The Effects of Activation Conditions on Physical Properties of Activated Carbon

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Porous carbons with a high porosity were successfully produced from fast pyrolysis pine wood char *via* a thermochemical method in which KOH was used as chemical activator. The effects of various weight ratios of KOH to pyrolysis char (0.65:1, 0.7:1, 1.0:1, 1.35:1, and 1.7:1) on the physical properties of activated carbons were investigated. When the weight ratio of KOH to pyrolysis char was 1.35:1, the prepared activated carbon had the highest surface area of 1140 m^2/g with a total pore volume of 0.71 cm^3/g, a microporous surface area of 957 m^2/g, and a microporous specific volume of 0.51 cm^3/g. As the weight ratio of KOH to pyrolysis char increased from 0.65 to 1.35, the prepared activated carbon had increases in total surface area, total pore volume, microporous surface area, and specific volume of micropores. However, there was a reverse trend when the weight ratio of KOH to pyrolysis char was higher than 1.35. The use of nitrogen as a flow gas resulted in much more developed activated carbon than without nitrogen. The experiment results suggested that activated carbon with high surface area could be prepared from pyrolysis char by adjusting the activation conditions.

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INTRODUCTION

As the amount of natural gas volume increases, developing effective processes to separate, purify, and store gas fuels and to convert them to chemical raw materials is challenging. As activated carbon possesses well-developed pore structure, high internal surface area, and plentiful functional groups on the surface, it has been widely applied to various areas such as separation and purification areas. Activated carbon is mainly made from fossil fuels such as petroleum and coal. However, with oil price fluctuations, serious environmental pollution, and political reasons, it is necessary to find other sustainable and environmentally friendly carbon-rich precursors to produce activated carbons (Li *et al*. 2008). The sustainable, carbon-rich, and environmentally friendly properties of biomass or biomass waste make it a possible source to prepare activated carbon (Li *et al*. 2008). In previous research, pyrolyzed wood has been used to produce 57 to 60 wt% yield of bio-oil, and bio-char accounting for 21 to 25 wt% yield treated as by-product was also produced (Luo *et al*. 2015, 2016a,b). Pyrolysis char without any treatment has been used as a soil remediation to improve soil aeration (López *et al*. 2013). Pyrolysis char can be converted to a more valuable product—activated carbon—by chemical, physical or chemical-physical methods (Luo *et al*. 2015). Fuller usage of pyrolysis char can be achieved with an integrated process that makes full use of biomass or biomass waste (Appels and Dewil

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2012).

There are three main methods to prepare activated carbon, namely, chemical, physical, and chemical-physical methods. Physical methods are performed at high temperatures ranging from 400 to 1000 °C for carbonization; activation occurs at 600 to 900 °C in the presence of an oxidizer gas, including air, CO_2, steam, and their mixtures. Although physical methods are environmentally friendly and cost less, they have not been utilized broadly due to higher temperature, longer process time, and uncontrolled pore structure of the products. Chemical methods are carried out by impregnating biomass, biomass waste, or pyrolysis char with chemical activators and then activating at a lower temperature, which produce activated carbons with high surface area and well-developed pore structure from carbon precursors. Physical-chemical methods combine the advantages of physical and chemical methods to improve the properties of activated carbon.

Chemical activators, including K_2CO_3, KOH, H_3PO_4, $NH4Cl$, HCl, NaOH, H_2SO_4, $ZnCl_2$, $FeCl_3$, and $MgCl_2$, have been widely investigated (Gomez-Serrano *et al*. 2005; Duman *et al*. 2009; Tsang *et al*. 2007; Luo *et al.* 2015). Gomez-Serrano *et al*. (2005) applied the chemical method and use H_3PO_4 as activator to process chestnut wood at 300 to 600 °C and different weight ratio of water/H_3PO_4 (1:1, 1:2, 1:3). The results showed that the micropore structure was more heterogeneous at the highest acid concentration for 300 °C and lower acid concentration for 600 °C, while the pore size distribution of the activated carbons in micropore ranges was similar at 400 and 500 °C regardless of the H_3PO_4 concentration. Duman *et al*. (2009) also produced activated carbon from pine cone by using H_3PO_3 and $ZnCl_2$ as activators. The surface areas and microspore volume of the activated carbon prepared by $ZnCl_2$ was a little higher than that of activated carbons produced using H_3PO_4. In order to cut activation time and activate the biomass sufficiently, researchers applied the chemical methods to treat with carbonized precursors rather than the original biomass. Tsang *et al*. (2007) compared the activation of the carbonization and wood waste itself in one step; there were almost no hardened cores formed in the carbonization step for 3 h because of sufficient reaction. The best products had the highest total surface area of 1230 m^2/g, a micropore surface area of 710 m^2/g, and a total pore volume of 0.58 mL/g.

According to previous research results (Luo *et al.* 2015, 2016a,b), KOH is a more effective chemical activator to prepare activated carbon with high surface area from pyrolysis pine wood char compared with the H_3PO_4 and H_2O_2 activators. In this study, the effects of KOH amount and the gas atmosphere on the properties of the synthesized activated carbon were studied.

EXPERIMENTAL

Loblolly pinewood (*Pinus taeda*) 2 to 3 cm was provided from Mississippi State University. Potassium hydroxide (KOH, pellets/Certified ACS), filter paper, and pH meter were purchased from Fisher Scientific (Hampton, NH, USA). Additionally, nitrogen (N_2, ultra-purity) and liquid nitrogen were purchased from NexAir (Columbus, MS, USA). Distilled water was prepared in the laboratory. The Autosorb iQ was purchased from Quantachrome (Boynton Beach, FL, USA), and the micro-reactor was purchased from Micrometrics Instrument Corp. (Norcross, GA, USA).

Treatment of the Pyrolyzed Pinewood Char

The production of pyrolysis pine wood char was described in detail in the previous research results (Ingram *et al*. 2007; Luo *et al*. 2016a,b). The pyrolyzed char ranging from 60 to 80 mesh was selected and dried at 100 °C overnight to remove moisture adsorbed onto the surface. Subsequently, different amounts of KOH were dissolved in water and then mixed with the treated char at room temperature for overnight. Finally, it was dried at 110 °C in a vacuum oven for 24 h (Luo *et al*. 2016a,b).

Gas atmosphere is supposed to have effects on the properties of the prepared activated carbon as the gas affects the pore development as well as the heat and mass transportation. In this research, the activation process with and without gas was carried out and the products were analyzed.

Thermochemical Activation of the Pyrolyzed Pinewood Char

The thermochemical activation of the pyrolyzed pinewood char was the same as described in the previous research (Luo *et al*. 2015). In each experiment, 0.3 g of the pyrolyzed pinewood char was placed in the reactor tube and a quartz wool bed 5 mm thick was respectively placed above and below the pyrolyzed char. The activation process was kept at 750 °C for 1 h.

The product yield was calculated by Eq. 1,

$$Yield \ (\text{wt\%}) = (m_1 - m_2) \ / \ m_1 \tag{1}$$

where *Yield* (wt%) is the activated carbon yield in terms of weight percentage, m_1 is the mass of pyrolyzed char placed into the micro-reactor before activation (g), and m_2 is the mass of the products after the activation (g).

The products were subsequently washed with hot distilled water several times in a beaker until the pH of the washed solution was 7 (Zabaniotou *et al*. 2008). The washed samples were dried at 110 °C overnight, and then samples of 60 to 80 mesh size were selected for adsorption-desorption isotherm and transmission electron microscopy (TEM) analysis (Chen *et al*. 2018; Fang *et al*. 2018; Wei *et al*. 2018).

Adsorption-Desorption Isotherm Characterization

Adsorption-desorption isotherms of nitrogen was applied to evaluate the porous properties of the prepared products by means of an AutosorbiQ gas sorption analyzer (Quantachrome). Before testing, the samples were degassed at 300 °C under a vacuum for 6 h. The apparent surface area of the activated carbon was calculated by the BET method (Gregg and Sing 1982). The microporous surface area was determined by the t-plot method. The total pore volume was determined by converting nitrogen gas adsorbed at a relative pressure of 0.99 to the volume of liquid adsorbate (nitrogen) (Luo *et al*. 2015).

Transmission Electron Microscopy (TEM) Analysis

The pore structure of the as-prepared product was examined using a high-resolution transmission electron microscope (JEOL JEM-100CX II, JEOL USA Inc., Peabody, MA, USA) operating at 200 kV and 112 µA. A small amount of sample was dispersed in ethanol at a concentration of 100% and sonicated for 30 min. One drop of this suspension was placed on a Formvar 300 mesh copper grid and allowed to air dry before TEM characterization was performed (Luo *et al*. 2015).

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RESULTS AND DISCUSSION

The Effects of Nitrogen on the Porosity of the Prepared Activated Carbon

Different weight ratios of KOH to pyrolysis char from 35% to 170% were prepared. To test the nitrogen effect on the properties of the activated carbon, 0.3 g of sample in each experiment was processed without nitrogen as flow gas, and the results are listed in Table 1. Similarly, another group of experiments were carried out in the same process conditions to prepare activated carbon, except for the application of nitrogen at the flow rate of 200 mL/min as flow gas, and the results are shown in Table 2.

The adsorption ability of activated carbons depends on the total surface area, the pore size distribution, and the functional groups of activated carbons. Generally, a higher surface area of activated carbons is an indication of the presence of a great amount of micropores, which is beneficial to smaller molecules adsorption. The total surface area, total pore volume, average pore size, external surface area, microporous surface area, and pore volume of the products prepared without or with nitrogen are presented in Tables 1 and 2. The results showed that all the products were not improved sufficiently to form well-developed pores, though the carbon yield was at least 79% when there was no flow gas. More specifically, the total surface area of all products was poor, which was less than 70 m^2/g, because less micropores and mesopores were developed in the products. Activated carbons obtained with nitrogen presented in Table 2 exhibited various levels of pore development. The total surface area increased from 465 to 1140 m^2/g with a large number of micropores and a portion of mesopores as well as a total pore volume ranging from 0.23 to 0.71 cm^3/g. In addition, the activated carbon yield was at least 64% when the nitrogen was applied. Therefore, the flow gas had significant and positive effects on the properties of the prepared activated carbon.

Table 1. Properties of Prepared Activated Carbon without Nitrogen as Flow Gas

KOH/pyrolysis char ratio	Yield (%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore radius (Å)	Micropore surface area (m^2/g)	External surface area (m^2/g)	Micropore volume (cm^3/g)
0.35/1	0.08	60.56	0.02	25.70	0.00	60.56	0.00
0.65/1	0.79	8.28	0.02	47.36	0.00	8.28	0.00
1/1	0.87	13.79	0.04	55.37	0.00	13.79	0.00
1.35/1	0.86	0.00	0.20	20.38	0.00	0.00	0.00
1.7/1	0.93	36.43	0.41	22.66	0.00	0.00	0.00

Table 2. Properties of Prepared Activated Carbon with Nitrogen as Flow Gas

KOH/pyrolysis char ratio	Yield	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore radius (Å)	Micropore surface area (m^2/g)	External surface area (m^2/g)	Micropore volume (cm^3/g)
0.35/1	0.64	465.94	0.23	11.25	396.19	69.75	0.21
0.65/1	0.70	840.80	0.47	11.20	751.36	89.44	0.40
1/1	0.77	903.64	0.53	11.36	743.84	159.80	0.40
1.35/1	0.81	1140.92	0.71	12.44	956.43	184.49	0.51
1.7/1	0.82	1059.45	0.68	12.85	872.11	187.35	0.47

The Effect of Ratios of KOH to Pyrolysis on the Porosity of the Activated Carbon

As shown in Table 2, all products were developed considerably, which means that the activated carbon presented a well-developed porous structure (BET area > 200 m^2/g, V_{Micro}>0.1 cm^3/g) (Amaya *et al*. 2007). The surface area of the activated carbons produced from pyrolysis char treated with various concentrations of KOH were much higher than those prepared with untreated pyrolysis char. In addition, the KOH amount affected the pore properties of activated carbons, and the weight ratio of KOH to pyrolysis char had an optimal value of 1.35 with a total surface area of 1140 m^2/g, a total pore volume of 0.71 cm^3/g, a microporous surface area of 956 m^2/g, and a mesoporous surface area of 185 cm^3/g. When the ratio of KOH to pyrolysis char increased from 0.35 to 1.35, all parameters of the prepared activated carbon, including the total surface area, the total pore volume, the microporous surface area, and the mesoporous surface area exhibited increasing trends. However, when the ratio was higher than 1.35, the total surface area, total pore volume, and microporous surface area decreased, but the mesoporous surface area increased slightly. One possible explanation is that some micropores widened to mesopores in the presence of the extra KOH. Consequently, the skeleton of the activated carbon was over eroded because of the extra KOH, resulting in a widely developed pore structure, which is consistent with the decreased microporous surface area and increased mesoporous surface area exhibited in Table 2.
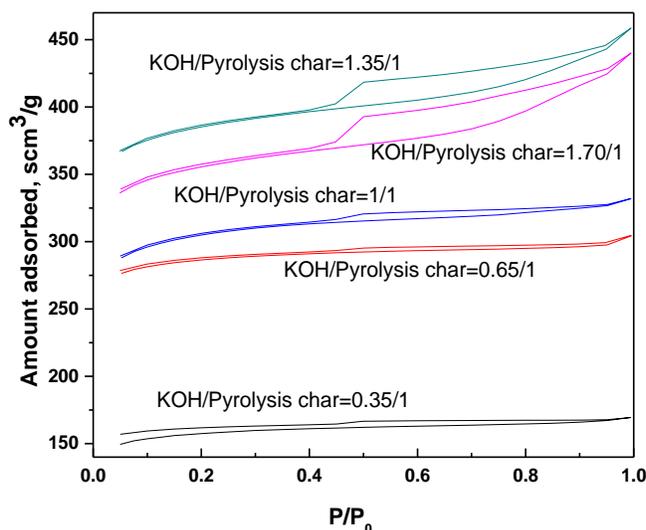

Fig. 1. Nitrogen adsorption-desorption isotherms for activated carbons prepared from pyrolysis char treated with various ratios of KOH to pyrolysis char with nitrogen as flow gas. KOH/Pyrolysis Char: 0.35/1, 0.65/1, 1/1, 1.35/1, and 1.70/1.

The isothermal curves shown in Fig. 1 were obtained from nitrogen adsorption-desorption isotherms for activated carbons which were prepared from pyrolysis char treated with various ratios of KOH with nitrogen as flow gas. An assessment of the properties of the activated carbons can be decided by the adsorption-desorption isotherms. The isothermal curve of activated carbons prepared with 0.35 ratio of KOH to pyrolysis char could be classified as intermediate between type I and type II, indicating microporous structure with a developed mesoporous structure but less mesopores, which corresponded

to the BET results listed in Table 2. When the KOH concentration was increased from 0.65 to 1.7, the isotherms range in general from Type I isotherms at lower KOH concentration to Type IV isotherms at higher KOH concentration. The isotherms suggest that a larger number of mesopores are developed as the KOH concentration increases (Williams and Reed 2006). The four isothermal curves show hysteresis loops (the desorption is not coexistent with adsorption isotherm), which indicate the presence of mesoporous-activated carbons. In addition, the hysteresis loops indicate that the pores are slit-shaped or that the carbons are comprised of plate-like material, perhaps graphene layers between which are the pores (Williams and Reed 2006). Moreover, the increase of the uptake at high relative pressure is large, corresponding to higher macroporous surface area listed in Table 2, which uncovers that a high development of meso and macroporosity (Gregg and Sing 1982; Amaya *et al*. 2007; Yang *et al*. 2010).
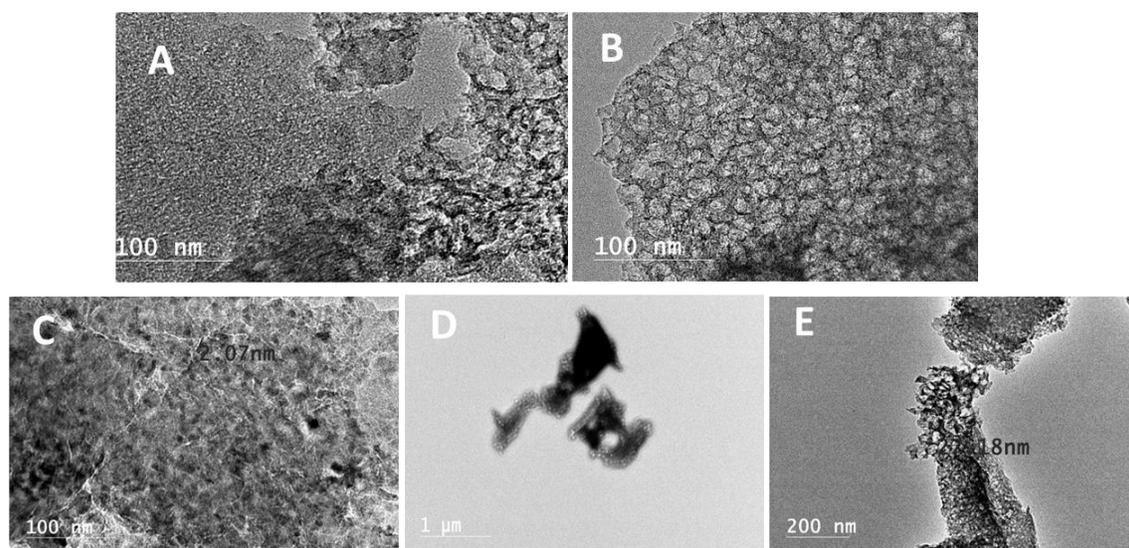

Fig. 2. TEM images of as-prepared activated carbons with nitrogen as flow gas. KOH/pyrolysis char ratio (A) 0.35/1, (B) 0.65/1, (C) 1.0/1, (D) 1.35/1, and (E) 1.7/1

The pore characteristics of activated carbon prepared by various ratios of KOH to pyrolysis char were examined by TEM shown in Fig. 2. According to the International Union of Pure and Applied Chemistry (Sing 1985), three types of pores are defined according to their pore size, including micropores with pore width less than 2 nm, mesopores with pore width ranging 2 to 50 nm, and macropores with pore width larger than 50 nm. Pore width refers to the distance between the walls of the slit-shaped pores or the radius of cylindrical-shaped pores. The mesopores can be defined by the hysteresis loops during adsorption and desorption at a high relative pressure (Williams and Reed 2006). Figures 2A and 2B show TEM photographs of the activated carbon prepared when the ratio of KOH to pyrolysis char was 0.35 and 0.7, respectively. The micropores were clearly developed, and some mesopores were observed. The predominant microporosity of this type of activated carbons resulted in a homogeneous morphology. Figure 2C shows a TEM image of the activated carbon prepared when the ratio of KOH to pyrolysis char was 1.0, showing that micropores and mesopores were clearly developed. Figure 2D shows the activated carbon when the ratio of KOH to pyrolysis char was 1.35, where micropores and mesopores were observed. Figure 2E represents activated carbon prepared when the ratio of KOH to pyrolysis char was 1.7. There was clear evidence of microporosity and

mesoporosity. Mesopores with larger diameter are found in the products shown in Figs. 2C to 2E), which confirmed the nitrogen adsorption and desorption results as shown in Fig. 1. This loss of micropores contributes to pore widening and the development of mesoporosity.

CONCLUSIONS

1. Activated carbon with a high porosity was prepared from fast pyrolysis pine wood char. The products in the presence of nitrogen resulted in well-developed pored compared with those without nitrogen.

2. The concentration of KOH activator had a great effect on the pore development of the activated carbon. Total surface area and total pore volume of the resulting carbons were found to increase with the weight ratio of KOH to pyrolysis char to a maximum of 1.35.

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