

USE OF ACTIVATED ANTHRACITES FOR CO₂ CAPTURE

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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 [1-3].

New solid-based sorbents are currently being investigated for CO₂ capture. Special attention is being paid to the cost of the sorbents, due to the large amount of sorbents required to control CO₂ emissions. It is anticipated that high- surface-area amine impregnated activated anthracites can satisfy this need and provide a superior low-cost CO₂ sorbent. The present paper focuses on the optimization of steam activation of anthracites to produce high surface area activated carbons (AC) and characterize their CO₂ capture capacity. The follow-up paper also published in this conference and titled "CO₂ Adsorption by Surface Modified Carbon Sorbents" discusses several surface treatment methods to modify the surface properties of the carbon sorbents in order to improve their CO₂ capture capacity.

Experimental

Three anthracite samples (PSOC-1468, AN-1 and AN-2) were used for this work. Table 1 shows the proximate analysis results. A fluidized bed was used for the activation experiments. N₂ adsorption isotherms at 77K were measured 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 CO₂ adsorption performance of the produced anthracite based activated carbons (AC) was conducted using a PE-TGA 7 thermogravimetric analyzer, as described elsewhere [4]. Adsorption capacity in mg-adsorbate/g-adsorbent was used to evaluate

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the adsorbent, where these values are calculated from the weight change of the sample in the TGA adsorption process.

Table 1. Proximate analyses of the anthracite samples studied

Name	Moisture wt%	Ash wt%	Volatile wt%	Fixed C wt%	Fixed C wt% daf*
PSOC-1468	4.51	6.83	3.65	89.52	96.9
AN-1	4.58	9.73	4.64	81.05	97.0
AN-2	5.04	6.43	3.36	85.17	95.9

* Calculated following ASTM D 388-99

Results and Discussion

Effect of activation conditions on the pore structure of the activated carbons

The effect of the activation parameters, including time, temperature and anthracite feedstock, on the pore structure of the activated carbons were investigated in this work. Figures 1-2 show the N₂ isotherms of the activated carbons made from PSOC-1468 at different activation times and temperatures, respectively. Table 2 lists the pore structure parameters (surface area and pore volume) of the produced activated anthracites.

The activation dramatically increases the surface area and pore volume of the anthracite. All the isotherms of the resultant ACs are Type I according to the BDDT (Brunauer, Deming, Deming, Teller) Classification [5]. This indicates that the ACs made from anthracite have mainly micropores and only a few mesopores. The ratio of micropore volume to total pore volume for all activated samples is larger than 90%, except for the sample activated at 890°C for 3 hours, which is 78%. Increasing activation temperature and longer activation time favor the development of larger micropores and smaller mesopores, as indicated by the more open knee at lower relative pressures of the isotherm.

Table 2 shows that the surface and pore volume first increase with increasing activation time and get to a maximum value after 3.0 hours activation (928m²/g and 0.442mL/g), and then decrease with increasing activation time (855m²/g and 0.412mL/g for AC with 3.5 hours activation time). This is consistent with the isotherm that shows a more open knee at lower relative pressure, indicating a broader pore size distribution with larger micropores and increasing mesoporosity (Figure 1).

The activation temperature shows a great effect on the pore structure of the activated anthracites (Figure 2 and Table 2), where the surface area of the ACs activated at 800, 850 and 890°C for 3hrs are 607, 928 and 639 m²/g, respectively. The micropore volume values follow a similar trend (0.271, 0.406 and 0.275 mL/g at 800, 850 and 890°C, respectively), indicating that the lower activation temperature (800 and 850°C) helped to produce highly microporous activated carbon from anthracite, while higher temperatures (890°C) developed more mesopores in the activated carbon. When considering both

the activation time and temperature, the optimum activation conditions for PSOC-1468 are 850°C and 3hrs in terms of maximizing the surface area and pore volume.

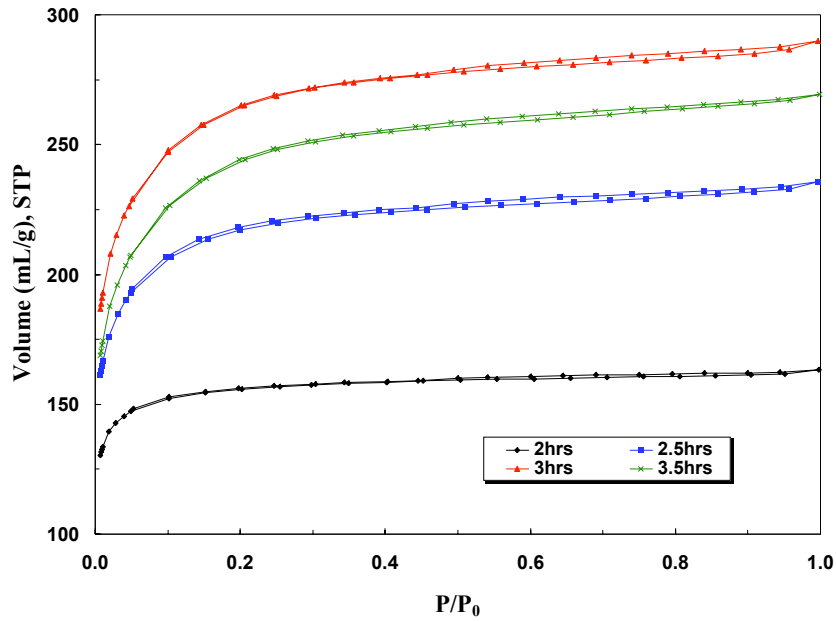


Figure 1. N₂ isotherms of ACs of anthracite PSOC-1468 activated at 850°C for different times

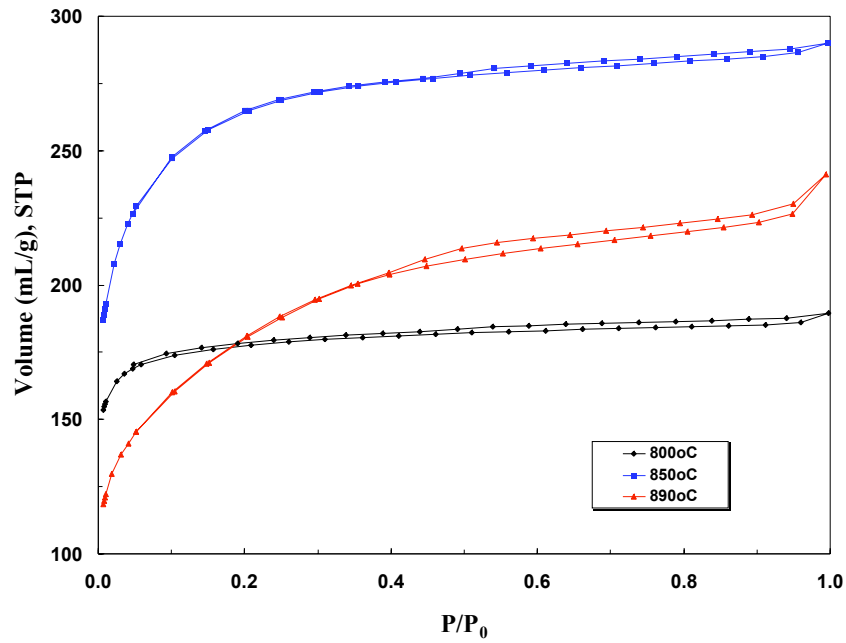


Figure 2. N₂ isotherms of ACs of anthracite PSOC-1468 activated for 3hrs at different temperatures

Table 2. Pore structure parameters of the ACs produced from anthracite PSOC-1468, including BET surface area (S_t), micropore surface area (S_{mi}), total pore volume (V_t), micropore volume (V_{mi}) and mesopore volume fraction (V_{me}/V_t).

Anthracite	Act. Temp. °C	Act. Time hr	S_t m ² /g	S_{mi} m ² /g	V_t mL/g	V_{mi} mL/g	V_{me}/V_t
PSOC-1468	850	2.0	540	529	0.250	0.239	0.044
PSOC-1468	850	2.5	762	733	0.360	0.330	0.083
PSOC-1468	850	3.0	928	891	0.442	0.406	0.081
PSOC-1468	850	3.5	855	814	0.412	0.372	0.097
PSOC-1468	800	3.0	607	591	0.287	0.271	0.056
PSOC-1468	890	3.0	639	564	0.351	0.275	0.216

CO₂ adsorption studies of the activated anthracites

Figures 3-5 shows the CO₂ adsorption capacity results of the produced anthracites activated at different times and temperatures. For all the cases, the CO₂ adsorption capacity decreases with increasing adsorption temperature. This indicates that the CO₂ adsorption of the all the ACs is physical adsorption and is mainly related to the pore structure of the ACs. Figure 3 shows the CO₂ adsorption capacities at 30, 50 and 75°C for the PSOC-1468 anthracites activated at 850°C for different times (2, 2.5, 3 and 3.5 hours). The CO₂ adsorption capacity increased with increasing activation time at low adsorption temperatures (30 and 50°C), while the adsorption capacity slightly decreases with increasing activation time at relative higher adsorption temperatures (75°C).

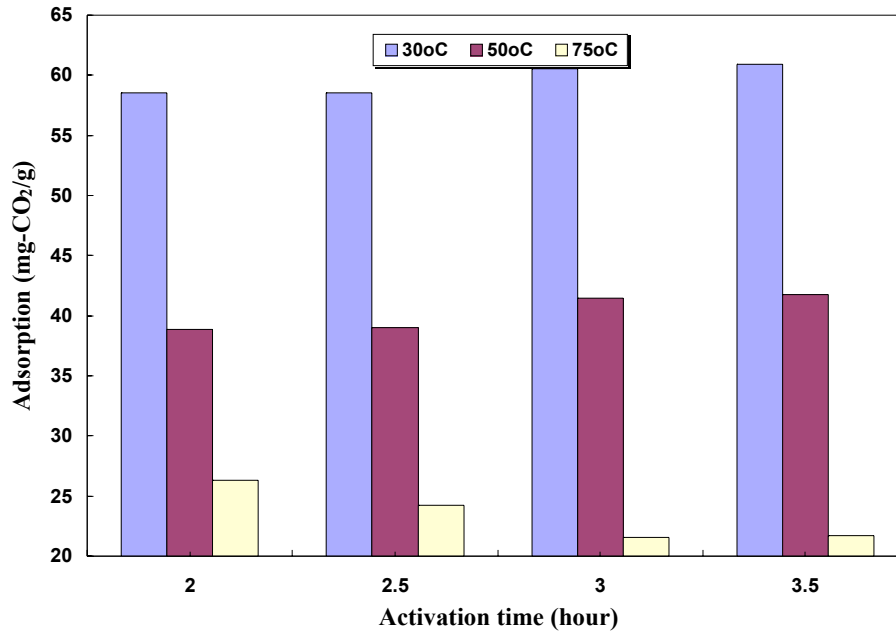


Figure 3. CO₂ adsorption capacities at 30, 50 and 75°C for the PSOC-1468 anthracites activated at 850°C for different times (2, 2.5, 3 and 3.5 hours).

Figure 4 shows the CO₂ adsorption capacities at 30, 50 and 75°C for the PSOC-1468 anthracites activated for 3 hours at different temperatures (800, 850 and 890°C). It can be seen that the CO₂ adsorption capacity decreases with increasing activation temperature for all the adsorption temperatures studied here. For example, at 30°C adsorption temperature, the adsorbed amount of CO₂ is 65.72, 53.14 and 34.34mg-CO₂/g-adsorbent for the anthracites activated at 800, 850 and 890°C, respectively.

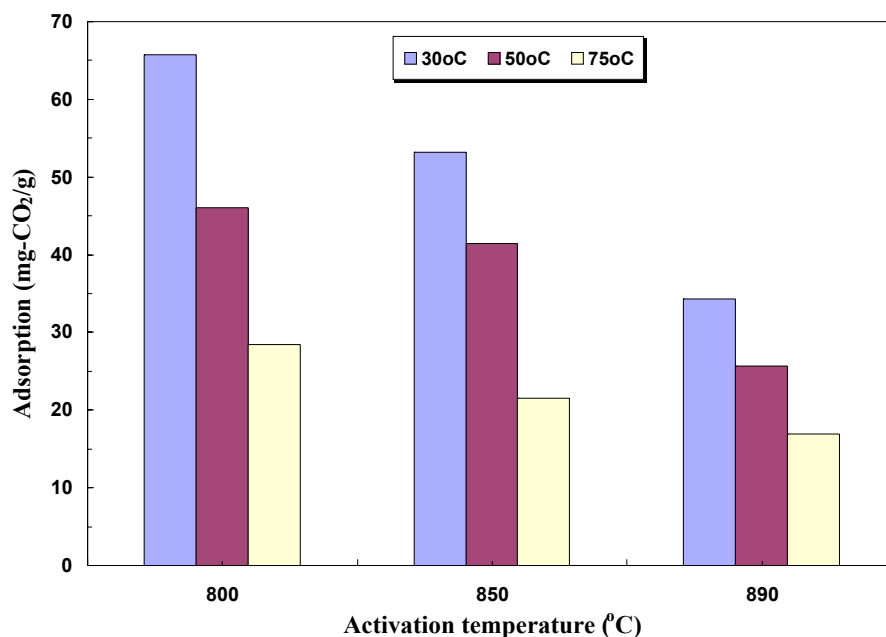


Figure 4. CO₂ adsorption capacities at 30, 50 and 75°C for the PSOC-1468 anthracites activated for 3 hours at different temperatures (800, 850 and 890°C).

The adsorption data presented here did not show a direct relation surface area and pore volume with CO₂ adsorption capacity. For example, the activated carbon made from PSOC-1468, which showed the best CO₂ adsorption capacity (65.72mg-CO₂/g-adsorbent at 30°C), corresponds to the sample activated at 800°C for 3 hours, while the sample activated at 850°C for 3 hours with the highest surface area and microporosity has a CO₂ capacity of only 53.14mg-CO₂/g-adsorbent at 30°C. Therefore, it is anticipated that there are additional factors (not only porous structure) that influence the adsorption of CO₂ by activated anthracites, such as surface functional groups.

The above CO₂ adsorption results show that the anthracite activated at 800°C has the highest CO₂ adsorption capacity. Therefore, this temperature was selected to further investigate the effect of different parent anthracites on the CO₂ adsorption. Figure 5 shows the CO₂ adsorption capacities at 30 and 75°C for the PSOC-1468, AN-1 and AN-2 anthracites activated for 3 hours at 800°C. The activated carbon made from PSOC-1468 has the highest CO₂ adsorption capacity (65.72mg-CO₂/g-adsorbent at 30°C), while the CO₂ adsorption capacity of the activated carbons made from AN1 and AN2 have similar values (55.37 and 58.31mg-CO₂/g-adsorbent, respectively at 30°C). The

three samples investigated (PSOC-1468, AN-1 and AN-2) belong to the anthracite coal rank (Table 1) and there seems to be no effect of the parent sample used on the CO₂ adsorption within the narrow rank investigated here.

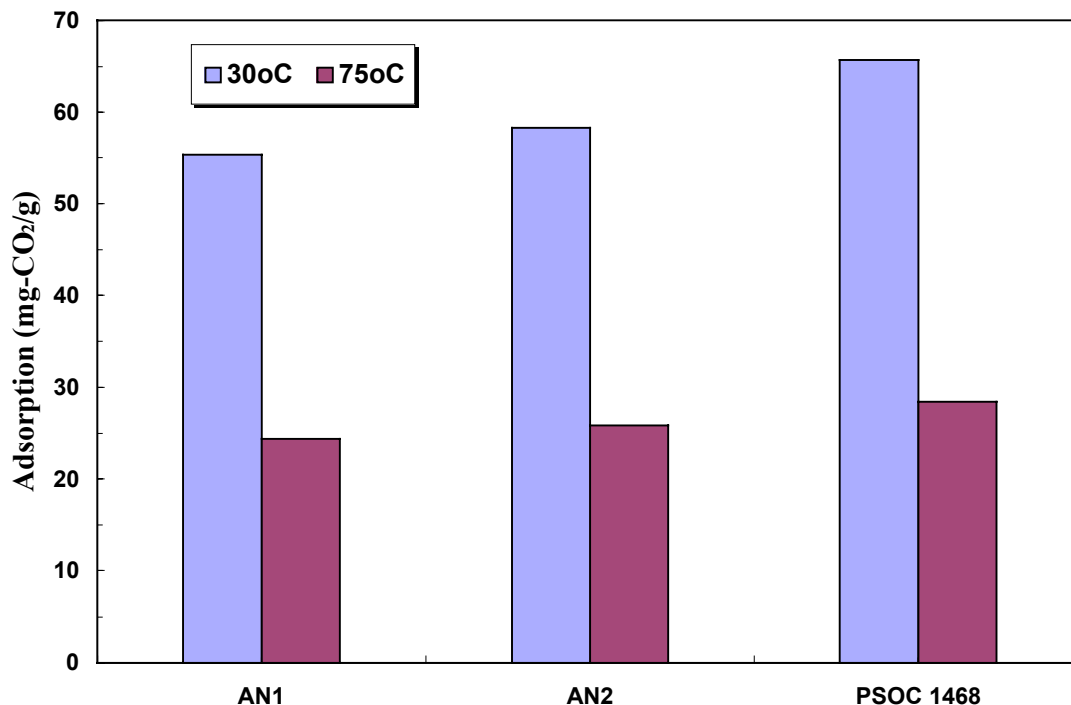


Figure 5. CO₂ adsorption capacities at 30 and 75°C for the PSOC-1468, AN-1 and AN-2 anthracites activated for 3 hours at 800°C.

Conclusions

The objective of this work is the optimization of steam activation of anthracites to produce high surface area activated carbons (AC) and characterize their CO₂ capture capacity. It has been shown that the activated carbons made from anthracite by steam activation have a highly developed microporous structure. The optimum activation conditions for PSOC-1468 are 850°C and 3hrs in terms of maximizing the surface area and pore volume. However, the highest CO₂ adsorption capacity was presented the PSOC-1468 sample activated at 800°C and 3 hours. Therefore, the CO₂ adsorption data presented here do not show a clear relationship between the CO₂ capture characteristics and the surface area and pore volume of the adsorbents. Finally, for the activated carbons made from the three different parent anthracites, under the same activation conditions, PSOC-1468 shows the highest CO₂ adsorption capacity. However, there seems to be no clear effect of the parent sample used on the CO₂ adsorption within the narrow rank investigated here.

Acknowledgements

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