# $CO_2$ CAPTURE USING ANTHRACITE BASED SORBENTS

*Zhong Tang, M. Mercedes Maroto-Valer and Yinzhi Zhang*

The Energy Institute and the Department of Energy and Geo-Environmental Engineering, Pennsylvania State University,
209 Academic Projects Bldg., University Park, PA 16802

## 1. Introduction

Activated carbons are sorbents used in a wide range of household, medical, industrial, military and scientific applications, including gas-phase and liquid-phase processes. The activation process together with the intrinsic nature of the precursors strongly determines the characteristics of the resulting activated carbons. Anthracites have inherent chemical properties, fine structure and relatively low price that make them excellent raw materials for the production of activated carbons [1-5].

New solid-based sorbents are currently being investigated for $CO_2$ capture. Special attention is being paid to the cost of the sorbent, due to the large amount of sorbent required to control $CO_2$ emissions. In this work, it is anticipated that high- surface-area powdered anthracites, which have been amine impregnated will satisfy this need and provide a superior low-cost $CO_2$ sorbent. Accordingly, this paper focuses on the optimization of steam activation of anthracites to produce high surface area activated carbons (AC) and characterize their $CO_2$ capture capacity.

## 2. Experimental

**2.1 sample characterization and activation.** One Pennsylvania anthracite (PSOC-1468) was obtained from the Penn State Coal Bank. Table 1 shows the proximate and ultimate analyses results, as provided by the Penn State Coal Bank. The anthracite was screened and the sample with particle size between 150-250μm was used for producing the activated carbon by steam activation. A fluidized bed was used for the activation experiments. The activation temperature was 850°C, and the steam concentration was 65.8% in the feeding gas stream. 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 total pore volume, $V_t$ was calculated from the amount of vapor adsorbed at relative pressure of 0.95, and the total surface area $S_t$ was calculated using the multi-point BET equation in the relative pressure range 0.05-0.35. The micropore (<2nm) size distribution and mesopore (2-50nm) size distribution were calculated by the DFT and BJH methods, respectively.

**2.2 $CO_2$ adsorption/desorption studies.** The adsorption and desorption performance of the produced activated anthracites (ACs) was conducted using a PE-TGA 7 thermogravimetric analyzer. The weight change of the adsorbent was followed to determine the adsorption and the desorption performance of the ACs. In a typical adsorption/desorption study, about 20-25mg of the AC was placed in a small platinum pan, heated to 100°C in $N_2$ atmosphere at a flow rate of 100mL/min, and held at that temperature for 30 minutes. Then the temperature was adjusted to the desired adsorption temperature and 99.8% bone-dry $CO_2$ adsorbate was introduced at a flow rate of 100mL/min. After adsorption, the gas was switched to 99.995% pure $N_2$ at a flow rate of 100mL/min to perform the desorption at the same temperature. Adsorption capacity in mg-adsorbate/g-adsorbent and desorption capacity in percentage were used to evaluate the adsorbent, where these values are calculated from the weight change of the sample in the TGA adsorption/desorption process.

## 3. Results and Discussion

**3.1 Effect of activation time on the porosity of the activated anthracites** In this study, the activation temperature was selected at 850°C according to previous studies conducted by the authors[5]. The typical isotherms of the resultant activated carbon with different activation time are shown in Figure 1. For comparison, the isotherm of the raw sample is also presented in Figure 1.

Figure 1 shows that the activation dramatically increases the surface area and pore volume of the anthracite. All the isotherms of ACs are Type I according to the BDDT (Brunauer, Deming, Deming, Teller) Classification[6]. This indicates that the ACs made from anthracite have many micropores and only a few mesopores. With increasing activation time, the isotherm shows a more open keen at lower relative pressure of the isotherm, indicating a broader pore size distribution with larger micropores and increasing mesoporosity.

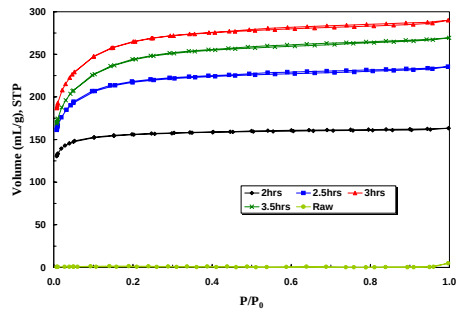


**Figure 1.** $N_2$-77K isotherms of the raw anthracite and its steam activated carbons produced at 850°C using different activation times.

Figures 2 and 3 show the micropore and mesopore size distribution of the activated anthracites, respectively. It can be seen that there are no micropores and few mesopores for the raw anthracite. In contrast, after activation, there is a significant amount of mesopores in the ACs (Figures 2 and 3). For the AC after 2 hours activation time, there is a large peak between 0.4-1.0nm. For the ACs produced after 2.5 and 3.0 hours activation time, the peak between 0.4-1.0nm is still there, and there are some additional peaks at 1.6 and 2.0 nm, and also a peak at 2.4 for the AC sample produced after 3 hours steam activation. Furthermore, for the AC sample produced after 3 hours activation time, the largest peak moves to 1.2nm, and the height of the peaks at 1.6, 2.0 and 2.4nm increases. Due to technical limitations of the instrument, it is not possible to get adsorption data at very low relative pressure, and therefore the pore size distribution < 0.4nm cannot be calculated by the DFT method. However, the results indicate that the pore development during activation includes pore opening followed by pore enlargement.

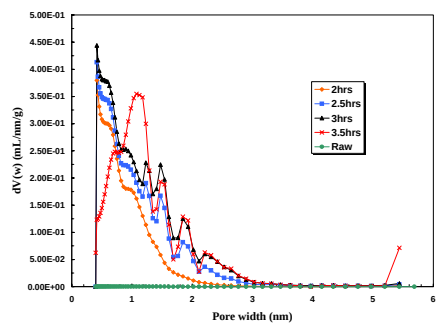


**Figure 2.** Micropore size distribution of the raw anthracite and its steam activated carbons produced at 850°C using different activation times.

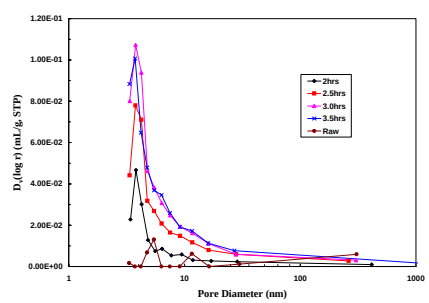


**Figure 3.** Mesopore size distribution of the raw anthracite and its steam activated carbons produced at 850°C using different activation times.

Figure 3 shows that all the ACs with different activation time have the same mesopore distribution profile. This indicates that the ACs have similar mesopore structure and mesopore size.

The surface areas and pore volumes for the activated carbons produced by steam activation of anthracite are presented in Table 2. It can be seen that the surface and pore volume first increase with increasing activation time and get to a maximum value after 3.0 hours activation (928m$^2$/g and 0.442mL/g), and then decrease with increasing activation time (855m$^2$/g and 0.412mL/g for AC with 3.5 hours activation time). However, the ratio of micropore surface area over total surface area and the ratio of micropore volume over total pore volume keep decreasing with increasing activation time. For instance, the ratio of micropore surface area decreases from 98.0% to 95.3%, when increasing the activation time from 2 to 3.5 hours. Similarly, the ratio of micropore volume to total pore volume decreases from 95.6% to 90.3% when increasing the activation time from 2 to 3.5 hours. This indicates that larger pores were produced with increasing activation time.

**3.2 $CO_2$ adsorption/desorption of the activated anthracites** Table 3 lists the $CO_2$ adsorption and desorption results of the ACs at 30 and 75°C. Because the $CO_2$ adsorption is mainly a physical process, the adsorption capacity decreases with increasing adsorption temperature, and the $CO_2$ capture capacity of the ACs at 30°C is about half to one-third to that of the ACs at 75°C. It can be seen that at 75°C, the AC with 2.0 hours activation time has the highest $CO_2$ capture value (26.32mg-$CO_2$/g-AC), while at 30°C, AC after 3.5 hours activation has the highest $CO_2$ capture value (60.90mg-$CO_2$/g-AC). However, it was expected that the AC with the highest surface area would give the highest $CO_2$ capture value. Table 2 shows that the surface area of AC after 2.0hrs activation is only 540m$^2$/g, which is the smallest among the four ACs studied here. Furthermore, the surface area of AC after 3.5hours activation is also not the highest among the ACs.

If all the total pore volume was effectively used to adsorb $CO_2$, it can be calculated that the theoretical maximum amount of the $CO_2$ adsorbed by the ACs would be 232.7mg/g, 334.2mg/g, 412.4mg/g and 384.2mg/g for the four ACs produced here after 2.0, 2.5, 3.0, and 3.5 hours, respectively. For this calculation it is considered that the liquid density of $CO_2$ is 0.93g/L, and the adsorbed $CO_2$ changes to the liquid phase due to capillary condensation[7]. However, Table 3 shows that the adsorbed amount of the $CO_2$ is much lower than the theoretical values. This indicates that not all the surface area or the pore volume of the AC contribute to the adsorption of the $CO_2$ and only some pores are used to adsorb $CO_2$. However, it remains unclear whether the preferred pore size is close to the $CO_2$ molecular diameter (0.208nm) or whether it should be larger than the $CO_2$ molecular diameter. Finally, Table 3 shows that for all the samples the desorption is higher than 97%, indicating that these ACs can readily desorb the $CO_2$ and be reused.

## 4. Conclusions

An anthracite sample (PSOC-1468) was selected for this study to make activated carbon as adsorbents for $CO_2$ capture. A lab scale fluidized bed was used for the activation and the activation temperature used was 850°C. The $N_2$-77K isotherms show that the ACs made from anthracite have highly developed microporosity and a small amount of mesopores. The surface area can get up to 928m$^2$/g with 3 hours activation time. However, extending the activation time beyond 3 hours decreases the surface area. A TGA instrument was used to characterize the $CO_2$ capture capacity at 30 and 75°C. The $CO_2$ capture capacity was 60mg-$CO_2$/g-sorbent for the AC with 3.5 hours activation time at 30°C adsorption temperature. Contrary to expected, the $CO_2$ capture results do not show any clear relationship with the surface area. The desorption capacity of the ACs are very high (>97%), indicating that these samples can be reused for $CO_2$ capture.

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**Table 1. Proximate and ultimate analyses of the anthracite sample used (PSOC-1468).**

| Proximate analysis | | | | Ultimate analysis | | | | |
|---|---|---|---|---|---|---|---|---|
| Moisture Wt% | Ash wt% | Volatile wt% | Fixed C wt% | C % | H % | N % | S % | O % |
| 4.51 | 6.83 | 3.65 | 89.52 | 96.2 | 1.40 | 0.84 | 0.49 | 1.55 |

**Table 2. Surface areas and pore volumes of the raw anthracite and its steam activated carbons produced at 850°C using different activation times.**

| Sample number | Activation time, hr | $S_t$ m$^2$/g | $S_{mi}$ m$^2$/g | $V_t$ mL/g | $V_{mi}$ mL/g | Average pore diameter, nm |
|---|---|---|---|---|---|---|
| Raw | | 1 | | | | |
| 1 | 2.0 | 540 | 529 | 0.250 | 0.239 | 1.85 |
| 2 | 2.5 | 762 | 733 | 0.360 | 0.330 | 1.89 |
| 3 | 3.0 | 928 | 891 | 0.442 | 0.406 | 1.91 |
| 4 | 3.5 | 855 | 814 | 0.412 | 0.372 | 1.93 |

**Table 3. $CO_2$ capture results for the produced ACs at 30 and 75°C.**

| AC sample | 30°C | | 75°C | |
|---|---|---|---|---|
| | Adsorption mg-$CO_2$/g-sorbente | Desorption % | Adsorption mg-$CO_2$/g-sorbente | Desorption % |
| Raw | 38.21 | 89 | 16.05 | 100 |
| 2.0hrs | 58.52 | 97 | 26.32 | 97 |
| 2.5hrs | 58.51 | 97 | 24.24 | 98 |
| 3.0hrs | 53.14 | 99 | 21.55 | 99 |
| 3.5hrs | 60.90 | 99 | 21.68 | 99 |