, Z.; Maroto-Valer, M.M.; Andrésen, J.M. and Schobert, H.H., Energy & Fuels, 2003, 17, 369.
(3) Zhang, Y., Maroto-Valer M.M., Lu, Z., Andrésen, J.M. and Schobert, H.H., Proceeding of American Carbon Society, Carbon'01, 2001, CD-Rom Zhang38.1.pdf
(4) Zhang, Y., Tang, Z., Maroto-Valer, M.M. and Andrésen, J.M., Prepr. Pap. - *Am. Chem. Soc., Div. Fuel Chem.*, **2003**, *48(1)*, 65-66.
(5) Zhang, Y.; Wang, M.; He, F. and Zhang, B. *J. Mater. Sci.* ***1997,*** *32*,6009
(6) Kruk, M.; Jaroniec, M.; Gadkaree, K.P., J. Colloid Interface Sci., 1997, 192, 250
(7) Tang, Z., Zhang, Y., Maroto-Valer, M.M., Prepr. Pap. - *Am. Chem. Soc., Div. Fuel Chem.*, **2004**, *49(1),* In this volume.
(8) Hill, R.L.; Sarkar, S.L.; Rathbone, R.F.; Hower, J.C. Cem Concr. Res., 1997, 27(2), 193.