Short Communication

Corn stalks char from fast pyrolysis as precursor material for preparation of activated carbon in fluidized bed reactor

Zhiqi Wang, Jingli Wu, Tao He, Jinhu Wu*

Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, China

HIGHLIGHTS

- Corn stalks char from fast pyrolysis was activated in a fluidized bed reactor.
- Different pore structures were obtained depending on different reaction mechanisms.
- The physically activated carbons have microporous structure with S_{BET} of 880 m²/g.
- The chemically activated carbons have mesoporous structure with S_{BET} of 600 m²/g.

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ABSTRACT

Corn stalks char from fast pyrolysis was activated by physical and chemical activation process in a fluidized bed reactor. The structure and morphology of the carbons were characterized by N₂ adsorption and SEM. Effects of activation time and activation agents on the structure of activation carbon were investigated. The physically activated carbons with CO₂ have BET specific surface area up to 880 m²/g, and exhibit microporous structure. The chemically activated carbons with H₃PO₄ have BET specific surface area up to 600 m²/g, and exhibit mesoporous structure. The surface morphology shows that physically activated carbons exhibit fibrous like structure in nature with long ridges, resembling parallel lines. Whereas chemically activated carbons have cross-interconnected smooth open pores without the fibrous like structure.

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1. Introduction

Fast pyrolysis of biomass is a rapid thermal decomposition process in the absence of oxygen to produce liquid organic compounds, gas and char. Researches on fast or flash pyrolysis have shown that high yields of primary liquids could be obtained from biomass (Meier and Faix, 1999; Bridgwater and Peacocke, 2000). Consequently, the lower value solid char from traditional slow pyrolysis can be replaced as much as possible by higher-value fuel oil and fuel gas from fast pyrolysis. Recently, the exploration to effectively utilize the production of value-added products from the fast pyrolysis of biomass is very attractive (Reyhanitash et al., 2014). There is no doubt that liquid products have the most attraction, but the char is also an attractive byproduct, with production of activated carbons, and sorption of heavy metals from wastewater.

There is only less literatures on the treatment of char obtained from fast biomass pyrolysis to promote the char by-products value (Liu et al., 2012). Bio-chars obtained from fast pyrolysis without further treatment, were investigated as adsorbents for the removal of the toxic metals and a long-term carbon sequestration agent (Mohan et al., 2007; Bruun et al., 2011). Though these fast pyrolytic bio-chars can be used as adsorbents without further treatment, the bio-char structure tends to be underdeveloped due to short residence times in the fast pyrolysis process thereby impacting its full potential application as a value-added by-product. Therefore, activation could enhance their adsorption capacity. There are a large number of studies regarding the preparation of activated carbons from raw biomass (Schroder et al., 2007; Gao et al., 2011; Foo and Hameed, 2012). Little data is available in the literatures describing the activation of the byproduct char from the fast pyrolysis of biomass (Lima et al., 2010).

In this study, corn stalks char, a fast pyrolytic by-product during bio-oil production, is as intermediate material precursor for preparing activated carbon. The char obtained from fast pyrolysis of corn stalks at about 550 °C for high yields of bio-oil, was activated

* Corresponding author. Tel.: +86 53280662763; fax: +86 532 80662761.

E-mail addresses: wangzq@qibebt.ac.cn (Z. Wang), wujh@qibebt.ac.cn (J. Wu).

by physical and chemical activation process in a fluidized bed reactor. The structure and morphology of the activated carbons were characterized. The effects of preparing parameters such as activation time, and activation agents on the structure of activation carbon were investigated.

2. Methods

2.1. Biomass char materials

Corn stalks char was obtained from fast pyrolysis of biomass to produce bio-oil in a fluidized bed reactor with a feeding rate of 10 kg/h at about 550 °C. The obtained corn stalks char was used as the precursor material for preparation of activation carbon without treatment except the char particles were sieved to size range between 40 and 120 meshes. The average elemental and proximate analyses of the properties of corn stalks char are as following: C, 72.28 wt%; H, 3.14 wt%; O, 22.47 wt% (by difference); N, 1.09 wt%; S, 0.9 wt%; moisture, 4.36 wt%; ash, 16.73 wt%, volatile matter, 23.79 wt%; fixed carbon, 55.12 wt%; BET-N₂ surface area (dry basis), 89.4 m²/g.

2.2. Preparation method

The received char was activated to preparing activated carbon in a bubble fluidized bed reactor (50 mm in diameter, 1200 mm height). In the chemical activation process, the char was dipped with H₃PO₄ solution with the weight ratio of H₃PO₄/char equal to 1.0 and then used as precursor material after drying and evaporating at 80 °C for 24 h, and N₂ was employed as fluidization gas, whereas, CO₂ was selected as fluidized and reaction gas for physical activation process.

The temperature of fluidized bed reactors, made of stainless steel tube, was controlled by external electric heater with intellectualized temperature controller and fluidization gas preheating. The bubble fluidized bed reactor was first charged with about 100 g silica sand (60–120 mesh, minimum fluidization velocity: 0.092 m/s), which helped in stable fluidization and keeping the reactor temperature uniform, then the electric heater and gas pre-heater were turned on to heat reactor. When the desired temperature was reached, the N₂ or CO₂ flow rate was controlled to the desired level and about 50 g char was fed in the reactor. The operating fluidization gas velocity was 0.198 m/s, and the activation temperature was 850 °C with the activation duration ranged from 60 to 120 min.

2.3. Characterization of char and activated carbons

The textural heterogeneity of the prepared activation carbons was characterized by N₂ adsorption–desorption isotherm measurements at 77 K using a Quantachrome Instruments (Model Nova 2000, USA) to determine the specific surface area and pore volume of the samples. The specific surface area (*S*_{BET}) was calculated by multipoint BET method using the N₂ adsorption isotherm data below the relative pressure range of 0.15. The total pore volume (*V*_T) was estimated on the basis of the liquid volume of nitrogen adsorbed at a relative pressure of 0.98. The micropore volume (*V*_{HK}) and the mesopore volume (*V*_{BJH}) were determined according to the HK method and BJH method, respectively. Pore size distribution was determined by the DFT (Density Functional Theory) method. The surface morphology characteristics of the activation carbons were analyzed using scanning electron microscopy (SEM, Hitachi S-4800F, Japan). The burn-off mass loss *X*_m (%) was found as the ratio (*m*₀–*m*)/*m*₀, where *m*₀ and *m* are the initial and final masses of the bio-char and the carbon product, respectively. Iodine

number was determined according to ASTM D4607-94. The uptake of methylene blue (MB) from aqueous solution was evaluated by adding a previously weighted amount of carbon to MB solution. The mixture was stirred for 30 min at 50 °C and the adsorbent was then removed by filtration. The dye concentration in the remaining solution was determined by measuring the absorbance at 670 nm in an UV–vis spectrophotometer.

3. Results and discussion

3.1. Effect of activation time on the porous texture and surface area of physically activated carbons

The adsorption–desorption isotherms of N₂ at 77 K for both the original bio-char and the series of activated carbons prepared with different activation times at activation temperature of 850 °C using CO₂, are presented in Fig. 1. According to the classification of physiosorption isotherms recommended by the International Union of Pure and Applied Chemistry (IUPAC), the shape of the adsorption isotherms for N₂ at 77 K is a typical type I isotherm, which indicates the activated product is an essentially microporous solid. The first three isotherms upon activation carbons are similar. These isotherms show that the adsorption capacity of the activated carbons is much more dependent on the activation times. *S*_{BET} and the total pore volume obtained from the nitrogen adsorption isotherms and the burn-off are listed in Table 1. The N₂ adsorption capacity is increased with the prolongation of the duration of activation, and the burn-off is also increased. *S*_{BET}, as expected, follows the same trend as the burn-off. After activation for 120 min, a value of 880 m²/g is reached. The burn-off at this activation time is already very high (77%). With the increase of activation time, *V*_T, *V*_{HK} increase obviously. In contrast, the increase of *V*_{BJH} is not so prominent.

The pore size distribution (PSD) is a key element in the characterization of porous carbons. According to the classification recommended by the IUPAC, pores within porous materials are normally classified into micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). The PSD of the activated carbons with CO₂ activation is shown in Fig. 2. As shown in Fig. 2, the sharp increase in the PSD curves toward the smallest pore diameter for the activated carbons indicates the formation of micropores. The PSD calculated from DFT shows that the micropores in the activated carbons from physical activation with CO₂ are very narrow, and all the samples have a sharp peak. All carbon samples have pore sizes centered between 0 and 5 nm, but the intensity and region

Fig. 1. N₂ adsorption–desorption isotherms of physically activated carbons (ACP-6, ACP-9 and ACP-12 are the physically activated carbons with activation time for 60 min, 90 min and 120 min, respectively).

Table 1

Variances in the some properties of activated carbon samples.

Samples	S_{BET} m ² /g	V_{T} cm ³ /g	V_{HK} cm ³ /g	V_{BJH} cm ³ /g	Iodine number g/g	MB number g/g	Burn-off%
ACP-6	559	0.472	0.215	0.059	320	204	66.7
ACP-9	672	0.548	0.297	0.071	453	217	72.5
ACP-12	882	0.599	0.353	0.082	811	243	77.1
ACC-6	410	0.327	0.155	0.112	265	217	69.6
ACC-9	532	0.368	0.177	0.141	292	240	75.3
ACC-12	607	0.415	0.223	0.165	364	269	80.4

Fig. 2. Pore size distribution of the physically activated carbons.

of PSD for various samples have a little difference. ACP-12 has higher distribution intensity between 0 and 2.5 nm compared with the other samples, which shows that ACP-12 has a high micropore volume.

SEM was taken for corn stalks char and activated carbons prepared by physical activation with different activation times to examine their surface morphology. Bio-char exhibits smooth surfaces without a porous structure, however, the activated carbon samples show cavities on their external surface. The activated carbons with physical method give fibrous like structure in nature with long ridges, resembling a series of parallel lines. The carbon surface appears to be more etched with prolonged activation time, the external surfaces of all carbon samples are found covered with open pores of different sizes.

3.2. Effect of activation time on the porous texture and surface area of physically chemically activated carbons

The adsorption–desorption isotherms of N₂ at 77 K for the series of activated carbons prepared with different activation times at activation temperature of 850 °C using H₃PO₄, are presented in Fig. 3. At higher pressures, the isotherms exhibit hysteresis loop which indicates that the pore structure is mostly mesoporous. The hysteresis loops have no sharp knees indicating absence of mesopores of uniform size. According to the IUPAC classification, the isotherms approach the Type IV and also exhibit a Type H4 hysteresis loop. As shown in Fig. 3, all curves have obvious smearing effect, and the reason is that there are some mesopores in the samples, and when the relative pressure P/P_0 is close to 1, smearing effect will be caused by capillary effect. When the activation time is prolonged, the slope of the curve gradually increases with wider a hysteresis loop. It seems that prolongation of active time can promote the formation of mesopores. This can be linked to the formation of a greater fraction of mesoporosity which is confirmed by the mesopore volume (V_{BJH}) presented in Table 1. With the increase of activation time, S_{BET} , V_{T} , the burn-off and V_{HK} increase obviously.

Fig. 3. N₂ adsorption–desorption isotherms of chemically activated carbons (ACC-6, ACC-9 and ACC-12 are the chemically activated carbons with activation time for 60 min, 90 min and 120 min, respectively).

The PSD of the activated carbons with H₃PO₄ chemical activation process is shown in Fig. 4. The dominant pores of all the samples are in the range of <10 nm with the maxima at approximately 5 nm. Therefore, the active carbons derived from cornstalks char are typically mesoporous. Notably, ACC-9 and ACC-12 two samples have wider PSD region, and the distribution intensity of the two samples between 2.5 and 15 nm are higher than that of ACC-6. So it can be concluded that the PSD of the activated carbons intend to present a mesoporous nature with the increase of duration of activation treatment. The distribution intensity of ACC-12 between 2.5 and 15 nm is the highest in all samples, which shows that ACC-12 has the largest mesopore volume.

The results of the adsorption on different activated carbon samples in Table 1 show that MB and iodine values increase gradually with the increase of the activation time. It has been reported that the MB and iodine molecules are accessible to the pores with diameters larger than 1.5 nm and 1 nm, respectively (Bacoui et al.,

Fig. 4. Pore size distribution of the chemically activated carbons.

2001; Aygun et al., 2003). The increase rate of iodine value in physical activated carbons is much bigger than that of chemical activated carbons. However, the increase of MB value in chemical activated carbons is much bigger than that of physical activated carbons. Therefore, it can be concluded that the number of pore diameter bigger than 1.5 nm increases with the increase of the chemical treating time for bio-char.

SEM analysis shows that the surfaces of the chemically activated carbons are covered with smooth open pores of different sizes and it is composed of different layers of differentiated structure, all of them with an important presence of macropores, while the fibrous like structure is absence. The surfaces of the chemically activated carbon samples appear as friable and shows signs of structure weakness, as evidenced by rupture of walls and disintegrated particles.

4. Conclusions

The different pore structures of the activated carbons prepared from physical and chemical activation were obtained using corn stalks char from fast pyrolysis as precursor material. Activation with CO₂ mainly develops micropores and a S_{BET} value of 880 m²/g is reached. However, Activation with H₃PO₄, mainly develops mesopores and a S_{BET} value of 600 m²/g is reached. The surface morphology shows that physically activated carbons exhibit fibrous like structure in nature with long ridges, resembling parallel lines. Whereas chemically activated carbons have cross-interconnected smooth open pores with friable and rupture of walls, but without fibrous like structure.

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