

Use of Unburned Carbon in Fly Ash as Precursor for the Development of Activated Carbons

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KEYWORDS: unburned carbon, activated carbons.

ABSTRACT

The increasing role of coal as a source of energy in the 21st century will demand environmental and cost-effective strategies for the use of carbonaceous waste products from coal combustion. The carbonaceous residue in fly ash, unburned carbon (UC), is a potential precursor for the production of adsorbent carbons, since it has gone through a devolatilization process while in the combustor, and therefore, only requires to be activated. Accordingly, this paper demonstrates the potential for converting unburned carbon from coal combustion waste to activated carbons. The three parent UC samples that were examined, have surface areas between 30-40 m²/g. After steam activation at 850°C, the unburned carbon samples generated activated carbons with microporous structure and surface areas up to 443 m²/g. Despite the low particle size of the UC samples, the solid yields are relatively high, since the UC has been previously devolatilized in the combustor. The inherent porosity of the UC samples is highly mesoporous, with the mesopore volume accounting for ~ 66% of the total pore volume. The activation process promotes the development of micropores, with the micropore volume accounting for over 60% after steam treating.

INTRODUCTION

The US electric power industry relies heavily on the use of coal as the primary energy source. In 1997, around 90% of the total US coal production was used in coal-fired units to generate over 55% of the total electricity.¹ Furthermore, coal is the most abundant fossil fuel resource in the US, and therefore it will even play an increasing role as a source of energy in the 21st century.² However, the use of coal for energy generation faces environmental challenges due to the emissions of pollutants such as NO_x and SO_x from coal combustion furnaces and such pressures will only intensify in the next century. 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 regulations. In particular, the implementation of these regulations concerning NO_x emissions is being addressed in coal combustion furnaces mainly by a combination of low-NO_x burners and catalytic reduction systems. Although low-NO_x burner technologies efficiently decrease the emissions level by lowering the temperature of combustion, they also reduce the combustion

efficiency, resulting in an increase in carbonaceous waste product.³ In 1997, the combustion of 830 million tons of coal generated around 75 million tons of coal combustion by-products (CCBPs), mainly fly ash containing unburned carbon.⁴ 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.

The carbonaceous residue in fly ash, unburned carbon, is a potential precursor for the production of adsorbent carbons, since it has gone through a devolatilization process while in the combustor, and therefore, only requires to be activated. The present global consumption of activated carbons is over 350,000 tons and it is estimated to rise 7% annually.⁵ The main reason for this expanding market is the ubiquitous use of activated carbons as adsorbent materials in a broad range of increasing household, medical, industrial, military and scientific applications. These range from gas-phase adsorption in household air conditioning equipment and industrial emissions control, to liquid-phase adsorption for water treatment and even gold recovery. 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.² However, for these new precursors to compete effectively with the conventional raw materials like coal and wood, they must be inexpensive, have a low mineral matter content and be easily converted into activated carbons. The unburned carbon in the ash furnishes satisfactorily all these conditions, since it can be easily obtained from the utility industries as a by-product, it can be beneficiated from the fly ash by commercially available techniques and it has already gone through a devolatilization process in the combustor and, therefore, only requires to be activated. Furthermore, the average price for a ton of activated carbon ranges from \$500 up to \$4000,⁵ which implies a potential 50-400 fold increase compared to the price of the ash (currently \$10-20/ton). Therefore, the use of unburned carbon as precursor for the production of activated carbons would help the utilities to offset the cost of installing and running a beneficiation process. Accordingly, this work addresses the potential use of unburned carbon from coal combustion as precursor for the production of adsorbent carbons.

EXPERIMENTAL

Three unburned carbon samples, UC-KY, UC-WI and UC-PA, obtained from power plants at Kentucky, Wisconsin and Pennsylvania, respectively, were investigated. A series of preliminary enrichments were conducted on UC-KY (Dale unit #3 operated by Eastern Kentucky Power) to increase the amount of carbon in the ash, including an initial screening of the sample with a 140 mesh sieve (106 μm), with the 140+ fraction being triboelectrostatically separated to obtain a sample with an inorganic matter content below 10 %. The UC-WI (Wisconsin Electric Power Co.) sample was processed directly through the triboelectrostatic separator without the initial screening step and also presented a glass content of $\sim 10\%$ vol. These carbon-enriched samples were then used as feedstock for the production of activated carbons. UC-PA was collected from Shawville station Unit #4 operated by GPU Genco. This sample was collected from cool-side

hopper number 22, since previous studies by the authors have demonstrated that cool-side hoppers exhibit higher LOI contents than their hot-side counterparts.⁶ UC-PA has an LOI value of 42%.

The activation of the samples was carried out in an activation furnace, that consists of a stainless steel tube reactor inside a vertical tube furnace. Typically 3 g of sample was held isothermally at 850°C for periods of 60 minutes in flowing steam (~1.0-0.3 g/min). The porosity of the samples was characterized conducting N₂ adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The BET surface areas were calculated using the adsorption points at the relative pressures (P/P₀) 0.1 - 0.25. The values reported were corrected to a mineral-free basis using the 6 m²/g surface area measured for a high content ash sample and the TGA-derived inorganic contents for the respective density fractions.⁷ The total pore volume, V_{TOT}, was calculated from the amount of vapor adsorbed at the relative pressure of 0.95. The mesopore (pores 2-50 nm in width) and micropore (pores <2 nm in width) volumes were calculated using the BJH and DR equation, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the N₂-77K adsorption isotherms for the three UC samples and illustrates the inherent porosity of these materials. All the adsorption isotherms are Type II according to the BDDT classification and they are typical for nonporous or macroporous adsorbents, on which unrestricted monolayer-multilayer adsorption can occur.

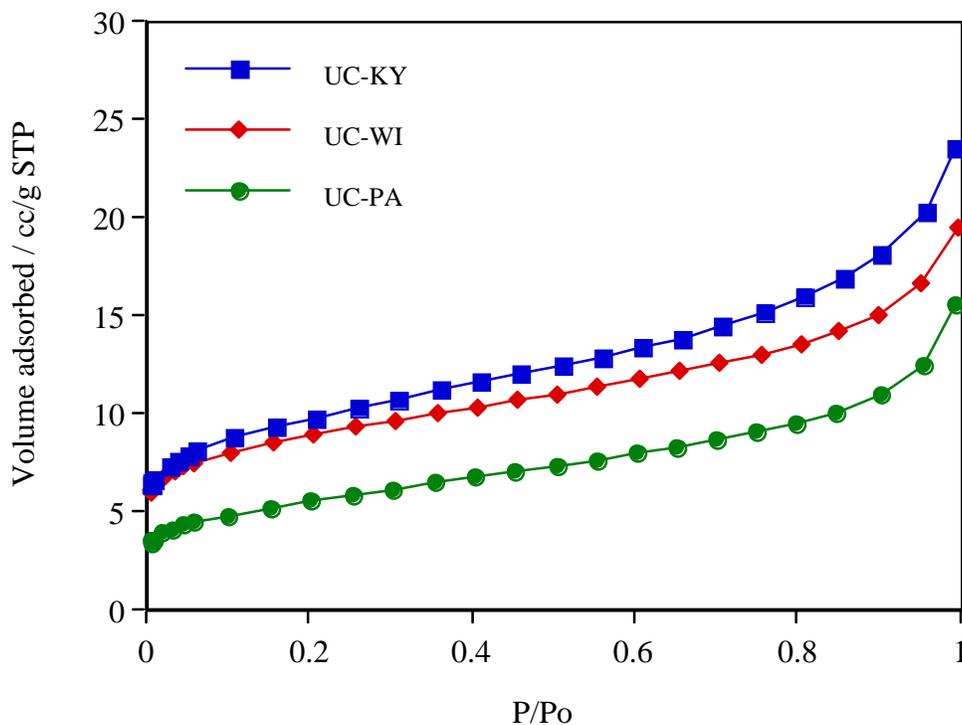


Figure 1 N₂-77K adsorption isotherms for the three UC samples.

Table 1 lists the BET surface areas (SA) and total pore volume (V_{TOT}) for the precursors. The three UC samples have surface areas between 30-40 m^2/g . Previous studies conducted by the authors on a range of fly ashes and Density Gradient Centrifugation concentrates have shown that the extensive and rapid devolatilization that coal undergoes in the combustor, seems to promote the generation of meso- and macropores.⁷ Pore size distribution studies were also conducted and showed that the pore volume is mainly due to mesopores, with the mesopore volume accounting for over 60% of the total pore volume.⁷

Table 1 Solid yield, BET surface area and total pore volume for the unburned carbon samples and their activated counterparts.^a

Sample	Activation time / min	Solid yield / % weight	BET S.A. / m^2/g	V_{total} / cc/g
UC-KY	--	--	40	0.03
UC-WI	--	--	38	0.03
UC-PA	--	--	30	0.02
UC-KY-Act	60	73	332	0.15
UC-WI-Act	60	55	443	0.14
UC-PA-Act	60	79	110	0.04

^a The solid yields and surface areas are expressed in ash free basis.

The solid yields of the UC samples activated for 60 minutes are also listed in Table 1. Despite the low particle size of the UC samples, the solid yields are relatively high, since the UC has undergone devolatilization in the combustor. This makes the UC an attractive precursor for the production of activated carbons, since they present much higher solid yields than conventional precursors, such as wood. UC-KY and UC-PA present higher solid yields than UC-WI (73% vs. 55%), due to their larger particle size (200 μm vs. 45 μm). Previous studies have shown that the particle size of the precursor strongly affects the solid yields of the resultant activated samples, with higher yields for bigger particle size fractions.⁸

Figure 2 shows the N_2 -77K adsorption isotherms for the steam activated UC samples. The isotherms are Type I, concave to the P/P_0 axis, that are typical for microporous materials. However, the isotherms do not reach a plateau at high relative pressures, indicating the presence of some meso- and macro-porosity. The activated carbons generated from the samples UC-KY and UC-WI present higher adsorption isotherms than that of UC-PA. This is reflected in UC-KY-Act and UC-WI-Act exhibiting surface areas and pore volumes higher than that of UC-PA-Act (332 and 443 m^2/g vs 110 m^2/g , Table1). This may be due to the lower steam flowrates used for the first two samples, resulting in more favorable conditions for the production of activated carbons. The higher ash content of UC-PA compared to that of UC-KY and UC-WI may also play a detrimental role in the activation of this sample. Further activation studies are being conducted to ascertain the role of the ash in the activation process of the unburned carbon.

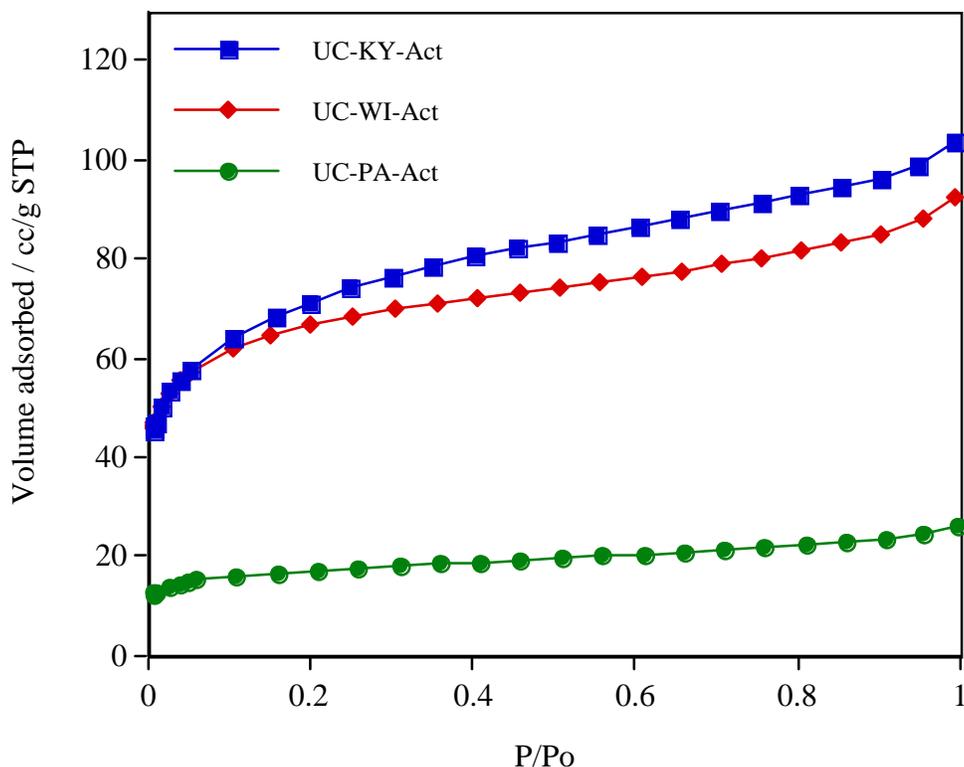


Figure 2 N₂-77K adsorption isotherms for the activated samples

Figure 3 compares the meso- and micropore volume for the precursors and the activated samples. As previously described, the inherent porosity of the UC samples is highly mesoporous, with the mesopore volume accounting for ~ 66% of the total pore volume. The activation process promotes the development of micropores, with the micropore volume now accounting for over 60% of the total. Pore size distribution studies and CO₂ porosity measurements are in progress.

CONCLUSIONS

The work reported here has demonstrated the ability of unburned carbon from coal combustion waste to generate activated carbons by steam activation. The inherent porosity of the parent unburned carbon samples with surface areas between 30-40 m²/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 m²/g. Despite the low particle size of the UC samples, the solid yields are relatively high, since the unburned carbon has already gone through a devolatilization process in the combustor. The activation process can tailor the inherent mesoporosity of these materials into the desired porosity for a specific application. For example, the mesopore volume accounted for ~ 66% of the total pore volume for the parent samples, while after activation the micropore volume accounted for over 60% of the total. Furthermore, ongoing work is presently developing other possible routes for the use of unburned carbon as filler for the production of carbon artifacts. Work conducted in this novel area is also presented in these Proceedings.⁶

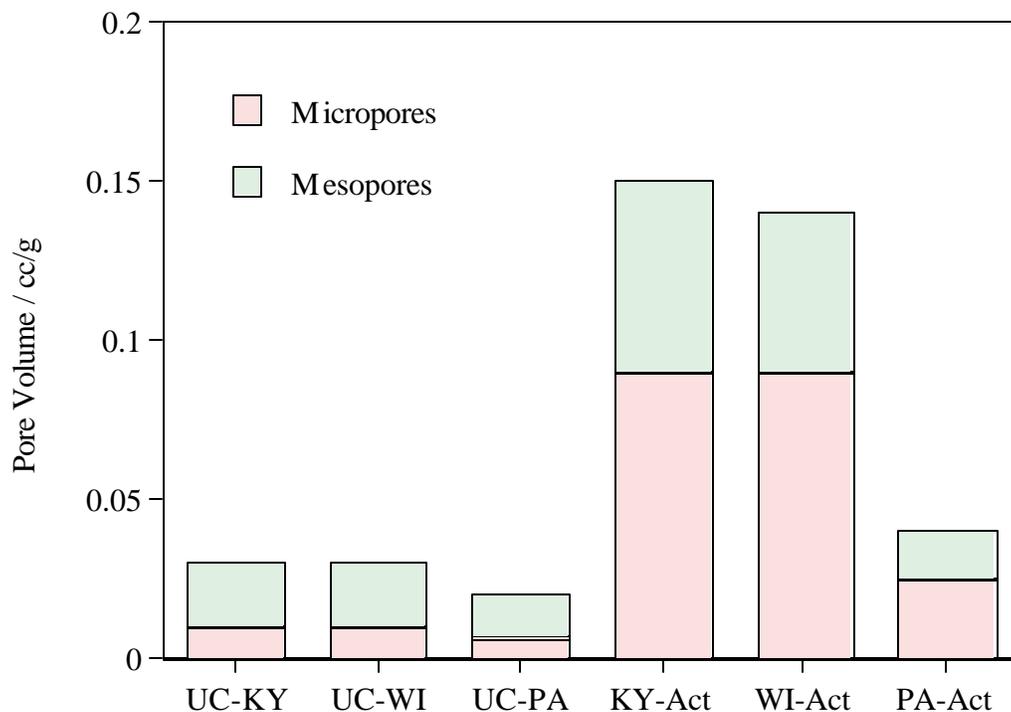


Figure 3 Distribution of the micro- and mesopore volume of the UC and their activated samples.

ACKNOWLEDGMENTS

The authors wish to thank the Research Council of the Basque Government and the Consortium for Premium Carbon Products from Coal (CPCPC) at The Pennsylvania State University for financial support.

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