

ONE STEP ACTIVATION OF COAL COMBUSTION WASTE

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Introduction

With the expanding market for activated carbons (AC) due to their enlarging environmental applications, a great interest has been developed to seek more steady and cheaper feed stocks for the manufacture of AC, including the focus on by-product and waste materials. Such routes do not only generate cheaper precursors for AC, but will also consume the waste materials and therefore reduce disposal costs.

At the same time, 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. This carbonaceous residue, also refer to as unburned carbon, is a potential benign 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. Our previous papers have shown the possibilities of producing AC from coal combustion waste by a one step steam activation process⁽¹⁾. Based on the preliminary activation results and the analysis of the properties of unburned carbon, the present study has improved the simple one step steam activation method by adding a pretreatment process of the unburned carbon. The pretreatment resulted in the AC with higher surface area and microporosity.

Experimental

The unburned carbon sample (A) investigated was impregnated with potassium hydroxide (KOH) and dried at 110°C for 6 hours (A-KOH), and compared to a none treated sample. 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, as previously described⁽¹⁾. Typically 3g of sample with or without pretreatment was held isothermally at 850°C for 1-3 hours in flowing steam. The codes of the resultant AC and the activation conditions are listed in Table 1. The porosity of the samples was characterized by conducting N₂ 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 the relative pressure of 0.95. The mesopore (pores 2-50nm in width) surface area and micropore (<2NM) volume were calculated using the

t-method. The micropore and mesopore size distributions were calculated by H-K and BJH methods, respectively⁽²⁾.

Results and Discussion

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 promotes the generation of meso- and macropores in the unburned carbon^(3,4). Pore size distribution studies were also conducted and showed that the surface area and pore volume of unburned carbon are mainly associated with mesopores⁽³⁾. For the unburned carbon A listed in Table 1, the BET surface areas are only 40m²/g, and the pore volume was 0.03ml/g.

1. The effect of activation time on the microstructure of resultant activated carbon

Figure 1 shows the N₂-77K adsorption isotherms for the steam activated carbons produced from the unburned carbon A with different activation time. With increasing activation time, the isotherm changes from Type 1 for A-60 into Type 4 for A-180. For the isotherm of A-60, the adsorbed volume increases rapidly at low relative pressure, while at higher pressure, the adsorbed volume increases very slowly, which implies that most of the pores in the samples are micropores. But for the isotherm of A-180, the adsorbed volume keeps increasing progressively with the relative pressure, and there is a distinct hysteresis loop in the isotherm, which indicates that the sample has the prevailing mesoporosity.

The microstructure parameters listed in Table 1 calculated from the t-method give more detailed information. After 1 hour activation, the resultant activated carbon surface area was 332m²/g, where about 87.4% were from micropores (i.e. 290.2m²/g). Similarly, the micropores contributed 74.3% to the total pore volume (i.e. 0.237ml/g). But when the activation time increased to 2 hr, the proportion of both the micropore surface area and volume of the resultant AC decreased, and the proportions drop to as low as 62.2% and 46.2%, respectively. At the same time, its total surface area and pore volume increase to 540m²/g and 0.500ml/g, respectively, indicating that most of the increase is due to the development of mesopores. When the activation time was increased to 3 hr, the surface area was similar to that for 2 hr, but the pore volume increased to 0.556ml/g and the proportion of micropores kept decrease. This indicates that some micropores have widened into mesopores and some

mesopores have widened into macropores with the activation time.

The micropore size distribution curves calculated from the H-K method are shown in Figure 2. As expected, for A-60, most micropores are ultramicropores (<0.7nm), while with increasing activation time to 2 hours, A-120, most micropores shift to supermicropores (>0.7nm). For the activation time of 3 hours, A-180, the micropores decrease severely. The mesopore size distribution curves calculated from the BJH method are shown in Figure 3. For all the AC from unburned carbon, there is a peak at around 4nm, similar to mesoporous PAN-ACF⁽²⁾. The peak of A-60 is smallest, but for A-180, the peaks not only enlarged, but also there was a shoulder in the larger pore size region.

Considering the fact that unburned carbon in fly ash has already gone through temperatures above 1200-1300°C while in the combustor, and that the elemental analysis showed its oxygen concentration is less than 0.01%, there should only be a very small amount of reaction active sites on the unburned carbon surface. This indicates that an increase in the activation time only results in widening the micropores into mesopores. Hence, chemical pretreatment may introduce more reactive sites.

2. The effect of KOH pretreatment on the activation results

Based on the above experimental results and analysis, chemical pretreatment with KOH was performed to increase the reactivity of the unburned carbon. Certain amounts of KOH were loaded on the unburned carbon followed by steam activation. The isotherms of resultant AC are shown in Figure 4. With 1.5wt% KOH, the resultant AC, A-KOH-1.5, has an isotherm with similar shape to that of A-60, although it has larger adsorbed volume, which suggests a similar high microporosity as A-60. As listed in Table 1, with only 1.5wt% KOH, compared to that without pretreatment A-60, the surface area of AC can increase 35.5% (450m²/g vs. 332m²/g), and keep the very similar micropore proportion (87.4% for without pretreatment vs. 85.8% for 1.5wt% KOH).

But with further increase in the KOH content, the surface area decreases and there are more mesopores formed. This may be due to the limited amount of active sites on the surface of unburned carbon, which can adsorb KOH. Hence with more burn-off, the gasification reaction still happens on the same active site, with the result of widening the exist pores, that makes micropores into mesopores and mesopores into macropores.

Conclusions

Following the previous work that demonstrated the ability to generate activated carbons by steam activation of coal combustion waste, the work reported here gives further results of the one step activation process using chemical pretreatment. After 2 hours activation, activated carbons with surface area up to 540m²/g has been generated from the unburned carbon in combustion waste. By pretreating the unburned carbon with 1.5%KOH, the surface area of the resultant activated carbon increased 35.5% and at the same time kept the similar high proportion of microporosity (86%). Longer activation time at 850°C only contributed to the formation of mesopores.

References

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Table 1. Microstructure parameters for the AC made from unburned carbon in fly ash.

Sample	KOH content wt%	Activation time hr	Solid yield wt%	S _{BET} m ² /g	S _{mi} m ² /g	S _{mi} /S _{BET} %	V _t ml/g	V _{mi} ml/g	V _{mi} /V _t %
A	-	-	-	40	-	-	0.03	-	-
A-60	-	1	73.2	332	290.2	87.4	0.237	0.176	74.3
A-120	-	2	34.8	540	335.9	62.2	0.500	0.231	46.2
A-180	-	3	30.6	533.8	171.9	32.2	0.556	0.110	19.8
A-KOH-1.5	1.5	1	61.7	450	386.1	85.8	0.316	0.227	71.8
A-KOH-6.0	6.0	1	42.3	427.1	276.8	64.8	0.359	0.154	43.0

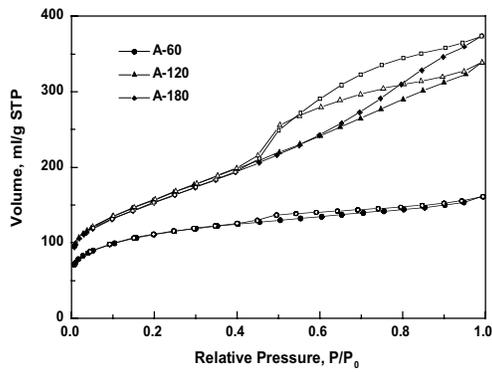


Figure 1. The isotherms of AC made from the unburned carbon A without pretreatment.

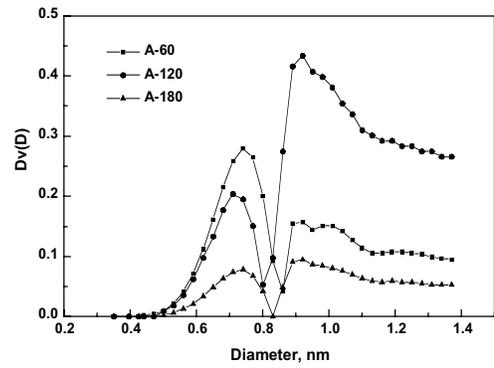


Figure 2. The micropore size distribution curves of AC made from the unburned carbon A without pretreatment.

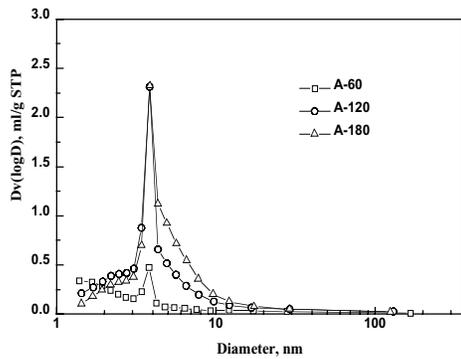


Figure 3. The mesopore size distribution curves of AC made from the unburned carbon A without pretreatment.

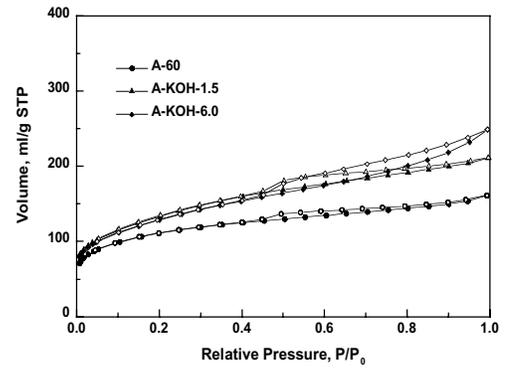


Figure 4. The isotherms of AC made from the unburned carbon A with pretreatment.