

An Improved Process for Preparing Activated Carbon with Large Specific Surface Area from Corncob

Y. Sun^{*,**,+}, J.-P. Zhang^{*,**}, G. Yang^{*,**}, and Z.-H. Li^{*}

^{*}National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100080, P. R. China

^{**}Graduate School of the Chinese Academy of Sciences, Beijing, 100039, P.R. China

Original scientific paper

Received: July 4, 2006

Accepted: March 1, 2007

In this study, the fluidized bed reactor was used to carbonize corncob in the carbonization step of producing carbon adsorbent with large specific surface area. The experiment showed that not only the efficiency of carbonization, but also the value of specific surface area and specific pore volume of the produced carbon were obviously increased. The experimental operating conditions were as follows: carbonizing the corncob in the preheated fluidized-bed at $T = 350$ °C for 5 min using N_2 as carrier gas; impregnating the char with KOH solution; activating the mixture at $T = 800$ °C for 60 min in the tubular furnace. Under the optimal conditions, the specific surface area and specific pore volume reached $s = 2880$ $m^2 g^{-1}$ and $v = 1.664$ $cm^3 g^{-1}$, respectively. Comparison was made between this work and other literature on the preparation of activated carbon with large specific surface area.

Key words:

Carbon adsorbent, corncob, fluidized-bed

Introduction

With the appearance of many new technologies such as preparation of electric double-layer polar material with super high capacity and low resistance, storage of hydrogen energy etc., the carbon adsorbents (CA) with common specific surface area which are around $s = 1000$ – 1600 $m^2 g^{-1}$ can not meet these growing demands.¹ In the past few years, investigations into the preparation of CAs with large specific surface area from corncob were extensively. It is generally agreed that the two-step process (precarbonization followed by chemical activation) can produce CA with larger specific surface area from corncob than the one-step chemical activation process.² According to literature reported, the CA with large specific surface area was produced from corncob through precarbonization in a fixed bed reactor at $T = 450$ °C for 4 hours followed by impregnation with KOH and activation at 850 °C¹, the specific surface area of CA produced from this process can reach $s = 2700$ $m^2 g^{-1}$. The CA with large specific surface area was also produced by precarbonizing the corncob in a sealed ceramic oven at 450 °C for 1.5 h followed by chemical activation with KOH at 780 °C plus CO_2 gasification,³ the specific surface area of resulting CA

reached 2844 $m^2 g^{-1}$, which might be the highest among the literature reported previously. However, their relatively longer carbonization time from 1.5 to 4 h at 450 °C in the fixed bed reactor may hinder these processes of manufacturing CA with large specific surface area. How to effectively increase the efficiency of the carbonization step seems very important in manufacturing CA with large specific surface area from corncob.

The fluidized-bed reactor is thought to yield a uniform product due to its efficient heat and mass transfer that minimizes temperature variation and ensures good mixing.⁴ These advantages are so compelling that the application of a fluidized bed to the carbonization step can be attractive for producing CA with large specific surface area. Therefore, such an attempt was made in this work. The condition of carbonizing corncob in the fluidized bed reactor is studied. The effect of preparation conditions upon the specific surface area and specific pore volume of the CA is also investigated.

Experimental

Materials

Corncocks, the main composition and elements of which are shown in Table 1, were collected in the HeBei province in northern China and sieved to about 0.15–0.30 mm in size after drying at 110 °C for 6 h in oven.

⁺Corresponding author. Address: National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, 100080 Beijing, P. R. China. Tel.: +86 01 62525607; Email address: ysun@home.ipe.ac.cn

Table 1 – Main components and contents of corncob

Composition	Mass fraction, w/%
cellulose	32.44
hemicellulose	40.12
lignin	23.43
ash	4.01
C	43.41
H	5.83
N	0.56
O (estimated by difference)	50.20

Apparatus

Figure 1 illustrates the experimental apparatus system for carbonization of raw materials. A quartz glass column was used as a fluidized bed reactor. The diameter and height of the fluidized bed reactor in the bed section were 30 mm and 300 mm, respectively, and those in the expanding section were 55 mm and 90 mm, respectively. The distribution plate was made of 2-mm thick stainless steel which contained 25 holes, each 0.1 mm in diameter. The N_2 was fed into the bed through a pressure regulator, a calibrated rotameter, and a heating furnace controlled by a programmable thermostat heating at the rate of temperature change $\dot{T} = 30\text{ }^\circ\text{C min}^{-1}$. A U-tube manometer was used to measure the pressure drop of the bed. The fluidized-bed reactor was first heated to the preset temperature and then maintained until thermal equilibrium was achieved.

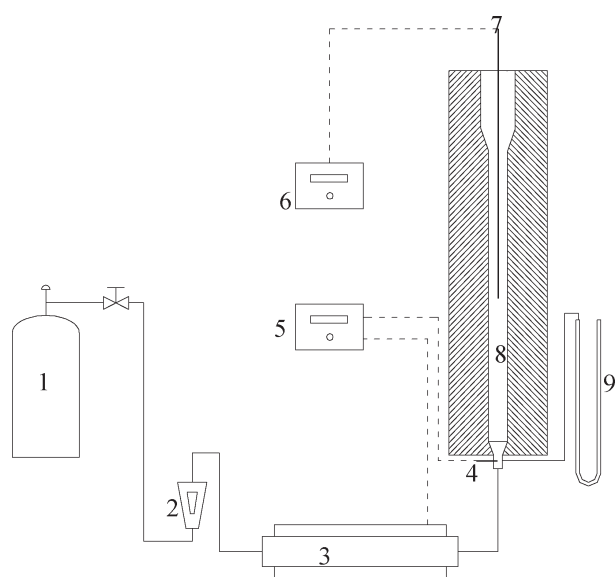


Fig. 1 – Experimental setup (1) N_2 ; (2) flow meter; (3) heating furnace; (4) thermocouple; (5) programmable thermostat; (6) programmable thermostat; (7) thermocouple; (8) fluidized bed; (9) U-tube manometer.

Preparation of carbon adsorbent with high specific surface area

(1) Approximately $m = 10\text{ g}$ of powdered corncobs were placed in the preheated ($T = 350\text{ }^\circ\text{C}$) fluidized-bed reactor through its top. N_2 was used at a flow rate of $Q = 8\text{ L min}^{-1}$. This condition was maintained for $t = 5\text{ min}$ to carbonize the raw materials, and the char was taken out once the reactor had cooled to room temperature. (2) 1 g char was mixed with 4 g KOH and 5 ml distilled water in an alumina crucible boat. The mass ratio of KOH to char was $\xi = 4:1$ in this research, since this ratio was adopted in many studies of the preparation of CA with large specific surface area.⁵ The mixture was stirred to form slurry. The alumina crucible boat and its contents were placed in the tubular furnace, heated from 500 to 900 $^\circ\text{C}$ at a rate of temperature change $\dot{T} = 30\text{ }^\circ\text{C min}^{-1}$ under the protective flow of N_2 of $Q = 90\text{ ml min}^{-1}$ for 60 min. (3) The products were washed with hot distilled water until neutralized, and then filtered and dried at 120 $^\circ\text{C}$.

The one-step KOH chemical activation was also conducted for the sake of comparison. The corncob was directly impregnated with KOH with an impregnation ratio of 4, then activated at 800 $^\circ\text{C}$ in the tubular furnace for 60 min under the protective gas of N_2 . The resulting carbon was washed with hot distilled water until neutralized, then filtered and dried at $T = 120\text{ }^\circ\text{C}$.

Characterization and measurements of activated carbon

N_2 adsorption and desorption Characterization: The specific surface areas and porosities of samples for the activated carbon were determined by nitrogen gas adsorption-desorption at 77 K with Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Corporation USA). The nitrogen adsorption-desorption isotherms of activated carbon were obtained through calculating their Brunauer-Emmett-Teller (BET) surface areas by assuming the area of the N_2 molecule was 0.162 nm^2 . The BET surface area was assessed within the range of relative pressures from $\dot{p} = 0.05$ to 0.3. The micropore volume and external surface area (mesoporous surface area) were measured by the t -plot method,⁶ the total pore volume was calculated as the liquid volume equivalent to the volume of N_2 adsorbed at a relative pressure of $\dot{p} = 0.99$. The Horvath and Kawazoe (HK) method for micropore size distribution was used for characterizing the resulting carbon. The Barret-Joyner-Halenda (BJH) method was used for pore size distribution of the resulting carbon in the mesoporic range.

Thermogravimetric Analysis: TG was performed on a Shimadzu TGA-50 under a nitrogen ($Q = 20$ ml/min) atmosphere at $T = 10$ °C min⁻¹.

Surface Morphology: Surface morphology was taken by HITACHI S-450 scanning electron microscope.

Results and discussion

Determining the carbonization conditions of corncob

The thermogravimetric analysis of corncob is shown in Fig. 2. The maxima of the mass loss rate of the corncob under N₂ atmosphere appears in the temperature range of $T = 250$ – 350 °C, and a slight change of the mass loss of the sample occurs in the range of 350 – 600 °C. This experiment adopts 350 °C as the carbonization temperature to carbonize the corncob in the fluidized bed, since most volatile components are expelled from the corncob in the temperature range of $T = 250$ – 350 °C. Fig. 3 shows pressure drop and burn-off rate of corncob as a function of carbonization time in the fluidized bed

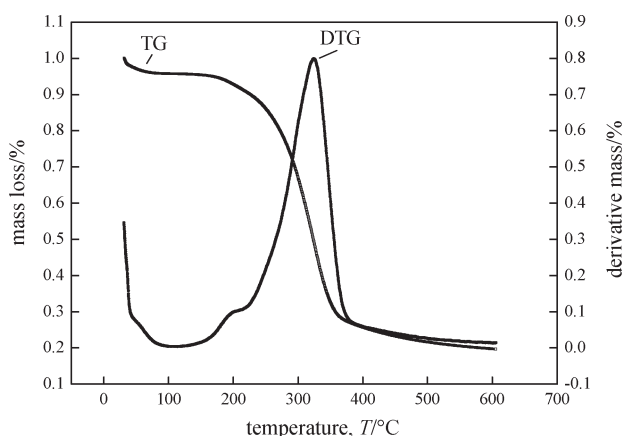


Fig. 2 – Thermogravimetric analysis of corncob

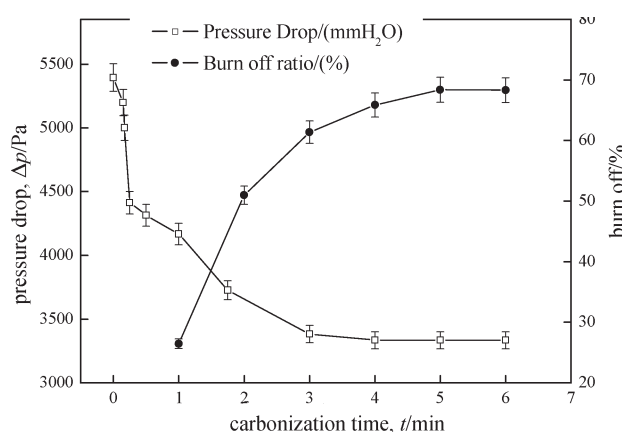


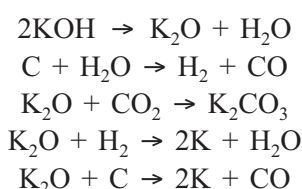
Fig. 3 – Pressure drop and burn off as function of carbonization time

at $T = 350$ °C. It shows that the burn-off rate does not change appreciably after the first 5 min of carbonization, neither does the pressure drop. This means that after the volatile matter had been removed in the first 5 min of carbonization, the volatilization largely reduced. Therefore, it was chosen to carbonize the corncob for 5 min prior to activation.

Comparing literature with this work on the preparation of CA with large specific surface area from corncob, the application of a fluidized-bed reactor to the carbonization step can definitely increase the efficiency of carbonization, which shortens the carbonization step from more than $t = 4$ h to about 5 min. When the KOH-impregnated char was activated at 800 °C in this work, the specific surface area and specific pore volume of $c = 2880$ m² g⁻¹ and $v = 1.664$ cm³ g⁻¹ were obtained, respectively. This improved process of carbonizing corncob in the fluidized bed shows obvious advantages, such as shorter carbonization time, lower carbonization temperature which used to be 450 °C, larger specific surface area and pore volume.

Determining the optimum conditions of activation

The surface area of the carbon depends largely upon the activation temperature. With the increase of activation temperature, the reaction rate between KOH and the char is faster.⁷ The following reactions may take place during the activated processes under high temperature⁸



The specific surface area and specific pore volume of CA activated at different temperatures are shown in Fig. 4 and Fig. 5, respectively. The optimum activation temperature of achieving the largest specific surface area and specific pore volume is 800 °C. Fig. 4 shows that the specific surface areas increase from $T = 500$ to 800 °C and then decrease with a further increase of temperature. Fig. 5 shows the pore volumes (micropore volume and mesopore volume) of CA increasing with activation temperatures up to 800 °C. This indicates that the pores enlarge up to this temperature. Above 800 °C, the excess enlargement results in a decrease of micropore volume, and increase of mesopore volume.

The specific surface area and pore volume of 800 °C activation can reach $s = 2880$ m² g⁻¹ and $v = 1.664$ cm³ g⁻¹, respectively. Although the acti-

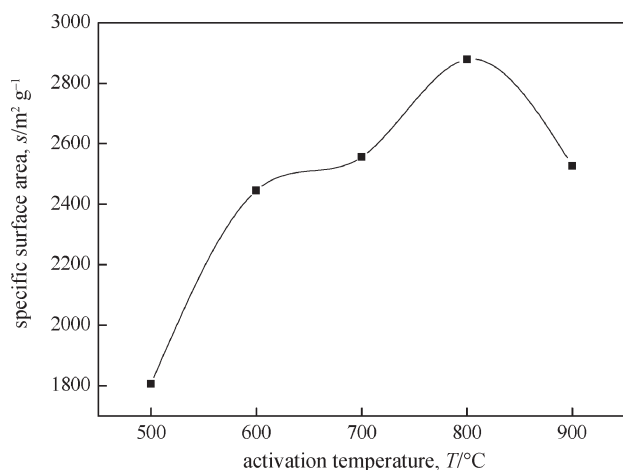


Fig. 4 – The effect of activation temperature on the specific surface area of CA

vation step of this improved process shows no obvious difference from other literature about preparing CA with large specific surface area from corncob, the time used for the carbonization step is largely reduced, thus the total time of preparing the CA is shortened. The comparison between this work and other literature about preparation conditions of producing CA with large specific surface area is listed in Table 2. It is obvious that the separated-step of KOH chemical activation of corncob yields somewhat larger BET specific surface area and pore volume than the one-step KOH chemical activation of corncob. Comparing the value of porosities of the carbon the precursor of which is Spanish anthracite,¹⁰ the BET specific surface area and pore volume of that carbon can reach 3290 m² g⁻¹ and 1.450 ml g⁻¹, respectively, which is even larger than the carbon produced from our process. This is due to the different precursor adopted as raw material. Considering the shorter operation time, lower temperature of carbonization, the larger specific surface

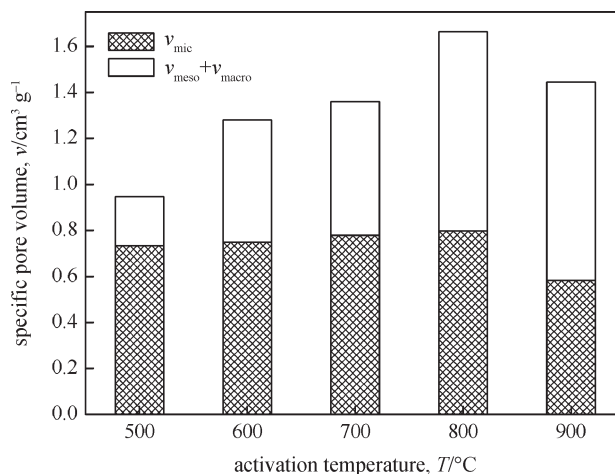


Fig. 5 – The effect of activation temperature on the specific pore volume of CA

area, and specific pore volume, the advantages of our improved process are obvious.

Characterization of the CA with the largest specific surface area

The specific surface area of the CA activated at 800 °C is $s = 2880 \text{ m}^2 \text{ g}^{-1}$. The adsorption and desorption isotherms of this carbon are shown in Fig. 6. According to Brunauer-Deming-Deming-Teller (BDDT) classification,¹¹ this carbon exhibits the type I isotherm. According to the t -plot method, the corresponding micropore and mesopore surface area of this carbon are $s = 2016$ and $864 \text{ m}^2 \text{ g}^{-1}$, respectively. In Fig. 7, a large proportion of the pores of this CA is in the microporous range, i.e. mainly in the range of 1.0 ~ 1.2 nm. There are also some proportions of wider pores like mesopores (> 2.0 nm) in CA as shown in Fig. 7b. Those data confirm that micropores play a key role in CA having a large specific surface area. The micropore and total spe-

Table 2 – Comparison of preparation conditions and the main parameters of the CA with large specific surface from corncob

Preparation condition	Carbonization	s_{BET} m ² g ⁻¹	v_{pore} cm ³ g ⁻¹	Reference
Carbonization at 450 °C for 4 h. Char activation by KOH at 850 °C	450 °C 4 h	2700	–	1
Carbonization at 450 °C for 1.5 h. Char activation by KOH at 780 °C	450 °C 1.5 h	2595	1.430	2
Carbonization at 450 °C for 1.5 h. Char activation by KOH at 780 °C plus CO ₂ gasification	450 °C 1.5 h	2844	1.533	3
One-step KOH chemical activation at 800 °C plus CO ₂ gasification	800 °C 1 h	1806	0.870	9
KOH chemical activation of Spanish anthracite at 750 °C for 1 h with impregnation ratio of 4	700 °C 1h	3290	1.450	10
One-Step KOH chemical activation at 800 °C with impregnation ratio of 4.	800 °C 1 h	1975	0.945	This work
Carbonization at 350 °C for 5 min. Char activation by KOH at 800 °C	350 °C 5 min	2880	1.664	This work

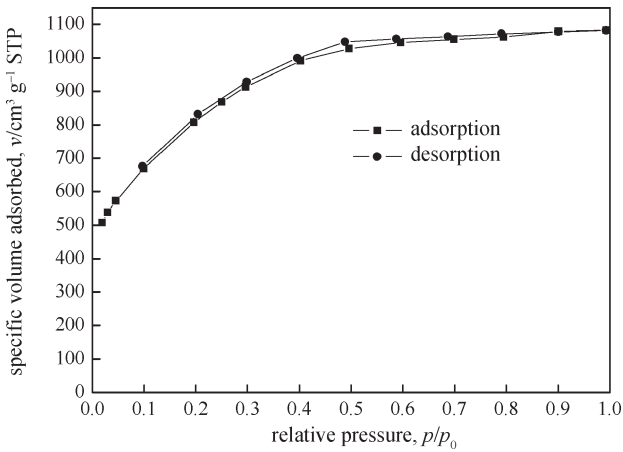


Fig. 6 – Adsorption/desorption isotherm of nitrogen of the CA with the largest specific surface

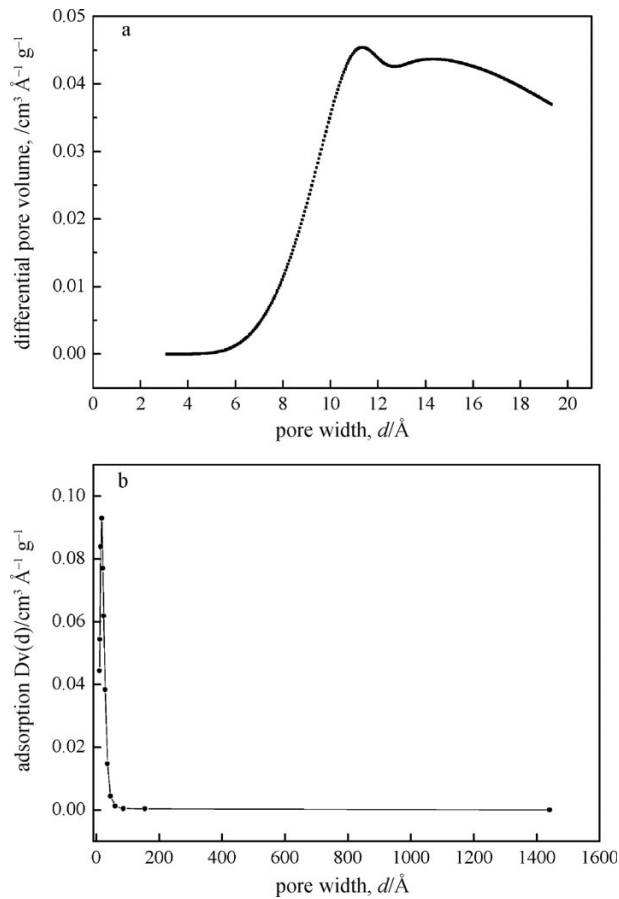


Fig. 7 – (a) Micropore size distribution; (b) the method of BJH for the pore size distribution of CA

cific pore volume are $v = 0.7974$ and $1.664 \text{ cm}^3 \text{ g}^{-1}$, respectively. Fig. 8 shows the surface morphology of the char and the CA activated at $800 \text{ }^\circ\text{C}$. Comparing these two carbons, the CA activated at $800 \text{ }^\circ\text{C}$ displays a highly irregular surface structure and good formation of the pores. It is clear that the opening of the pores should be due to the reaction between the carbon and KOH during the activation step.

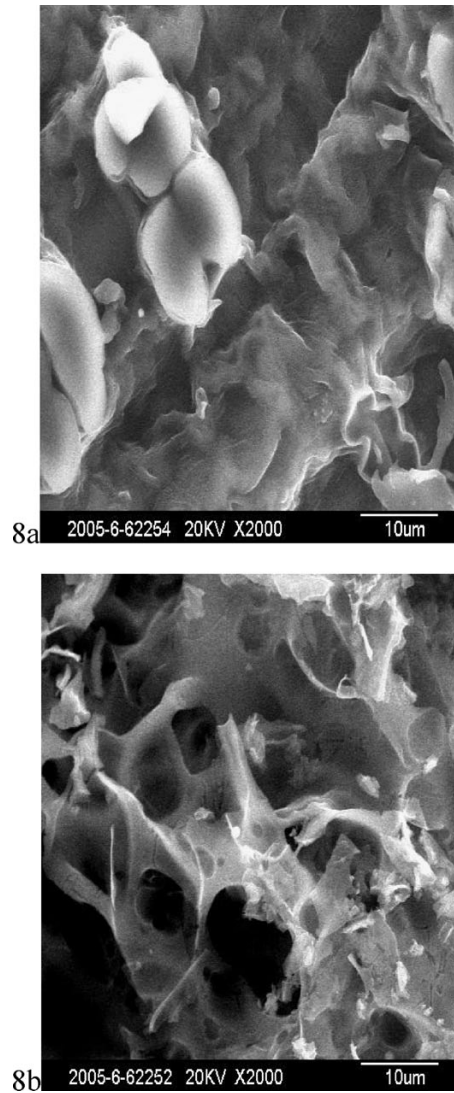


Fig. 8 – Scanning electron micrographs of (a) precarbonized corncob, and (b) CA activated at $800 \text{ }^\circ\text{C}$

Conclusions

The improved process of carbonizing corncob in the fluidized-bed reactor and subsequently activating in the tubular furnace can produce CA with very large specific surface area and specific pore volume, which reaches $s = 2880 \text{ m}^2 \text{ g}^{-1}$ and $v = 1.664 \text{ cm}^3 \text{ g}^{-1}$ respectively. The optimal conditions are carbonizing corncob at $T = 350 \text{ }^\circ\text{C}$ for $t = 5 \text{ min}$ in a fluidized bed with $Q = 8 \text{ L min}^{-1} \text{ N}_2$, impregnating the char with the KOH solution at a ratio of 4.0 (KOH/char), and activating at $800 \text{ }^\circ\text{C}$ for 60 min with N_2 as protective gas. The application of the fluidized bed to the carbonization step can greatly shorten the time of carbonization step, and thus increase the efficiency of the preparation conditions. This improved process is a promising process for producing activated carbon with large specific surface area from corncob.

ACKNOWLEDGEMENTS

Financial support for this work was provided by the National Basic Research Program of China (2004CB719701) and Innovation funds of the Process Engineering Institute of the Chinese Academy of Sciences (No: 062702). Authors also wish to thank Miss Yue Wu, for her help with constructive comments.

List of symbols

m	– mass, g
\dot{p}	– relative pressure p/p_0
Q	– volume flow rate, L min ⁻¹
s	– specific surface area, m ² g ⁻¹
t	– time, min, h
T	– temperature, °C
\dot{T}	– rate of temperature change, °C min ⁻¹
v	– specific pore volume, cm ³ g ⁻¹
ζ	– mass ratio

References

1. Qing, C., Ke-Chang, X., Yong-Kang, L., Wei-Ren, B., *Bioresource Technology* **97** (2006) 110.
2. Tseng, R. L., Tseng, S. K., *Journal of Colloid and Interface Science* **287** (2005) 428.
3. Tseng, R. L., Tseng, S. K., Wu, F. C., *Colloid And Surfaces A* **279** (2006) 69.
4. Al-Khalid, T. T., Haimour, N. M., Sayed, S. A., Akash, B. A., *Fuel Processing Technology* **57** (1998) 55.
5. Yang, S. B., Hu, H. Q., Chen, G. H., *Carbon* **40** (2002) 277.
6. Badie, S. G., Samya, S. Y., Ashraf, M. S., *Materials Letters* **57** (2002) 164.
7. McKee, D. W., *Fuel* **62** (1983) 170.
8. Guo, Y. P., Yang, S. F., Zhao, J. Z., Wang, Z. C., Zhao, M. Y., *Chemical Journal of Chinese Universities* **21** (2000) 335.
9. Tsai, W. T., Chang, C. Y., Wang, S. Y., Chang, C. F., Chien, S. F., Sun, H. F., *Resources, Conservation and Recycling* **32** (2001) 43.
10. Lozano-Castelló, D., Lillo-Ródenas, M. A., Cazorla-Amrós, D., Linares-Solano, A., *Carbon* **39** (2001) 741.
11. Gregg, S. J., Sing, S. W., *Adsorption, Surface Area and Porosity*, second edit. Academic Press, New York, 1982, pp. 195–228.