

AN INVESTIGATION ON PREPARATION OF ACTIVATED CARBONS MADE BY STREAM AND SUPER-CRITICAL WATER FROM HAW-STONE RESIDUE AND WASTE TYRE RUBBER

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This paper studies on the preparation of activated carbon produced from haw-stones residue and waste tyre rubber char, and the effect of different activation conditions on its porosity and adsorption characteristics. The haw-stones have been widely used for food and medical industries as additives. The mechanical strength of haw-stones residue obtained from industries is high enough, but it is treated as a waste by far, because no appropriate way may be used to deal with it. Meanwhile, huge amount of used tyres are produced annually in the world [1]. The disposal of this waste stream may cause a major environmental problem throughout the world. In the present work, activated carbons were prepared from haw-stones residue and waste tyre rubber by means of traditional steam activation and super-critical water activation. Based on pore structure characterization of the samples by N₂ adsorption technique, we compared the influences of two different activation processes on the evolution of pore structure. Our results illustrated that BET surface areas and total micropore volumes of activated carbon produced from haw-stones residue increased continuously with the temperature of activation to reach the values up to 1277m²g⁻¹ and 0.31cm³g⁻¹, respectively. Rubber-derived carbons activated by both super-critical water and by traditional steam have high proportion of mesopore.

Raw materials employed in this work were waste haw-stones residue and tyre rubber which had been carbonized as industrial wastes. Both of the two raw materials were ground and sieved into a diameter of 1mm as an average size.

Activation process

Some of samples (3g for each) were activated by steam. Activation was carried out in a vertical tube furnace. The precursors were heated at 5°C/min to a designed temperature from 650 °C to 900 °C under a flowing (at 100ml/min) nitrogen atmosphere. When the temperature was reached, the inert atmosphere was rapidly substituted by flowing steam/nitrogen (at the ratio of 1:1). Different reaction durations were then applied for the generation of each sample.

Activation for other samples was performed in a super-critical activation furnace,

heating the precursor to a designed temperature between 400°C and 700°C at a rate of 3°C/min, then keeping at the temperature for some time. Water was infused into the reactor at a flow rate of 2.5ml/min until the temperature reached the required value. Pressure was controlled at about 24 MPa during the activating process. Different carbon samples are denoted by their series reference code followed by their activation time in hours. For example, the haw-stones residue carbon produced by traditional steam for 4 hours at 650°C was denoted as TH650-4. Here, T represents traditional steam activation, H means haw-stones residue. SH650-4 denotes the haw-stones residue carbon activated by super-critical water under the same conditions.

Characterization

Carbon samples were characterized for their surface and pore characteristics by using continuous volumetric nitrogen gas adsorption at liquid nitrogen temperature of 77K. Analyses were conducted in the ASAP2010 (Micrometrics, USA) in order to determine the specific surface areas and pore structure parameters. Total surface areas were determined by application of the BET equation [2] to the adsorption data in the p/p_0 range of 0.06~0.2. The amount of N_2 adsorbed at a relative pressure ($Pr=P/P_0$) of 0.1 [3] was applied to determine the micropore volumes. The total pore volume was obtained by converting the nitrogen adsorption amount at a relative pressure of 0.95 to the liquid nitrogen volume [2].

Results and discussion

Table 1 shows the haw-stones residue carbons' structural parameters. The carbons possess the BET surface areas in a range between $452m^2g^{-1}$ and $1277m^2g^{-1}$, the total volumes in a range from $0.24cm^3g^{-1}$ to $0.81cm^3g^{-1}$. Table 1 also illustrates the proportion of mesopores is increasing with the increase of activation temperature. And also, traditional steam shows much better results comparing with super-critical water for haw-stones residue's activation. Fig.1 shows N_2 isotherms of the samples prepared by traditional steam activation and Fig.2 shows their BJH pore size distribution.

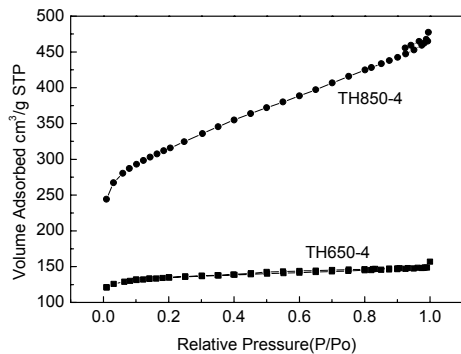


Fig 1 Nitrogen isotherm of the samples prepared by traditional steam activation

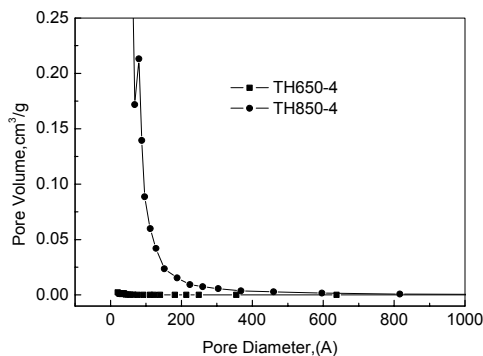


Fig 2 BJH pore size distribution of the samples prepared by traditional steam activation

Table 1. The pore parameters of activated carbons prepared from haw-stones residue

Sample No	S_{BET} m ² /g	S_{mic} m ² /g	V_{tot} cm ³ /g	V_{mic} cm ³ /g	V_{mes} cm ³ /g	R %	Yield%
TH650-4	452	377	0.24	0.18	0.025	11	57
TH650-10	519	427	0.27	0.2	0.03	12	52
TH850-4	1079	583	0.71	0.27	0.25	35	26
TH850-6	1277	665	0.81	0.31	0.29	35	24
SH650-4	493	383	0.25	0.18	0.034	13	39
SH650-10	572	379	0.31	0.18	0.062	20	24
SH700-1	395	320	0.21	0.15	0.06	29	45
SH700-6	587	408	0.34	0.19	0.079	24	30
SH700-10	650	414	0.37	0.19	0.096	26	25

BET surface area of the waste tyre rubber carbon might have a maximum value of 1070m²g⁻¹ as reported in ref [4]. In our work, the high mesopore proportion has been determined as a maximum of 52%.

The present results show that haw-stones can be used for preparing activated carbon with developed pore structure and high mechanical strength. When pulverized, it could be used for the filter tip of the cigarettes, or water clearing and air purifying. Super-critical water activation would reduce the consumption of energy and produce activated carbon without pollution. Waste tyre rubber can be made into high performance activated carbon with high mesopore proportion.

Acknowledgements

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References

- [1] Guillermo SM, Geoffrey DF, Marco Dall'Orso, Christopher JS. Porosity and surface characteristics of activated carbons produced from waste tyre rubber. *J Chem Technol Biotechnol* 2001;77:1-8
- [2] Gregg SJ, Sing KSW. Adsorption, surface area and porosity. London: Academic Press, 1982.
- [3] Rodriguez-Reinoso F, Lopez-Gonzalez JD, Berenguer C. Activated carbons from almond shells: I. Preparation and characterization by nitrogen adsorption. *Carbon* 1982;20(6):513-8.
- [4] Guillermo SM, Geoffrey DF, Christopher JS. A study of the characteristics of activated carbons produced by steam and carbon dioxide activation of waste tyre rubber. *Carbon* 2003;41:1009-1016.