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Additivity of pore structural parameters of granular activated carbons derived from different coals and their blends

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ABSTRACT

A series of granular activated carbons (GACs) were prepared by briquetting method from Chinese coals of different ranks and their blends, with coal pitch as the binder. Pore structural parameters including BET specific surface area (S_{BET}), total pore volume (V_T) and average pore diameter (d_a) were measured and calculated as well as process parameters such as yield of char (CY) and burn-off (B). The relationship between the pore structural parameters of the GAC from coal blend (BC-GAC) and the ones of the GACs from corresponding single coals (SC-GACs) was analyzed, in which an index, the relative error (δ), was presented to define the bias between fitted values and experimental values of these parameters of the BC-GACs. The results show that the BC-GAC keeps qualitatively the pore structural features of the SC-GACs; as concerned as the quantitative relationship, the pore structural parameters of the BC-GAC from coal blend consisting of non-caking coals can be obtained by adding proportionally the pore structural parameters of the SC-GACs with δ less than 10%. Meanwhile, for the BC-GAC from coal blend containing weak caking bituminous coal, the δ increases up to 25% and the experimental pore size distribution differs greatly from the fitted one.

1. Introduction

Granular activated carbons (GACs) are irreplaceable in some industrial applications such as flue gas desulphurization and water treatment for their high density, high strength and suitable particle size and/or size distribution [1–3]. However, in some cases, it is the porosity that determines the application and application efficiency of activated carbons [4], in other words, it is the porosity of activated carbon that makes it the right adsorbent for a given application.

The porosity of an activated carbon is highly affected by the preparation processes as well as the starting materials [5]. For instance, by chemical activation, activated carbons with specific surface area up to 2000–3000 m^2/g can be obtained from coals [6–11] while the specific surface area of activated carbons originating from lignocellulosic materials can hardly be greater than 1000 m^2/g for their lower carbon content [12–15], unless these lignocellulosic materials were carbonized previously [16]. Meanwhile, steam activation process generally produces activated carbons with specific surface area less than 1500 m^2/g [17–19].

In terms of GACs, coals of different ranks are the most important raw materials [9,20–23]. In some cases, the GACs can be obtained by carbonizing and/or activating directly crushed coarse coals or chars of appropriate particle size or size distribution. However, by briquetting method, which means to extrude or briquet the mixture of coal powder and binder(s) and then crush the formed briquettes to satisfactory particle size or size distribution, higher strength and density can be provided for GACs. In particular, when the briquetting pressure is in the range of 150–200 MPa, the amount of the binder can be less than 10% by weight, or even binder free [24]. It is well known that most GACs are prepared by steam activation [25–27]. The mechanism of steam activation can be described as the process by which carbon atoms free from bonding with surface complexes are removed by the gasification agent (steam), which means the structure of "graphene layers" in the char is preserved [28]. On the contrary, KOH activation separates the graphene layers, leading to a very high specific surface area but extremely low density and making the activated carbons flocculent [29].

Thus, the porosity of GACs is primarily determined by the properties of the raw coals, though it may be influenced to a certain extent by several specific chemicals when these chemicals are added into the coal powders prior to carbonization and/or activa-

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tion as shown in some studies [17,30,31]. A cost-efficient approach to regulating the porosity of GACs is to use different raw coals, or to blend different kinds of coal powders. So far, a great deal of effort has been made to elucidate the effects of properties of raw coals on the derived activated carbons, and considerable achievements in understanding the relationship between activated carbon's porosity and raw materials have been obtained [5,16,32–35]. Although it is predictable that the porosity of the GAC from coal blend (BC-GAC) combines the porosity of GACs from corresponding coals constituting the coal blend (SC-GACs), the relationship between the main pore structural parameters of BC-GAC and the ones of SC-GACs is quantitatively indistinct.

The objective of this paper is to clarify the relationship between the porosity of GAC from coal blend (BC-GAC) and the porosity of GACs from coals constituting the coal blend (SC-GACs), on the basis of detailed characterization of the porosity of these GACs. Specifically, the additivity of the pore structural parameters including BET specific surface area (S_{BET}), total pore volume (V_T) and average pore diameter (d_a) as well as the process parameters such as yield of char (CY) and burn-off (B), was checked.

2. Experimental

2.1. Raw materials

Coals of different ranks were chosen as the raw materials for the GACs and coal pitch from Shanxi province, China, was used as the binder, and the results of their proximate analysis and ultimate analysis are shown in Table 1.

Among these five coals, DT-coal, SM-coal and SL-coal were regarded as the main components in the blends, representing bituminous coal, subbituminous coal and lignite, respectively. Being the auxiliary components, TX-coal and LW-coal were used to adjust the porosity of the GACs.

2.2. Preparation of GACs by briquetting method

The raw coal and the pitch were ground to 0.075 mm and then mixed at the mass ratio of 100:10. Then the powdered mixture was pressed (p = 200 MPa) into pellets with thickness of 8 mm and diameter of 25 mm. These pellets were finally crushed into particles of 3–10 mm. The crushed coal briquettes were carbonized and activated in a tube furnace (R50/500/12, Nabertherm, Germany). The parameters of blending, carbonization and activation are compiled in Table 2.

2.3. Characterization of chars and GACs

The porosity of the GACs is characterized by a N_2 adsorption–desorption isotherm at 77 K, with a gas adsorption analyzer (Quantachrome Autosorb-iQ, USA). The GAC samples were outgassed at 573 K for 3 h and the relative pressure p/p_0 (i.e. abscissa of the isotherm) was set as 10^{-7}–1. Specific surface area and total pore volume were calculated by BET equation and $V_{liq} = Pa \cdot V_{ads} \cdot V_m/RT$. Modificatory QSDFT equation (silt/cylinder pores model, provided by Quantachrome) was used to calculate pore size distribution.

X-ray diffraction (XRD) analysis of the char samples was carried out by Rigaku D/MAX-RB (Japan) equipment with Cu X-rays (λ = 0.15406 nm). The generator voltage, the current, the step size and the scan range were 40 kV, 150 mA, 0.02° and 10–85°, respectively. The minerals in the chars were identified by the standard method and the crystallite parameters of "graphene layers" structure were calculated based on the Scherrer equation.

2.4. Additivity analysis

In this paper, relative error (δ) was used to analyze the additivity of the pore structural parameters as defined in Eq. (1).

$$\delta = \frac{A_f - A_e}{A_e} \times 100\% \tag{1}$$

where A_e is experimental value of the pore structural parameter of GAC from coal blend (BC-GAC); and A_f is fitted value of the pore structural parameter of GAC from coal blend (BC-GAC).

The "A" in Eq. (1) can represent yield of char (CY), burn-off (B), BET specific surface area (S_{BET}), total pore volume (V_T), and average diameter (d_a). "A_f" is calculated based on the hypothesis that the two coals in the blend are carbonized and activated independently and have no effect on each other. Thus, the fitted parameter A_f is calculated by the proportional addition of the values of the parameters of GACs from corresponding coals constituting the coal blend

Table 1
Proximate analysis and ultimate analysis of coal samples (%).

Sample ID	M_{ad}	A_d	V_{daf}	FC_{daf}	C_{daf}	$H_{da\ f}$	O_{daf}	N_{daf}	$S_{t,d}$
DT-coal	2.12	5.10	30.03	69.97	85.45	5.61	6.71	1.18	1.00
SM-coal	7.29	9.66	38.54	61.46	80.35	7.06	10.63	1.39	0.53
SL-coal	28.80	17.32	44.13	55.87	74.94	12.72	9.42	1.48	1.19
TX-coal	0.74	3.29	8.31	91.69	94.11	3.90	0.64	1.08	0.26
LW-coal	10.22	8.52	36.06	63.94	80.00	6.54	11.40	1.10	0.89
Coal pitch	0.16	0.11	61.46	38.54					0.44

Table 2
Parameters in the preparation processes of GACs.

Mass ratio of coal blends	Carbonization parameters	Activation parameters
DT:TX:pitch = 50:50:10	Mass of coal briquette = 40 g	Mass of char = 30 g
DT:LW:pitch = 50:50:10	Carbonization temperature = 600 °C	Activation temperature = 900 °C
SM:TX:pitch = 50:50:10	Heating rate = 10 °C/min	Steam flow rate = 0.75 mL/(g h)
SM:LW:pitch = 50:50:10	Carbonization time = 60 min	Activation temperature = 900 °C
SL:TX:pitch = 50:50:10	N_2 flow = 100 mL/min	
SL:LW:pitch = 50:50:10		